Synthesis and characterization of in situ reinforced Al - AlN composites produced by mechanical alloying

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Abstract. This research is focused on the production of aluminum matrix composites (AMCs) reinforced with various percentages of aluminum nitride (AlN). For this purpose, aluminum powder was milled at room temperature for a total time of 5 hours. The percentage of reinforcement is varied by milling under different periods of vacuum followed by ammonia gas flow. X-ray diffraction analysis showed the benefits of using a combined milling atmosphere to form, after the heat treatment of the powder, a higher amount of AlN. Results showed that the period in vacuum determines the greater or lesser capacity to absorb nitrogen during the ammonia gas period. Even using shorter vacuum milling periods, the AlN formed after sintering can be increased.

1. INTRODUCTION

Aluminum alloys represent an important category of materials that have attracted the interest of aerospace and automotive industry due to their low weight. Since there is an increasing demand of light alloys with remarkable mechanical properties, research on processing and manufacturing of Al alloys is strongly required.

The development of aluminum matrix composites (AMCs) allows improving the performance of conventional aluminum alloys [1, 2]. In the last few years, AMCs have been successfully used both in structural and functional applications, mainly due to their low density, high strength to weight ratio, good formability and wear resistance [3, 4]. These properties, partially obtained through the attainment of a nanostructured Al matrix, represents a very attractive research line [5-8]. Furthermore, properties can be tailored to a specific application by choosing the processing route, as well as the suitable combination of matrix and reinforcements. AMCs can be manufactured by different routes such as accumulative roll bonding (ARB) [9], anodizing and ARB processes [10], stir and compo-casting procedures [11] and also by powder metallurgy [12]. The reinforcement in AMCs can be in the form of particles, whiskers, and continuous or discontinuous fibers.

Traditionally, aluminium has been reinforced by the dispersion of fine oxides and carbides particles [13-15], which can be carried out both in liquid and solid-state. However, the resulting

dispersoids distribution achieved by liquid methods is generally inhomogeneous, while solid-state routes based in reaction milling allow obtaining a much more homogeneous distribution.

Mechanical alloying (MA) is a solid-state powder processing technique carried out in a high-energy ball mill. It is usually a dry process that allows the production of homogeneous materials starting from elemental powder mixtures [16]. This technique has been employed to develop a variety of commercially useful and scientifically interesting materials [17-21]. Traditionally, in the powder metallurgy field, aluminum has been reinforced with a variety of directly-added particles [22, 23]. However, it has been proved that MA is a process capable of producing a direct reaction between the metallic powder and the milling atmosphere [24, 25]. As result, aluminum can be reinforced with finely dispersed phases through direct reaction giving rise to aluminum matrix composites [5].

In this paper, ammonia gas was used to prepare aluminum matrix composites reinforced by solid-gas reaction during mechanical alloying. The aim of the research is to study the reactivity of aluminum powders with the ammonia gas during milling as a function of the vacuum and ammonia gas flow time used. The effectiveness of producing aluminum nitride, depending of the duration of each one of the milling stages, was studied.

2. MATERIAL AND METHODS

The starting material was atomized elemental aluminium powder (AS 61, Eckart) with a purity higher than 99.7% and a mean particle size of 80.5 μm. A high-energy attritor ball-mill was used to process the Al powder, with a water-cooled stainless steel vessel having a capacity of 1400 cm^3. A 3 wt. % micropowder organic wax (ethylene bis-stearamide, EBS) was used as process control agent (PCA) to balance welding and fracture processes during milling. The mill contained 72 g of powder and 3600 g of balls (charge ratio 50:1). All milling experiments were performed with a rotor speed of 500 rpm, at room temperature, and for a total time of 5 hours. The experiments started under vacuum and, after a period between 1 and 4 hours, an ammonia gas flow (1 cm^3/s, purity higher than 99.96%, Air Liquide) was incorporated until the total time of milling was reached. For comparison purposes, samples of powders milled for 5 hours in vacuum were also consolidated.

Cylindrical (diameter: 12 mm; mass: approximately 4 g) compacts were produced from all milled powders by cold uniaxial pressing (850 MPa) and vacuum (5 Pa) sintering (650 ℃, 1 h), followed by furnace cooling. EBS wax was also used as die-wall lubricant during cold pressing.

Particle size distribution of powders was obtained by laser diffraction (Malvern Mastersizer 2000), whereas their morphology was studied using a scanning electron microscope (SEM, Philips XL-30). X-ray diffraction analysis (XRD, Bruker D8 Advance, using Cu-K$_\alpha$ radiation) was used to identify the different phases present in the materials. The density and hardness (Emco M4U-025) of the compacts were also determined.

3. RESULTS AND DISCUSSION

Mechanical alloying is a high-energy milling process involving an intense plastic deformation of aluminium particles, which leads to strain hardening and fracture. The particle size of the milled powder is a key factor during a subsequent sintering process, with a much higher tendency to sinter for particles with smaller sizes and higher specific areas. Under vacuum conditions, milling promotes a gradual increase of the aluminium brittleness, and thereby the particle size slowly decreases (Figure 1a). Thus, mean particle size is reduce in a 64% when as received Al (AR Al) powder is milled in vacuum for 5 hours (5V), going from 80.5 µm to 29 µm. However, if a flow of ammonia gas is incorporated to the milling process, particle size is further reduced. All mechanically alloyed powders with a sequence vacuum-NH_3 have, independently of the ammonia gas flow duration, a smaller particle size than 5V powders (Figure 1b). This behaviour occurs even for millings in which the ammonia gas flow only lasts one hour (4V+1A).
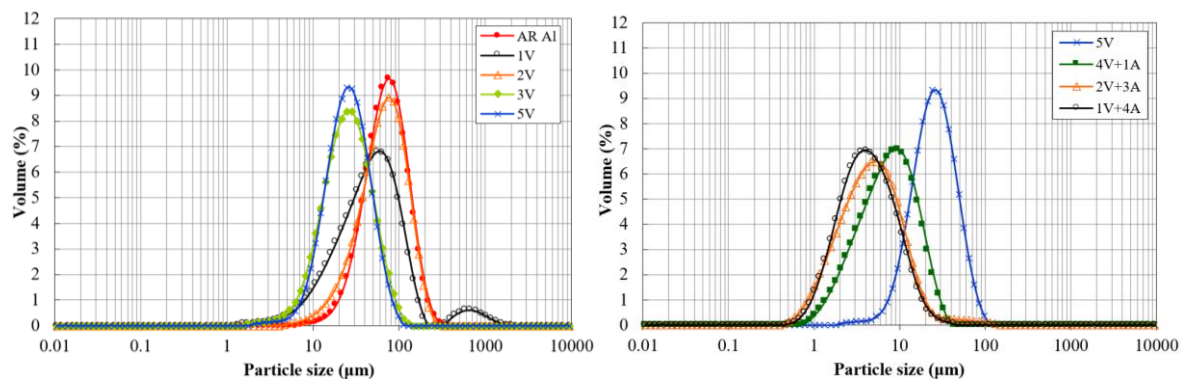

Figure 1. Particle size distribution of (a) AR Al and Al powders milled for different times in vacuum, and (b) Al milled under different combinations of vacuum and ammonia flow atmospheres.

Figure 2a shows that, for vacuum millings, the mean particle size increases with respect to AR Al during the first hour, and starts decreasing from the second hour. During milling, the powder particles are repeatedly flattened, cold welded, fractured and rewelded. After one hour, particles acquire a flake shape [8], most of them with a size smaller than AR Al, although, as shown in Figure 1a, a few of them tend to weld to each other forming very big agglomerates of 400 - 1000 µm, so that the mean particles size increases. After some time, particles harden and become brittle, so that their size decreases and their specific surface area increases. On the other hand, a high decrease in particle size is observed when NH_3 is incorporated to the milling atmosphere. Figure 2b show that the longer the ammonia milling time, the lower is the mean particle size and the higher the specific surface area. In this way, ammonia plays a key role in particle size reduction, allowing to obtain particle sizes smaller than 10 µm. Thus, an ammonia flow of one hour (4V+1A) allows achieving a particle size reduction of 68% with respect to the milling carried out exclusively in vacuum (5V). An additional reduction of 39%, respect to 4V+1A powders, is achieved when the ammonia flow time is prolonged for three more hours (1V+4A).
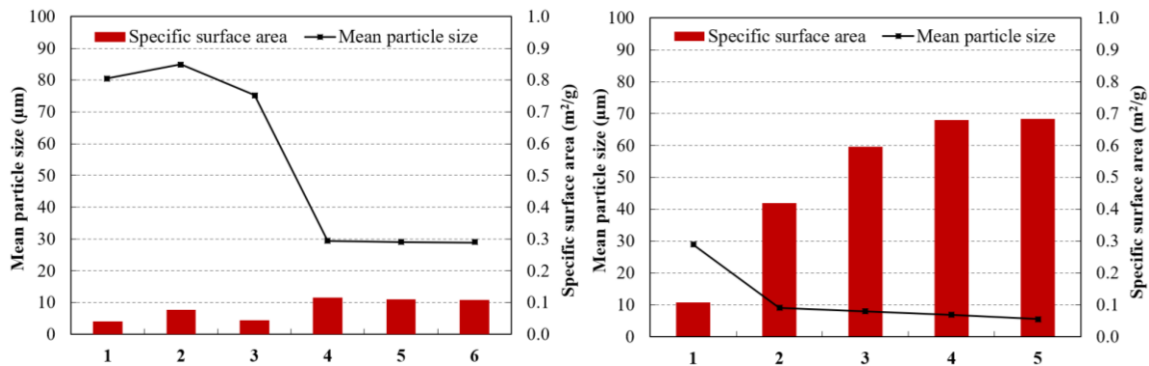

Figure 2. Mean particle size and specific surface area of (a) AR Al and Al powders milled for different times in vacuum, and (b) Al milled under different vacuum-NH3 sequences.

Indeed, SEM micrographs in Figure 3, corresponding to 5V and 4V+1A powders, allow to verify the aforementioned. In general, both powders have an equiaxial morphology, but milling with ammonia allows reaching a smaller size, despite the energy transferred during milling was the same for both experiences. Accordingly, ammonia gas has a direct effect on Al particle size reduction during the mechanical alloying process.
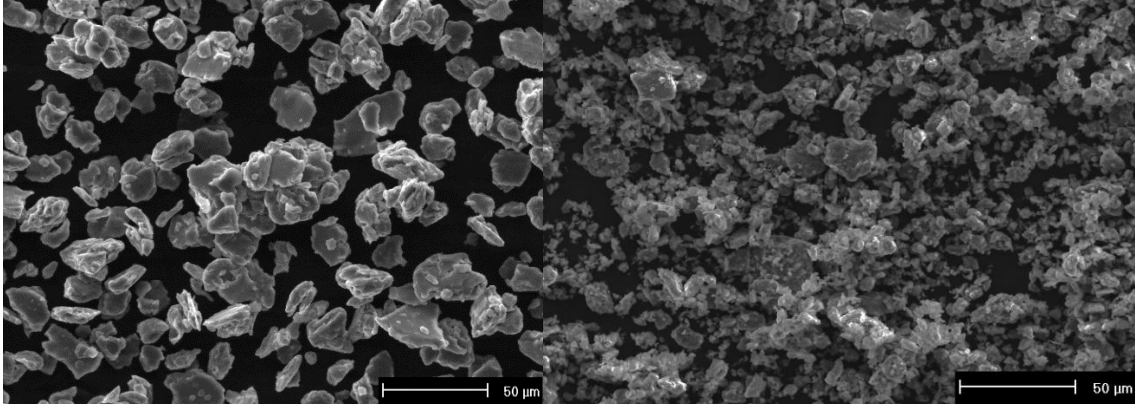
Figure 3. SEM-SE images of (a) 5V and (b) 4V+1A milled powders.

In addition to the ammonia effect on particle size, it is interesting to know the solid–gas reactions taking place during the milling process. To this end, XRD analyses were carried out on milled powders after being heat treated at 650 ºC for 1 hour (Figure 4). Thus, besides the Al peaks, reflections of aluminium carbide (Al_4C_3) and aluminium oxide (Al_2O_3) were detected in 5V powders. The carbides come from the organic wax used as PCA, while the oxides come from the Al particles surface. However, if ammonia is incorporated into the milling (4V+1A, 3V+2A, 2V+3A and 1V+4A), nitrogen-rich phases also appear, mainly aluminium oxynitrides and nitrides (Al_5O_6N and AlN, respectively). Furthermore, peaks corresponding to AlN grow, whereas those of Al_5O_6N very slightly decrease, as ammonia gas flow is prolonged.
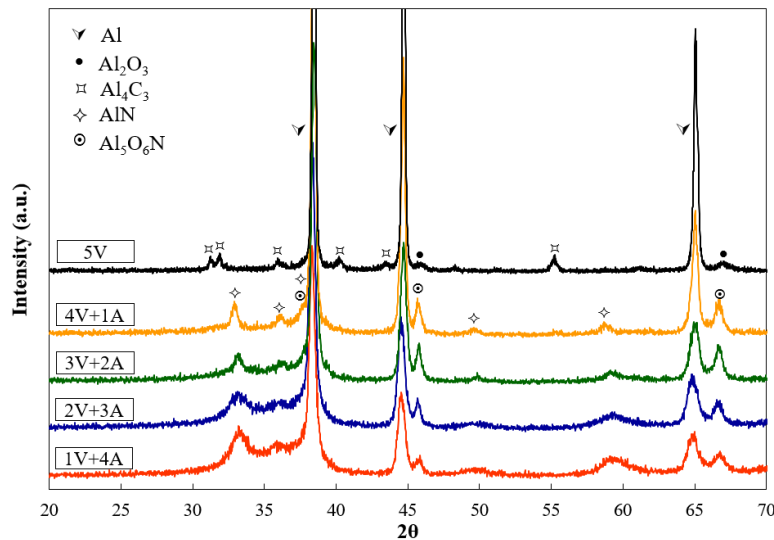

Figure 4. X-ray diffraction patterns of mechanically alloyed Al powders under different atmospheres after being heat treated at 650 ºC.

Therefore, results clearly show the reaction taking place between solid and gaseous elements contained in the milling vessel during the MA process. It should be taken into consideration that such reaction takes place due to the combination of two factors; firstly, the high energy of the MA process, which promotes the ammonia gas dissociation. And secondly, Al particles are broken and lose their Al_2O_3 layers during the milling period in vacuum, forming fresh Al surfaces. Moreover, as shown in the present study, milling provokes an increase of the specific surface area, which also helps intensifying the reactivity of the aluminium powders. The result is an Al powder with a high specific surface area and fresh surfaces avid to react, which favours the rapid adsorption of nitrogen and its incorporation into the Al crystal lattice, hardening it by solid solution [26]. Therefore, this effect strengthens the aluminum powders and is also responsible for the additional particle size reduction when the ammonia flow is incorporated to the milling process.

The XRD patterns were fitted via Rietveld refinement [27] to calculate the weight percentage of the phases formed during the heat treatment. Results reveal that the amount of Al decreases and that of AlN increases with the ammonia flow time (Table 1). Thus, 4V+1A powders have a 65 and 27 wt.% of Al and AlN, respectively. On the contrary, such amounts are reversed for 1V+4A powders, with a 28 wt.% of Al and 66 wt.% of AlN. It can also be observed that the weight percentage of AlN produced per hour of ammonia flow decreases with milling time, mainly from the third hour. As previously indicated, 4V milled powders have a specific surface area higher than 1V powders. Therefore, just at the beginning of the ammonia flow period, 4V+1A powders have a higher specific surface area to react than 1V+4A powders (Figure 2a), so the nitrogen incorporation to the Al lattice must be carried out in a more efficient way. However, after the first hour of ammonia gas flow, the reactivity of aluminium particles decreases, behaving as a solid solution which approaches to its saturation degree. Therefore, the amount of AlN formed during the rest of the heat treatment decreases.

Table 1. Weight percentage of the phases formed during the sintering process of the different materials.

Phase	Material				
	4V+1A	3V+2A	2V+3A	1V+4A	4V+4A
Al	65	47	33	28	43
AlN	27	45	60	66	50
Al_5O_6N	8	8	7	6	7

A new milling with a total time of 8 hours, four in vacuum and four under ammonia gas flow, was carried out to find out what period is most relevant during milling. The specific surface area is the same for 4V+1A and 4V+4A powders after the vacuum period (Figure 2a), therefore the weight percentage of AlN increases by extending the ammonia gas flow (Table 1). On the other hand, it is also interesting to compare this new milling (4V+4A) with that carried out with a shorter vacuum period followed by an ammonia gas flow of the same duration (1V+4A). In this case, a higher weight percentage of AlN is reached for 1V+4A powders, in spite that its specific surface area after the vacuum period is lower than that of 4V+4A powders. As can be observed in Figure 2a, a steady state is attained when AR Al powder is milled in vacuum for 3 or more hours, with particle size and specific surface area not changing any more. By contrast, if AR Al powder is milled for only 1 hour in vacuum, powder particles will tend to follow evolving during the period in ammonia gas flow, continuing with the fracture and cold welding processes. At the beginning of the ammonia period, the gas reacts with the fresh surfaces of aluminum particles, at the same time that external surfaces will become internal due to cold welding processes and new fresh surfaces will be form as result of fracture processes, favoring the additional nitrogen adsorption. On the other hand, at the end of the vacuum period, 4V+4A powders have already reached their steady state. Accordingly, the formation of new surfaces during the ammonia period is not so relevant, resulting in a lower nitrogen adsorption. Therefore, it can be concluded that both the period in vacuum and under ammonia gas flow are important, being the main parameter the vacuum milling time.

Figure 5 shows the weight percentage of AlN, relative density and Brinell hardness of the different sintered compacts obtained from milled powders. The low hardness of 5V powders makes possible to reach densities higher than 90% after the consolidation stage; however, increasing the milling time under NH_3 flow makes the powders to harden, reaching densities between 80 and 90%. The increase of compacts hardness is not only due to the strain hardening during mechanical alloying, because the milling time was the same for all millings (5 hours). The strengthening of the compacts obtained from NH_3 milled powder is, mainly, the result of the N solid solution and the Al-N reactions during the subsequent sintering process. As can be seen in Figure 5, hardness and weight percentage of AlN show the same trend as the ammonia flow time is prolonged. Thereby, hardness increases as ammonia flow is prolonged, reaching values as high as 151 and 204 HB for 4V+1A and 1V+4A compacts respectively. In contrast, 5V compacts only reach a hardness value of 81 HB.
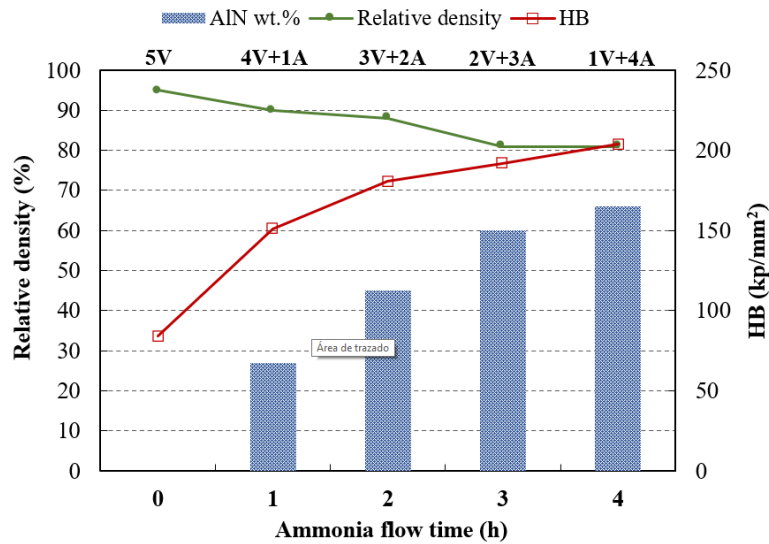
Figure 5. Relative density, Brinell hardness and weight percentage of AlN of sintered compacts obtained from milled powders.

4. CONCLUSIONS

In this paper, aluminum powder was mechanically alloyed both in vacuum and using a sequence of vacuum-NH_3 gas flow. Results show that ammonia gas plays a complementary role in particle size reduction, together with the strain hardening due to the milling lasting. Thereby, particle size of AR Al powder (80.5 µm) is further reduced when ammonia is incorporated to the milling process (10 µm) with respect to a milling carried out exclusively in vacuum (29 µm). In addition to the ammonia gas effect on particle size, a solid-gas reaction takes place during the milling process. Reflections corresponding to nitrogen-rich phases (AlN and Al_5O_6N) were detected by XRD analysis after heat treating the powders. Rietveld quantification shows that the weight percentage of AlN increases with ammonia flow time, reaching values as high as 60 wt.% and 66 wt.% for 2V+3A and 1V+4A samples, respectively. Results reveal that both the period in vacuum and under ammonia play a key role in Al powder reinforcement. However, the period in vacuum determines the greater or lesser capacity to absorb nitrogen during ammonia gas period. As result, the capability to absorb nitrogen is higher for 1V+4A powders than 4V+4A powders (66 wt.% vs. 50 wt.% of AlN, respectively), even though the period under vacuum lasted three hours less. Accordingly, compacts from 1V+4A powders reach a much higher hardness than compacts from 5V powders (204 HB and 81 HB, respectively).

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