

Use of Urea and Ammonia to Produce High-Strength PM Aluminium Parts

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Abstract. Two methods to obtain bulk nanostructured aluminium parts are compared. The first one consists on milling Al powder in an ammonia gas atmosphere. In the second method, the Al powder is milled in vacuum with the addition of solid urea. In both cases, the milled powders are consolidated to full density by a conventional press-and-sinter powder metallurgy (PM) technique. The produced composites consist on a nanostructured aluminium matrix reinforced with self-forming nanocrystalline nitrides dispersoids. Consolidated compacts reach full densification, and show a high tensile strength (up to 550 MPa) and an outstanding high-temperature behaviour.

INTRODUCTION

Mechanical alloying (MA) is a high-energy milling process capable of producing microstructurally fine composite metal powders. It allows, through mechanochemical synthesis, the dispersion of fine ceramic second phases in a metal matrix. The use of MA for the mechanochemical synthesis of materials has aroused the interest of many researchers in recent years [1,2]. The advantage of this technique is the performing of supervised mechanochemical reactions, resulting in the composites formation directly in the mill. One of the most relevant features of MA is that it can trigger reactions, that usually require a high temperature, at near-ambient levels [3].

Mechanically alloyed aluminium (MA Al) can be prepared by high-energy attrition milling of elemental Al powder in the presence of a wax, used as process control agent (PCA). The sinterability of MA Al powder is a must during the P/M shaping processes [4-6]. MA Al is a hard powder, covered by oxide and hydroxide layers that avoid interparticle contacts and, thus, hinder sintering. It is therefore necessary to break these surface layers, so that consolidation is usually carried out by complex processes that include a hot high-deformation stage, generally hot extrusion [7]. A simpler press-and-sinter consolidation method [8] has been employed in this work for these powders.

During the last few years, many researchers have focused their interest in the unusual properties of nanostructured and ultrafine-grained (UFG) materials [9,10]. However, a relatively small amount of work has been carried out about macroscopic properties, especially mechanical testing, of nanocrystalline materials. The reason is mainly due to the difficulties for producing large enough bulk samples. MA is one of the techniques that allows to obtain nanostructured or UFG powders in near commercial quantities. The challenge is avoiding grain growing during the powders consolidation.

In the present investigation, the production of nanostructured aluminium-based PM parts by two different developed methods is studied. The aim is to obtain a very hard and sinterable Al powder able to succeed in a simple press-and-sinter PM consolidation process.

EXPERIMENTAL

Atomised elemental aluminium powder, 99.7wt% purity, was used as starting material. The particle mean size is 44 µm, and the main impurity of the as-received Al powder (AR Al) was iron (0.2wt%Fe).

The Al powder was milled in a Szegvari vertical attritor, either in an atmosphere of 1.3 10⁵ Pa confined ammonia gas (MA Al A), or in vacuum (5 Pa) adding a 2.1wt% urea (MA Al U). Milling tests in the presence of urea were conducted in vacuum in order to avoid the effect of the milling atmosphere. For comparison, vacuum millings of Al powder, without additions of urea, were carried out (MA Al V). The duration of all the milling experiences was 10 h, and a 3wt% of ethylene-bis-stearamide (EBS)

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powder was added as PCA. A more detailed description of milling conditions can be found elsewhere [12]. Powders were characterized concerning particle size, grain size, presence of second phases and compressibility.

All milled powders were consolidated by a simple PM process. It consists on a cold uniaxial pressing stage at 850 MPa, and a vacuum (5 Pa) sintering at 650 °C for 1 h. Compaction was made using the EBS wax as die wall lubricant. The AR Al powder was consolidated by the same method, pressing at only 150 MPa.

Consolidated compacts were tested concerning relative density, hardness and tensile properties. Structural and fractographic studies were performed using X-ray diffraction (XRD, Bruker D8 Advanced, Cu K α radiation), scanning electron microscopy (SEM, Phillips XL30), and transmission electron microscopy (TEM, Phillips CM200) equipped with an energy dispersive x-ray spectrometer.

RESULTS AND DISCUSSION

Powder study

By monitoring the gas pressure variation during the MA Al A milling process, it can be determined the amount of ammonia present and, therefore, the nitrogen mass incorporated into the aluminium powder during the 10 h millings (0.722 g). To include the same amount of nitrogen in the urea millings, and taking into account the employed urea purity (98.5 %), a 2.1wt% of this substance has been added in MA Al U millings.

Powders milled in vacuum, in ammonia, or milled in vacuum with urea have a relatively equiaxed morphology (Fig. 1). In the three cases, milling produces an important decrease in powder particle size, falling to 16.7 μm for MA Al V, 12.6 μm for MA Al A, and 12.5 μm for MA Al U.

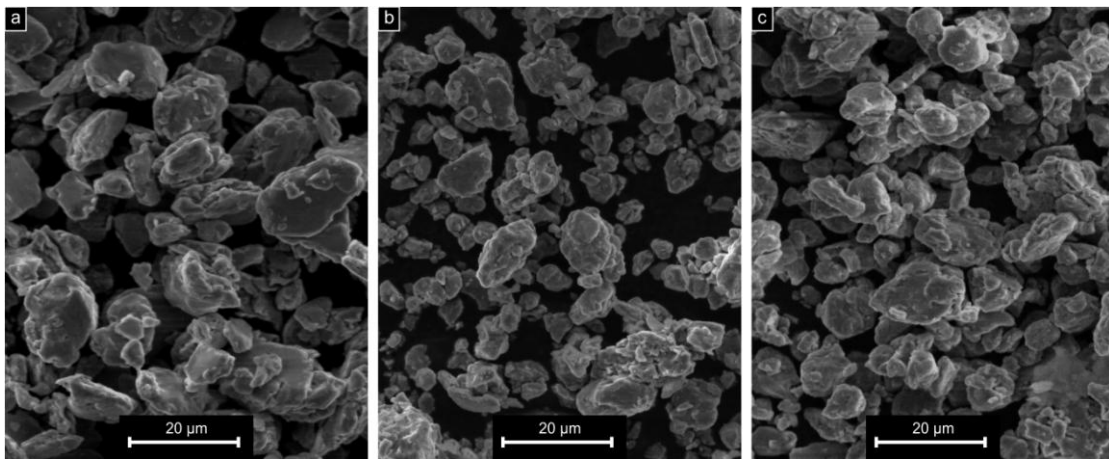


Fig. 1. SEM-SE micrographs of a) MA Al V, b) MA Al A and c) MA Al U powders.

During milling, Al particles undergo severe plastic deformation and they are brought into intimate contacts forming cold welds. With continued plastic deformation, grain size refinement and solid solution formation, the powder hardness increases and repetitive fracture occurs. At the same time, PCA covers powder particles preventing excessive welding, and establishing a dynamic balance between fracturing and welding.

In MA Al V millings, carbon coming from the PCA, gets into the aluminium lattice producing powder hardening [13]. This process increases *fracture/welding* ratio and, as a consequence, decreases the mean powder particle size. Smaller size of MA Al A powders is the result of additional enrichment in nitrogen, mainly, due to the NH₃ decomposition.

XRD of milled powders shows that no phases are formed during mechanical alloying (Fig. 2, bottom), independently of using vacuum, ammonia or adding urea. Therefore, in all cases, elements as carbon, nitrogen and oxygen are forming solid solutions with the milled aluminium. Applying the Williamson–Hall and Langford methods, after Rietveld adjusting of XRD patterns, it can be verified the nanostructured nature of the milled powders. The three milling conditions produce powders with a mean crystallite size of about 25 nm.

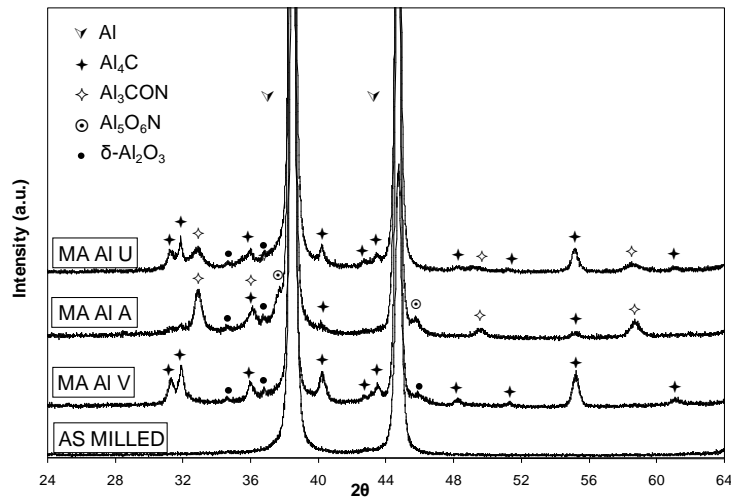


Fig. 2. XRD patterns of as-milled powders, and as-sintered MA Al V, MA Al A and MA Al U powders.

The nano-crystalline nature of milled powders was supported by TEM examination (Fig. 3). Powder particles were ultramicrotomed after being embedded in Spurr's resin. Image analysis of TEM micrographs gives values for the aluminium grain size (ca. 25 nm) that fit in with XRD results. No second phases were detected by TEM and therefore, as expected from XRD analysis, carbon, nitrogen and oxygen are in solid solution.

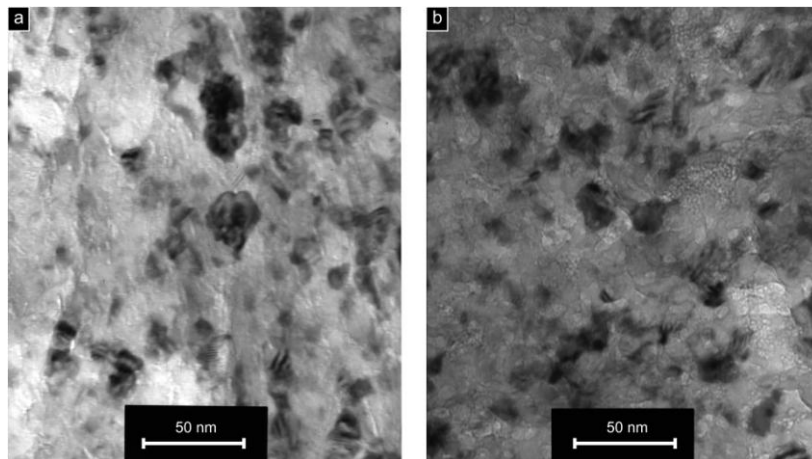


Fig. 3. Aluminium grains in a) MA Al A and b) MA Al U milled powders revealed by TEM.

Small particle size of powders prevented us from doing microhardness tests. However, hardness of milled powders can be indirectly measured by a compressibility test [13]. MA Al U (Fig. 4) is the least compressible (hardest), whilst the unmilled powder (AR Al) is the softest. Oxygen coming from the oxide film covering Al particles, and carbon and oxygen coming from PCA decomposition makes vacuum milled powder (MA Al V) harder than as-received aluminium. In MA Al A powders, nitrogen coming from ammonia increase powder hardness by solid solution with respect to MA Al V. Nitrogen content in powders milled with ammonia or urea is the same. Nevertheless, extra amounts of carbon and oxygen coming from urea decomposition makes this powder to be the hardest.

Although milled powders have different compressibility grades, a pressure of 850 MPa was chosen to compact all of them. This pressure can be employed in industrial plants, and permits the production of green compacts with a relative density of around 87 %. At this level of densification, the porosity in the green compacts is of the interconnected type, and this facilitates gas evacuation during the sintering process. The soft AR Al powder reaches the same relative green density when pressed at 150 MPa.

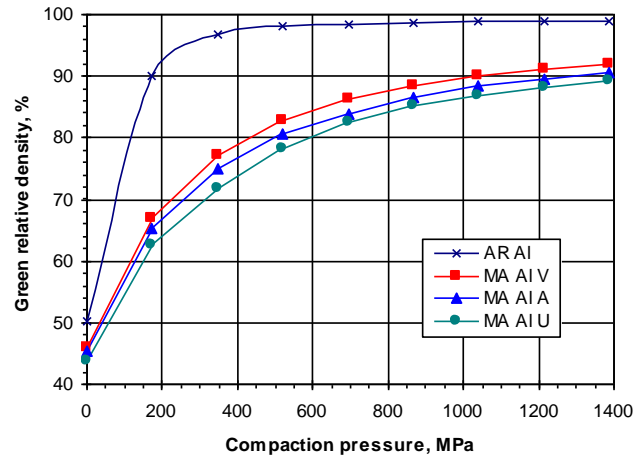


Fig. 4. Compressibility tests for as-received and milled aluminium powders.

Characterization of sintered samples

Crystalline second phases formation takes place, for all the studied materials, during powders sintering. In MA Al V compacts, carbon in solid solution combines with aluminium forming Al_4C_3 (Fig. 2). As shown in authors' previous works [12], aluminium carbide appears with its characteristic rod-like morphology and a size of approximately 150 nm. MA Al V can be considered an ultra-fine-grained material because the aluminium grains forming the matrix have a mean size of 550 nm.

The aluminium carbide (Al_4C_3), present in MA Al V sintered compacts, was virtually absent in MA Al A samples (Fig. 2). In fact, it was replaced by aluminium oxycarbonides (Al_3CON) and oxynitrides ($\text{Al}_5\text{O}_6\text{N}$). As occurs in MA Al V compacts, a small amount of $\delta\text{-Al}_2\text{O}_3$ is also present. It should be noted that these dispersoids were incorporated by milling in ammonia gas at room temperature, not needing techniques as cryomilling [14] to form them.

In the same Fig. 2, the XRD pattern for the MA Al U compacts shows a slight decrease in Al_4C_3 content in comparison with the MA Al V samples. However, the intensity decrease is smaller than in MA Al A. The MA Al U pattern includes reflections for Al_3CON , but such reflections are weaker than in MA Al A. The reflections for $\text{Al}_5\text{O}_6\text{N}$ are even weaker, practically imperceptible. Solid-gas reactions in millings with ammonia, more effective than solid-solid reactions produced in the case of using urea, seems to affect the formation of one or other phase.

The additional formation of aluminium carbonitrides and oxycarbonitrides in MA Al A sintered compacts highly restrains Al grain growth during sintering. Thus, the equivalent mean size of the aluminium grains, as measured by TEM, decreases from 550 nm in MA Al V [12] to 200 nm in MA Al A (Fig. 5a).

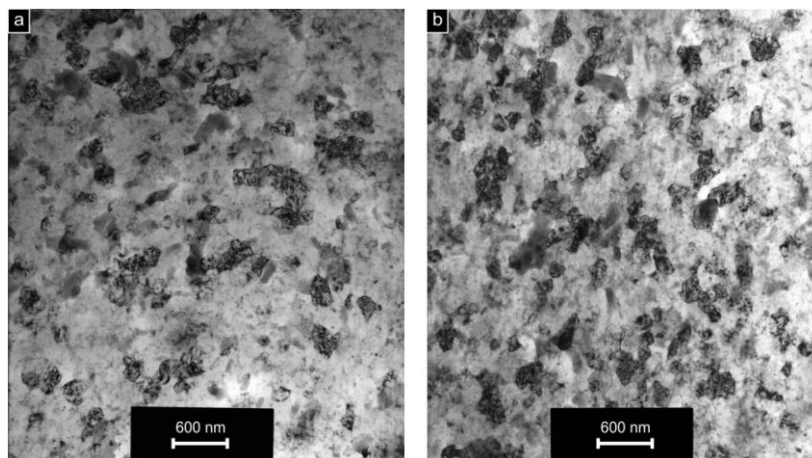


Fig. 5. TEM bright-field image of sintered a) MA Al A and b) MA Al U compacts showing their nearly nanometric structure.

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As can be seen comparing Figures 5a and 5b, the dispersoids formed in MA Al U compacts restrain Al grain growth, during sintering, in a manner similar to that made in compacts from powder milled in ammonia. The result is that the mean grain size of aluminum in compacts milled with urea is approximately 150 nm, according to the measurements based in TEM images analysis and XRD pattern quantification [15].

Macroscopic properties of sintered materials

Both the compacts from powder milled in ammonia and prepared with powder milled with urea can be considered nearly nanostructured materials reinforced by nanometric phases of ceramic nature. These features have a significant influence on macroscopic properties of compacts, being shown some of the most important in Table 1.

Table 1. Properties of consolidated compacts.

MATERIAL	D, %	At room temperature			At 250 °C	
		HB, kp/mm ²	UTS, MPa	E, %	UTS, MPa	E, %
AR Al	98.5	21	67	9.8	-	-
MA Al V	97.0	96	302	1.1	158	1.0
MA Al A	100	163	515	0.6	306	0.6
MA Al U	100	185	550	0.7	345	0.5

Compacts from MA Al V have a 3% of porosity, a hardness of 96 HB, a high ultimate strength (302 MPa) and a relatively low elongation (1.1%). The hardness and strength values of the MA Al V material are more than four and a half times higher than the corresponding values of the unmilled PM aluminum (AR Al). Basically, this is the result of the grain size refinement and dispersion strengthening (carbides and oxides) produced as a consequence of mechanical alloying. The elongation, as expected, is much lower than in the AR Al material.

On the other hand, the MA Al A specimens exhibits better sinterability than the MA Al V. This is seemingly related to a potentially beneficial effect of the aluminium oxycarbonitrides formed on the powder particles, as suggested by preliminary studies conducted in our laboratory and by other authors [16,17]. This improvement in sinterability, coupled with significant grain refinement (200 nm *versus* 550 nm, for MA Al A and MA Al V, respectively) and the dispersion strengthening, notably increases compacts hardness. Compacts from powder milled in ammonia have a Brinell hardness 70% higher than that of the compacts from powder milled in vacuum (Table 1). The same applies to the ultimate tensile strength, the 515 MPa reached by MA Al A compacts is well above the 302 MPa of MA Al V sintered parts.

A comparison of the hardness and tensile strength of the MA Al U compacts with those of the MA Al A compacts (Table 1) reveals that urea constitutes an effective replacement for ammonia. In fact, it additionally resulted in a similar compact density and a higher tensile strength (550 MPa *versus* 515 MPa). These differences can be ascribed to the chemical composition of urea, CO(NH₂)₂, that allows including an extra amount of carbon and oxygen in aluminium. Both MA Al A (0.6%) and MA Al U (0.7%) elongations are very low, and studies are being performed to improve them.

On the other hand, the use of commercial aluminium alloys is limited to applications below around 150 °C, due to their low mechanical performance at higher temperatures. The reason for this is that strengthening of these alloys is based on non-stable second phases. For instance, at 260 °C, the UTS of two wellknown high-strength wrought Al alloys, 7075-T6 and 2024-T6, is only 75MPa [18], due to overaging. However, bulk nanostructured MA Al U specimens retains a strength of 345MPa at a very similar temperature of 250 °C (Table 1), i.e., it is about 4.5 times stronger than high-strength commercial alloys.

The outstanding properties of the MA Al A and MA Al U materials are more remarkable considering the simplicity of the powder consolidation technique used, that is, a press-and-sinter method. In addition, these processing technique allows producing large series of parts without subsequent machining.

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CONCLUSIONS

The purpose of this work was to compare two methods to obtain high strength aluminium materials consolidated by cold pressing and sintering. In one of them, aluminium powder is milled in confined ammonia gas, while in the second case the milling is performed in vacuum but with the addition of urea. Results attained lead to the following conclusions:

- Both methods allow producing Al based bulk nanostructured materials, combining the grain size reduction during mechanical alloying and the in-situ formation of dispersoids.
- Aluminium matrix composites developed have extremely fine, homogeneously distributed and thermally stable phases providing high dispersion strengthening and elevated temperature properties.
- Properties reached by compacts from powder milled in urea are even slightly better than those of compacts from powder milled in ammonia. Thus, a handy and safe product as urea constitutes an effective replacement for ammonia in this process.

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