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Structure and properties of attrition-milled aluminium powder

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Aluminium powder has been attrition milled in the presence of 1.5 wt% of a wax. The aim was to achieve a mechanically alloyed powder amenable to powder metallurgy processing. Changes in particle size and form, microstructure, hardness and other properties of powders with milling time has been studied. Under the experimental conditions employed, a process time of 10 h was selected for the mechanical alloying of Al powder. The powder milled in this way shows a Vickers microhardness (127 HV) more than six times higher than the starting powder (20 HV), a coarser particle size (mean particle size is doubled) and a better flowability.

1. Introduction

Mechanical alloying (MA) is a high-energy milling process in which powder particles are heavily and repeatedly deformed, resulting in intimate alloying. This technique was originally developed around mid-1966 by Benjamin [1] to produce nickel-based superalloys combining oxide dispersion and intermetallic-compound strengthening. MA was later used to obtain dispersion-hardened aluminium by milling in the presence of a processing control agent (PCA), so as to establish a balance between fracture and welding of particles. These additives, such as methanol [2], lampblack [3] and a wax [4], prevent excessive welding of the metal particles and at the same time react with aluminium, during either milling or the subsequent heat treatment (degassing), introducing suitable dispersoids (Al_2O_3 and Al_4C_3) into the matrix [5]. Mechanically alloyed aluminium can be considered, in a certain way, an improvement on sintered aluminium powder, the first dispersion-strengthened aluminium material [6].

In recent years, MA has exceeded the scope of a method for producing composite metal powders with a fine microstructure. The process has been employed to obtain alloys with extended solubilities, amorphous materials and nanocrystalline structures and to synthesize inorganic compounds [7]. In fact, it has been known for a long time that the chemical reactivity of powders may be increased by milling. Important pioneering research work on this subject (mechanochemistry and mechanical activation) was carried out in Germany in the early 1960s by Naeser [8] and Schrader [9].

The properties of specific materials obtained by MA are very sensitive to experimental conditions (milling type, energy input, type and amount of PCA, atmosphere, etc.). In the present investigation, dispersion-strengthened unalloyed Al powder has been prepared by attrition milling in the presence of a wax. Once the experimental conditions had been chosen, the evolution of microstructure and properties of the powders with milling time is studied. The main purpose was to achieve a hard homogeneous powder amenable to powder metallurgy (PM) processing.

2. Materials and experimental procedure

The as-received material was a commercial-grade atomized Al powder, supplied by IJFESA, Madrid. The powder purity was greater than 99.5% Al and its particle size was below 150 μm. This powder was milled, together with a PCA, in a Szegvari attritor (Union Process). Hoechst Micropowder C wax ($H_{35}C_{17}CONHC_2H_4NHCOC_{17}H_{35}$; less than 40 μm) was used as PCA. The attritor [10] is a vertical ball mill, where the grinding balls are agitated by a rotating impeller (Fig. 1). The choice of the milling conditions, which are shown in Table I, was made on the basis of experimental results from preliminary studies on the variables involved in attrition milling.

Powder size distribution was measured using a Sedigraph 5100 from Micromeritics. This apparatus is based on particle sedimentation rate and X-ray absorption. For metallographic observations, powders were mounted and polished down to 1 μm diamond paste, followed by a final polishing with magnesium oxide. Polished specimens were eventually etched with Keller's reagent. Scanning electron microscopy (SEM) was performed with a Philips XL-30, operated at 15 kV. Vickers microhardness measurements were restricted to the 100–150 μm particle-size range, i.e., to individual particles large enough to accommodate the diamond pyramid indentation. They were made with a Zwick 3212 001 tester, under a load of 0.02 kgf. Each value is the mean of 20

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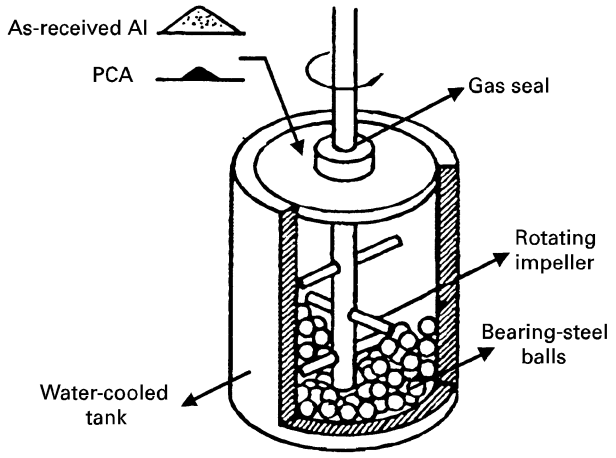

Figure 1 Attritor-type ball mill.

TABLE I Milling conditions of Al powder

Vessel volume (cm^3)	750
Mass of powder (g)	60
PCA (wt%)	1.5
Charge ratio = mass of grinding balls : mass of powder in mill	30 : 1
Steel ball diameter (mm)	4.65
Rotor speed (rev min^{-1})	500
Atmosphere	Sealed air
Refrigeration	Water
Milling time (h)	1–20

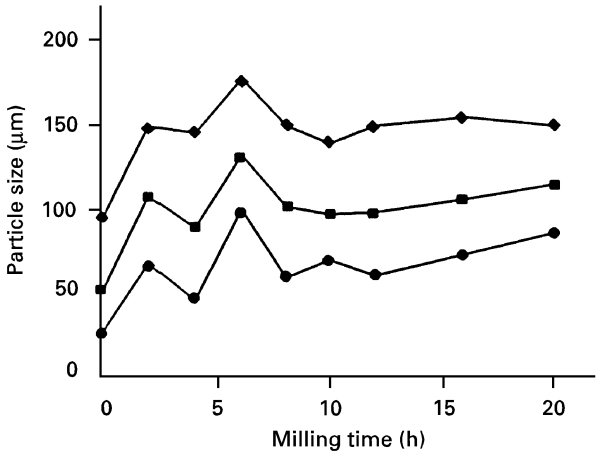

Figure 2 Powder size distribution versus milling time for various percentages of particles finer than the given size. (◆), 75 wt%; (■), 50 wt%; (●), 25 wt%.

measurements. PM properties such as apparent density, tap density and flowability of powders were eventually determined employing well-established common methods.

3. Results and discussion

The evolution of particle size, morphology and microstructure of Al powder with milling time was as follows. The powder size distribution continually changes during the first 10 h, presenting peaks and valleys, although with a clear trend to particle coarsening (Fig. 2). Then a relative steady-state size distribution is achieved, where only the finer size fractions still show a very slight tendency to grow. Thus, particle welding dominates the milling process through the first 10 h; afterwards, for times between 10 and 20 h, the processes of welding and fracture are quasi-balanced, although the proclivity for welding continues at a much lesser rate. It can be observed in Fig. 2 (curve of 50%) that, for a milling time of 10 h, the average particle size has increased from 50 to nearly 100 μm. The particle size data for as-received Al, milled for 10 h, are also plotted in Fig. 3. The results are presented as cumulative weight percentage of particles finer than a given size, and as the weight percentage of particles of a given size (screen opening). The coarsening introduced by 10 h milling is evident. The particle size distribution of mechanically alloyed Al powder (Fig. 3b) is monomodal and relatively narrow, around the 100 μm size, because small particles tend to weld and large particles to fracture.

Changes in powder particle morphology and structure that occur during attrition milling of Al powder up to 10 h are schematically shown in Fig. 4. They are also illustrated with SEM and optical micrographs in Figs 5 and 6, respectively. Four stages can be distinguished in the MA process. The as-received atomized Al powder particles (stage 0) are predominantly equiaxed and irregular in shape (some protuberances can be observed in Fig. 5a) and have a dendritic-type microstructure (Fig. 6a).

After milling for 1 h, the equiaxed particles flatten into flakes (stage 1). These plate-shaped particles (Fig. 5b) are of the same volume as the initial powder particles. They also conserve the dendritic microstructure (Fig. 6b). On the other hand, this flaky powder

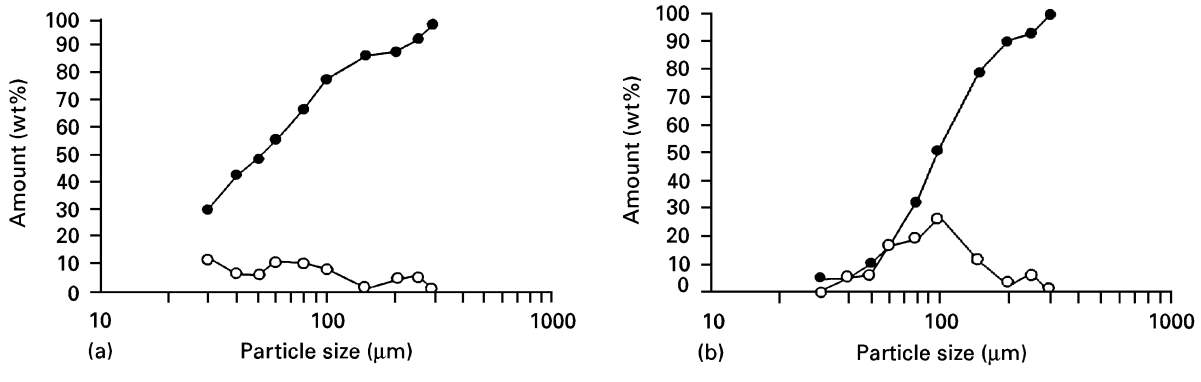

Figure 3 Cumulative weight percentage finer than a given particle size (●) and weight percentage of particles of a given size (○), for (a) as-received Al and (b) mechanically alloyed Al, milled for 10 h.

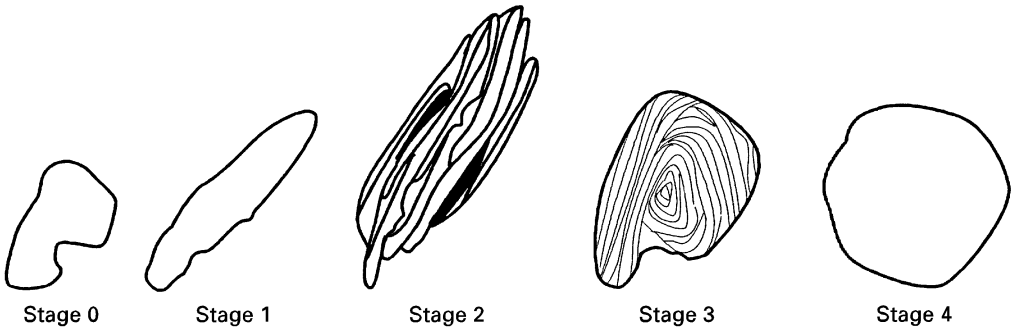

Figure 4 Schematic changing morphology of Al powder with milling time: (a) 0 h; (b) 1 h; (c) 2 h; (d) 4 h; (e) 10 h.

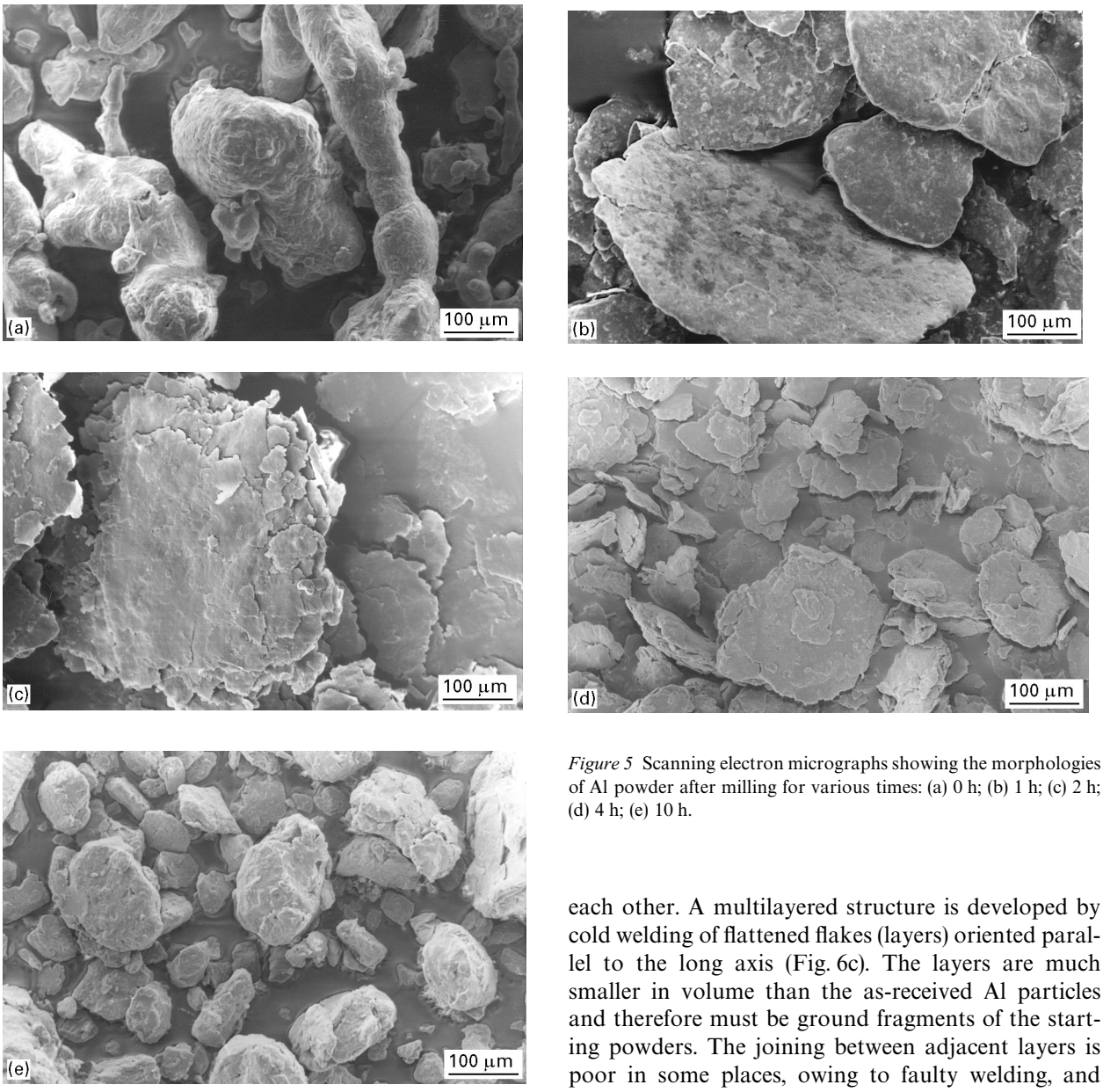

Figure 5 Scanning electron micrographs showing the morphologies of Al powder after milling for various times: (a) 0 h; (b) 1 h; (c) 2 h; (d) 4 h; (e) 10 h.

has an apparent density much smaller than that of the original powder (8.8 versus 36%), owing to difficulties in particle stacking (Fig. 7). It also lacks flowability (The as-received Al powder has zero Hall flowability, too.)

After milling for 2 h (stage 2), flake formation continues, especially for finer particles. Flakes weld to each other. A multilayered structure is developed by cold welding of flattened flakes (layers) oriented parallel to the long axis (Fig. 6c). The layers are much smaller in volume than the as-received Al particles and therefore must be ground fragments of the starting powders. The joining between adjacent layers is poor in some places, owing to faulty welding, and open spaces between themselves can be detected. These layers are very thin and the dendritic structure cannot be resolved by optical microscopy.

After the process has been under way for 4 h (stage 3), the multilayered elongated particles are transformed to a relatively equiaxed shape. The particles have a certain angular morphology, probably caused by fragmentation of their extremities. Multilayered flakes fold and/or break and reweld without any preferred orientation, causing a convoluted structure. The

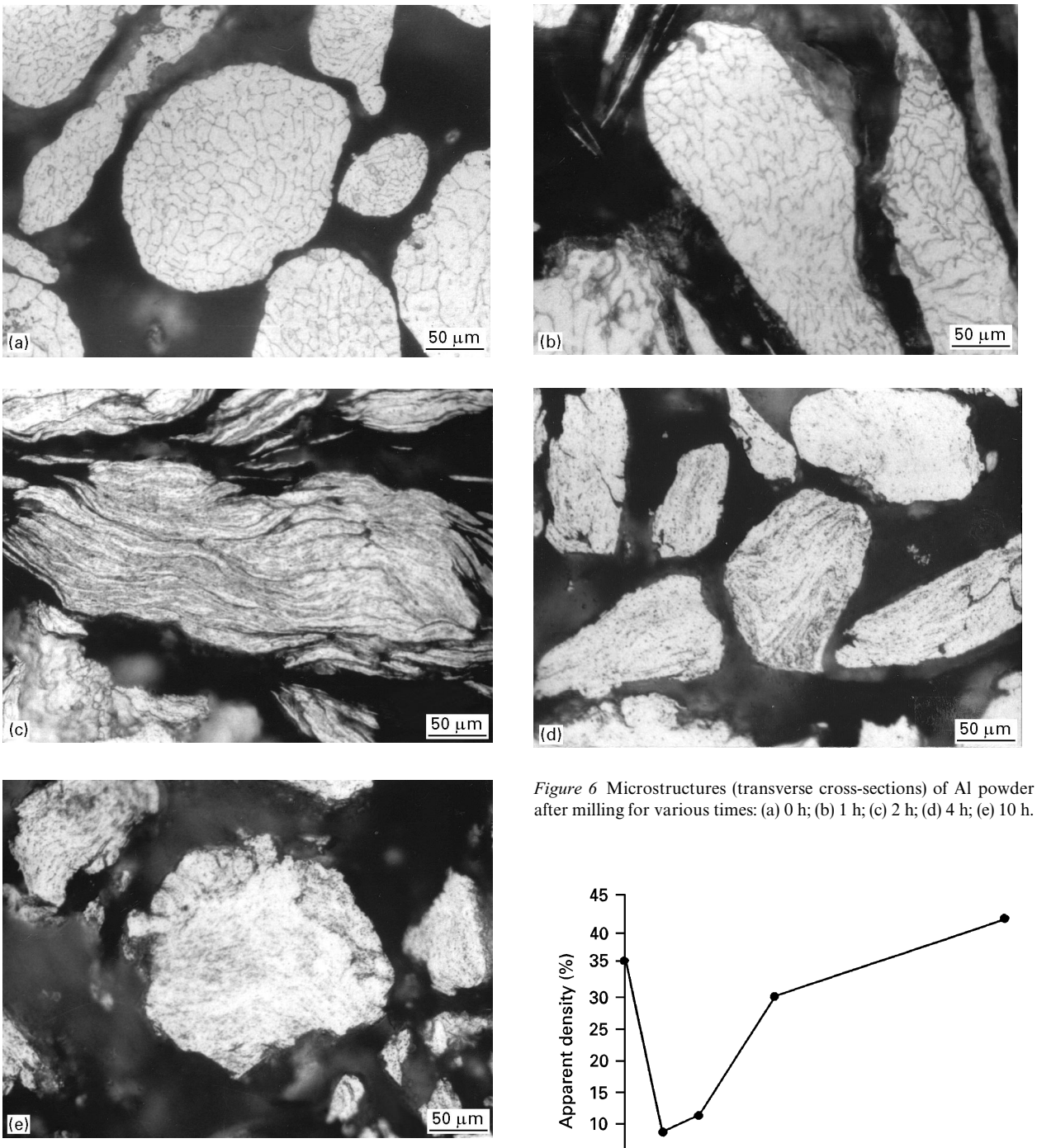

Figure 6 Microstructures (transverse cross-sections) of Al powder after milling for various times: (a) 0 h; (b) 1 h; (c) 2 h; (d) 4 h; (e) 10 h.

Figure 7 Apparent density of Al powder versus milling time.

layers, thus, become convoluted rather than being linear (Fig. 4d and Fig. 6d). Welding between layers is strong, but layer boundaries can be easily observed because of the alumina surface films remaining on them.

For milling times of longer than 10 h (stage 4), the powder is rather equiaxed and relatively spherically shaped (Fig. 5e). The internal layered structure has disappeared being replaced by a homogeneous dispersion of presumably alumina particles (Fig. 6e). These alumina particles ought not to be confused with the submicroscopic Al_2O_3 dispersoids. It may be concluded from these structural observations that the powder is mechanically alloyed. On the other hand, the mechanically alloyed Al powder has a relative apparent density of 42% (Fig. 7) and a Hall flowability of 60 s/50 g. Both values are appropriate for PM processing.

The changes in particle morphology and structure reported in this investigation are *a grosso modo* in agreement with the findings of Benjamin and Volin [11] during the MA of a mixture of Fe and Cr powders in a high-energy shaker mill.

The variation in microhardness with milling time is shown in Fig. 8. The data are widely scattered, but milling produces a rapid, almost linear increase in hardness over that of the starting powder. After milling for 10 h, the Vickers microhardness (127 HV) is more than six times that at the beginning of processing (20 HV). After milling for between 10 and 20 h, the

TABLE II Properties of as-received Al and mechanically alloyed Al (milling time, 10 h) powders

Property	Value for the following	
	As-received Al	Mechanically alloyed Al
Mean particle size (μm)	50	97
Apparent density (%)	36	42
Tap density (%)	56	54
Flowability (s/50 g)	No flow	60
Microhardness (load, 0.02 kgf) (kgf mm^{-2})	20	127

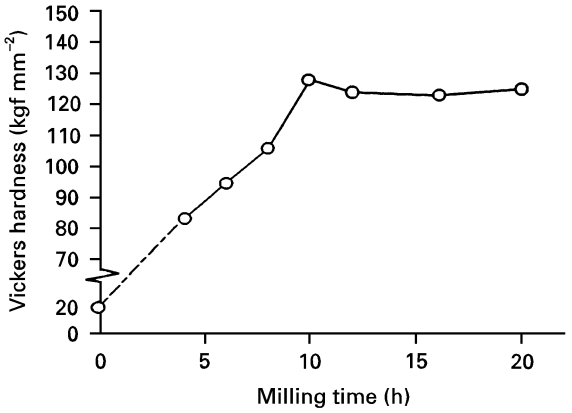

Figure 8 Microhardness of powder as a function of milling time (load, 0.02 kgf).

microhardness of the powder particles fluctuates around a value of 125 HV. The high hardness of mechanically alloyed Al is probably due to grain refinement and dispersion strengthening brought about by submicroscopic Al_2O_3 and Al_4C_3 particles [5]. The full cold-worked structure is most likely not retained, since high-energy grinding of Al may promote dynamic recovery. This could give rise to repeated subgrain formation and a final refined structure.

Properties of as-received Al and mechanically alloyed Al (milling time, 10 h) powders are shown in Table II. The average particle size increases with milling (from 50 to 97 μm) because the balance between cold welding and particle fracture is only partially attained. The particle rounding caused by milling could account for the higher apparent density (42 versus 36%) and flowability of mechanically alloyed Al in relation to the as-received powder (60 s/50 g versus no flow). Finally, the slightly lower tap density of mechanically alloyed Al (54 versus 56%) is in contradiction to its better roundness. It could be explained by the narrow particle size distribution of mechanically alloyed Al powder (Fig. 3). The variety of particle sizes favours a close stacking and, thus, a high tap density.

4. Conclusions

The evolution of microstructure and some properties of aluminium powder, milled in an attritor in the presence of 1.5% of a wax, has been studied. The particle size distribution varies with milling time in a clear tendency to particle coarsening during the first 10 h; subsequently, the mean particle size grows at a much lesser rate.

The starting irregular equiaxed particles change their morphology and structure through the stages of flattening, welding of parallel flakes, folding of multilayered flakes and formation of relatively equiaxed particles with a homogeneous structure.

The Vickers microhardness shows a substantial increase with increasing milling time up to 10 h (six times that of the starting powder); thereafter, a sort of saturation hardness is reached.

In view of these results (for the equipment and processing conditions employed) a milling time of 10 h was chosen for the mechanical alloying of the Al powder.

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References

1. J. S. BENJAMIN, *Metall. Trans.* **1** (1970) 2943.
2. J. S. BENJAMIN and M. J. BOMFORD, *Metall. Trans. A* **8** (1977) 1301.
3. G. JANGG, *Aluminium* **51** (1975) 641.
4. P. S. GILMAN, PhD Thesis, Stanford University, Stanford (1979).
5. R. F. SINGER, W. C. OLIVER and W. D. NIX, *Metall. Trans. A* **11** (1980) 1895.
6. E. A. BLOCH, *Metall. Rev.* **6** (1961) 193.
7. F. H. FROES and C. SURYANARAYANA, *Metal Powder Rep.* **49** (1994) 14.
8. G. NAESER, *Int. J. Powder Metall.* **6** (1970) J1.
9. R. SCHRADER, *Technik* **24** (1969) 88.
10. A. SZEGVARI, US Patent 2, 764,359, 25 September (1956).
11. J. S. BENJAMIN and T. E. VOLIN, *Metall. Trans.* **5** (1974) 1929.

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