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# 6061 Al reinforced with zirconium diboride particles processed by conventional powder metallurgy and mechanical alloying

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The homogenous distribution of the reinforcement phase is an essential condition for a composite material to achieve its superior performance. Powder metallurgy (PM) can produce metal matrix composites in a wide range of matrix reinforcement compositions without the segregation phenomena typical of casting processes. Particularly, mechanical alloying can be used to mix the matrix and reinforcement particles, enhancing the homogeneity of the reinforcement distribution. This work investigates the production of aluminium 6061 reinforced with zirconium diboride by mechanical alloying followed by cold pressing and hot extrusion, and compares the results with the same composite produced by conventional PM and hot extrusion. The incorporation of the $ZrB_2$ particles produces only a small increase in the material hardness, but a small decrease in the UTS when conventional PM is employed. Mechanical alloying breaks the reinforcement particle clusters, eliminates most of the cracks present in the surface of the reinforcement particles, decreases its size and improves its distribution. This enhancement of the composite structure, in addition to the metallurgical aspects promoted by mechanical alloying in the matrix, brings approximately 100% improvements in the composite UTS and hardness, compared with the composites obtained by PM. 

## 1. Introduction

Metal matrix composites (MMC) reinforced with ceramic materials usually have better service temperature, strength, creep resistance, wear resistance, and thermal stability, than the unreinforced matrix [1]. Particulate-reinforced composites, though not achieving the level of improvement of continuous fiber-reinforced composites, give isotropic materials with a better property/cost relation.

Particularly in the case of discontinuous MMCs, the homogeneous distribution of the reinforcing phase is an essential requirement [2]. Defects such as clusters of reinforcement particles impair the mechanical properties of the composite. Differences in particle sizes, densities, geometries, flow or development of an electrical charge all contribute to particle agglomeration [3]. Powder Metallurgy (PM) provides a better reinforcement distribution for a wide of reinforcement contents, when compared with casting process. In PM, the mixing of the matrix and reinforcement powders is the critical step towards a homogeneous distribution throughout the consolidated composite material, although subsequent processes, such as powder extrusion, can help to optimise the reinforcement distribution [4–6].

High-energy ball milling or mechanical alloying has been successfully used to improve particle distribution throughout the matrix [7–13]. Mechanical alloying, in which mixtures of powders are milled together in a high-energy mill, involves repeated deformation/welding/fracture mechanisms [14, 15].

Ceramic particles, mainly SiC and $Al_2O_3$, are the most widely used materials for reinforcement of aluminium alloys. More recently, new families of particle reinforcement have been used with promising results: intermetallic compounds (Al–Ni, Al–Fe, Al–Nb systems) [16, 17] and nitrides ($Si_3N_4$, AlN) [18–20].

However, new materials must be tested to optimise the composite strength and also other composite properties, such as wear behaviour and corrosion resistance. Zirconium diboride is a material of particular interest due its high melting point, high electrical and thermal conductivity, and chemical inertness [21, 22]. These properties make zirconium diboride an attractive candidate for reinforcement of aluminium alloys when corrosion and wear resistence is demanded.

The dual purpose of this work is the investigation of mechanical alloying followed by cold pressing and hot extrusion to produce composite materials, and the investigation of a new type of reinforcing material, $ZrB_2$. The composites produced by mechanical alloying are compared with similar composites produced by the conventional low-energy mixing process of matrix and reinforcement powders, as well as with the unreinforced alloy extruded from the as-received prealloyed aluminium alloy 6061 powder.

## 2. Experimental

Aluminium and zirconium diboride powders were used as matrix and reinforcement, respectively. The aluminium powder was supplied by Aluminium Powder Co. Ltd., West Midlands, England. Its chemical composition was: Mg: 0.96, Si: 0.69, Cr: 0.24, Cu: 0.19, Fe: 0.06. The maximum particle size was 75 $\mu$m. $ZrB_2$ particles have an average particle size of 7.9 $\mu$m and a theoretical density of 6.09 g/cm$^3$. Fig. 1 shows the morphology of the aluminium (a) and the $ZrB_2$ (b) powders. The reinforcement contents studied were 5 and 15% by weight.

The powders were mixed in a low-energy laboratory mixer (a horizontal ball mill) for 90 min at 150 rpm, and after that in a high-energy centrifugal ball mill (*Fritshc Gmbh*, model "*Pulverisette 6*"), with the following parameters: ball/charge ratio-6/1 (wt); ball diameter-20 mm; ball material-AISI 420 stainless steel; speed-700 rpm. As the process control agent (PCA), 1% (wt) of microwax was added. No atmosphere control was used. To observe how the reinforcement particles are incorporated into the matrix and determine the optimum milling time to achieve good reinforcement distribution, powder milled samples were withdrawn after 1.5, 3, 4.5, 6, 8, 10 and 12.5 h of high-energy milling. The obtained powders were characterized by SEM, X-ray and microhardness. The mixed powders obtained just after blending in the low energy laboratory mixer were taken as the non-milled mixed powders. The received aluminium and the mechanically alloyed powders were imbedded in resin; grinded and polished to perform microstructural analysis and microhardness tests.

After determination of optimum milling time for each composition, which is considered in the next section, the unmilled mixed powders and the composite powders were uniaxially cold pressed by slowly increasing pressure up 300 MPa, to obtain compacted samples of 25 mm diameter and approximately 16 mm height, hot extruded at 500°C, without canning and degassing, and cooled in stirred air at room temperature. The selected extrusion ratio was 25:1. Extruded rods of 5 mm diameter and approximately 400 mm length were produced.

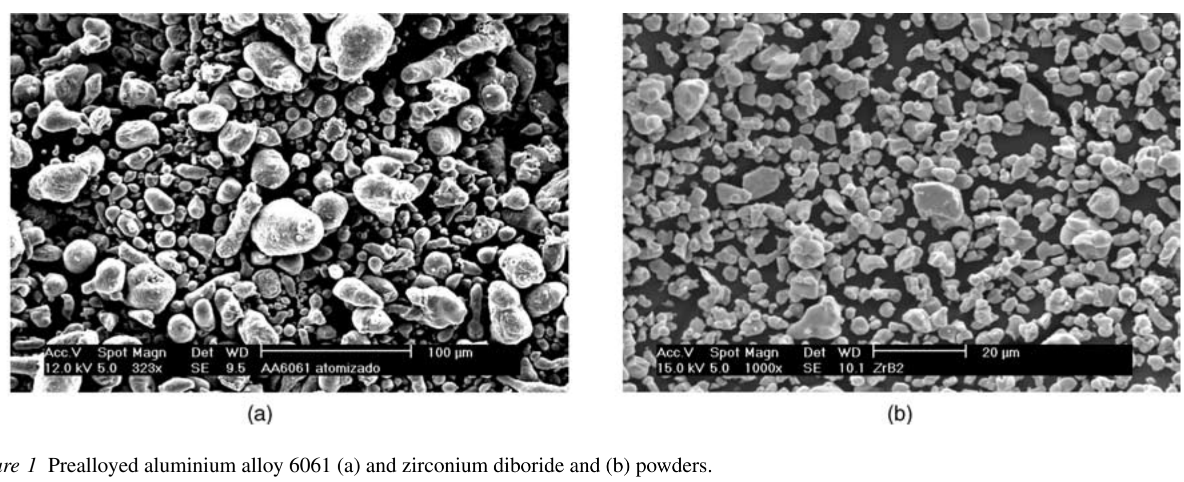
The composites extruded from the unmilled mixed powders were taken as the reference low-energy mixing materials, and the A6061 alloy extruded from the as-received prealloyed powder as the reference base material.

The extruded composites were characterised by tensile testing and hardness. Reported values are the mean of eight and twelve tests, respectively.

## 3. Results and discussion

Fig. 2 shows the evolution of the powder morphology during the high-energy milling. At the beginning of the mechanical alloying process in a ductile/brittle system, as is the case of Al and $ZrB_2$, the ductile particles (Al) undergo deformation, while brittle particles ($ZrB_2$) undergo fragmentation. At this stage, there is a morphological change of the ductile particles from being equiaxed (typical of the atomising process of fabrication of the powder) to being flattened. Fig. 2a shows reinforcement particles placed at the flattened aluminium 6061-particle surface, obtained after 1.5 h of high-energy milling of the mixture A6061/5% $ZrB_2$. When metal particles weld, they trap the reinforcement particle on the interfacial welding boundaries, as shown in Fig. 2b. At this point, the particle can be considered a composite particle.

The deformation and welding phenomena harden the material and consequently the tendency to fracture increases [23]. Longer milling times will provide equilibrium between welding and fracture, changing the




(a) (b)

*Figure 1* Prealloyed aluminium alloy 6061 (a) and zirconium diboride and (b) powders.

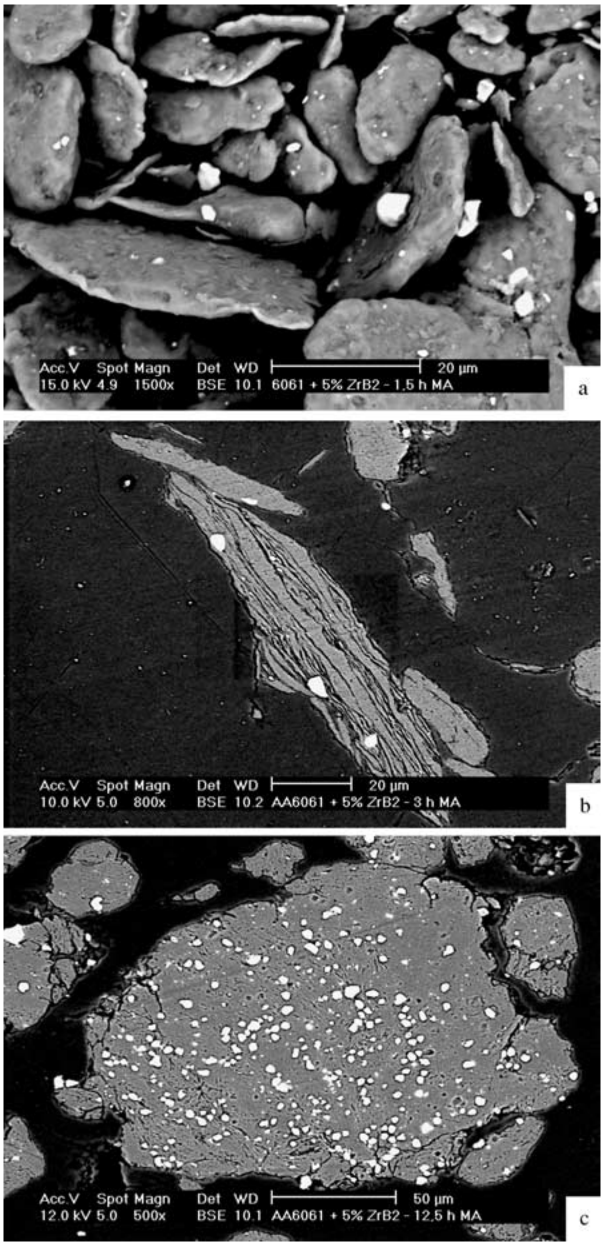



*Figure 2* Evolution of powder morphology: (a) $ZrB_2$ reinforcement particles located on the flattened aluminium A6061 particle surfaces, observed after 1.5 h of mechanical alloying, (b) $ZrB_2$ reinforcement particles trapped on the interfacial welding boundaries of aluminium particles, observed after 3 h of mechanical alloying, and (c) composite particles of A6061 reinforced with 5% $ZrB_2$ obtained after 12.5 h of mechanical alloying.

particle morphology from laminar to equiaxed [19]. After 12.5 h of high-energy milling, the process seems to reach a steady state, in which microstructural refinement can continue, but the particle size and size distribution should remain approximately unchanged. Fig. 2c shows the 5% $ZrB_2$ reinforced 6061 composite powder mechanically alloyed for 12.5 h. A homogeneous distribution of the reinforcement phase through the particle is observed. The study carried out with 15% $ZrB_2$ showed that only 10 h milling is required to produce a composite powder with a homogeneous reinforcement distribution. As demonstrated in a previous work [19], the presence of hard particles advances the phenomena involved in the mechanical alloying, due to the additional deformation imposed by these harder

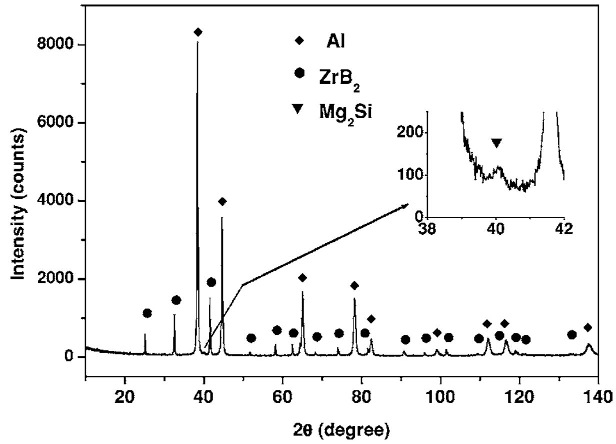



*Figure 3* X-ray diffraction pattern of the 5% $ZrB_2$ composite powder mechanically alloyed for 12.5 h.

particles upon the ductile ones. The higher hard phase content accelerates this advance, reducing the milling time necessary to achieve the steady state.

The proper determination of the milling time is very important to obtain the best results. A more difficult extrusion [24] and/or consolidated composite materials with non-optimised properties [20] can result when complete mechanical alloying is not carried out.

Fig. 3 shows X-ray diffraction of the 5% $ZrB_2$ composite powder mechanically alloyed for 12.5 h. The milling process did not produce significant contamination or oxidation, which would have been detected by XRD. The presence of $Mg_2Si$, typical of 6XXX aluminium alloys, is observed.

The as-received 6061 powder shows a fine dendritic microstructure resulting from the fast cooling rate imposed by the atomisation process. The hardening mechanisms of metals and alloys promoted by deformation, grain refinement and solid dispersion are well known. Mechanical alloying promotes a high degree of deformation, reduces the grain size to nanometer level and produces an extremely fine dispersion of oxides and carbides in the structure of the metal, which results in a dramatic hardening of the powder [14, 15]. After the process, the mechanical milled composite powder has an extremely refined microstructure, with a fine distribution of reinforcement, oxides and carbide throughout the particles, as well as high density of dislocations due to the high degree of deformation imposed by the process. The presence of the reinforcement $ZrB_2$ particles in the mechanical alloyed powder and the difference between the microstructures of the as-received and the mechanically alloyed powders produce a great difference in their hardness, as shown in Table I, a confirmation of the effectiveness of the high-energy milling process.

TABLE I Microhardness of the A6061 and A6061/5% $ZrB_2$ powders

| Material | Microhardness (HV) | Standard deviation |
|---|---|---|
| A6061 as-received atomised powder | 65.3 | 15.2 |
| A6061/5% $ZrB_2$ after 12.5 h of high-energy milling | 186.9 | 19.6 |

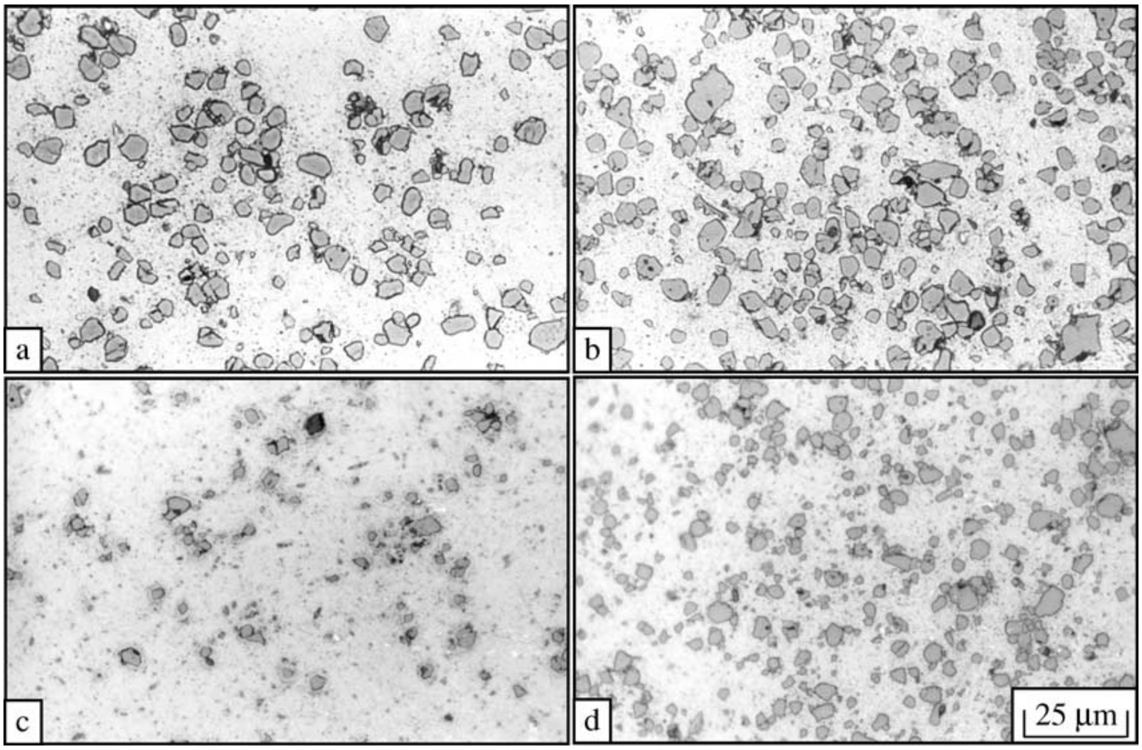



*Figure 4* Microstructures of A6061/5% $ZrB_2$ (a, c) and A6061/15% $ZrB_2$ (b, d) composites obtained through conventional PM (a, b) and mechanical alloying (c, d).

This result is in agreement with the results obtained by Hochreiter *et al.* [25], who report values of about 200 HV for A6061/15%$_{vol.}$ SiC mechanical-milled composite powder, as well as with previous results by the present authors on composites of A6061/AlN and A6061/$Si_3N_4$ [19].

Fig. 4 shows microstructures of the composites extruded from powders obtained by conventional PM and mechanical alloying. The extrusion process was able to produce practically full-density materials. It is confirmed that mechanical alloying produces a composite material with better distribution of the reinforcement particles, but only a small decrease in the size of reinforcement particles is observed. The higher energy involved in mechanical alloying should be sufficient to break the clusters of reinforcement particles, to eliminate most of the weak points, such as surface cracks, present in the reinforcement particles, and to promote a significant decrease in the reinforcement particle size [19]. These effects, however, are not so significant in the present case, in part due to the characteristics of the particulate reinforcement, such as its morphology, hardness and its presumable inherent toughness, and in part due to the presence of a ductile phase, which absorbs most of the energy of the ball collision, reducing its influence on the brittle particles. The use of even more brittle reinforcement particles should produce greater fragmentation, resulting in a finer distribution of the reinforcement phase [19].

Fig. 5 shows the UTS and hardness of A6061/5% $ZrB_2$ composites produced by extrusion of powders milled for 1.5 and 12.5 h in a high-energy mill, and A6061/15% $ZrB_2$ composites produced by extrusion of powders milled for 1.5 and 10 h. It also shows composites produced by extrusion of powders conventionally mixed and, for comparison, unreinforced A6061 in the as-extruded condition.

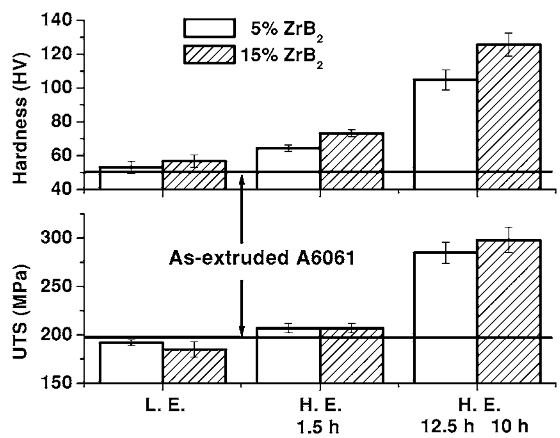



*Figure 5* UTS and hardness of A6061 in the as-extruded condition, and the extruded A6061/5 and 15% $ZrB_2$ composites produced by low-energy mixing (L.E.) and high-energy (H.E.) milling processes.

In the case of the composites obtained by low-energy mixing, the simple addition of $ZrB_2$ particles produces a small increase in the material hardness and a small decrease in the UTS. It is known that the incorporation of particulate reinforcements not always brings an increment in the material tensile strength [26, 27], in contrast with fiber or continuous reinforcements, which are able to promote the load transfer from the matrix to the reinforcement phase. Problems such as reinforcement clustering, cracks in the reinforcement surface, or poor bounding between matrix and reinforcements prevent the enhancement of the composite strength. Fig. 6 shows $ZrB_2$ particles in a aluminium matrix and a profile, obtained by EDS, of Al and Zr contents in the A6061/5% $ZrB_2$ composite extruded from low-energy

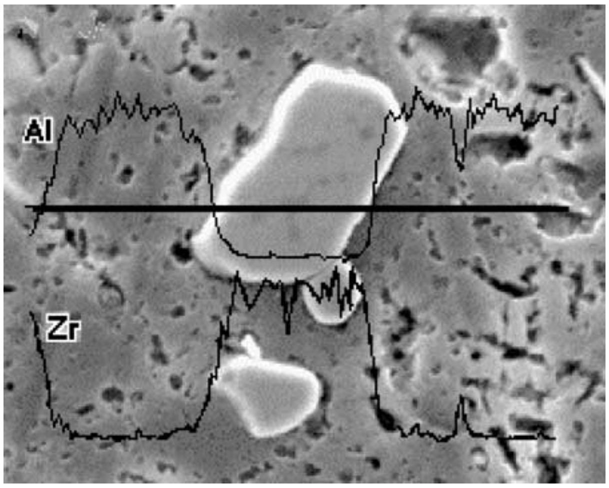



*Figure 6* Profile of Al and Zr contents in the A6061/5% $ZrB_2$ extruded composite produced from low-energy mixed powders.

mixed powders. The porosities observed in this microstructure are probably due to the pull out of the second phase, oxides or reinforced particles during sample preparation. The presence of a reaction layer between matrix and reinforcement is not verified, possibly due to the typical low temperatures involved in the PM techniques used. The absence of chemical bonding explains in part the lower strength of the conventional extruded composites as compared to the unreinforced material. The higher the reinforcement content the higher the probability of clusters and particle defects and, consequently, the composite strength decrease. Therefore, the UTS of the A6061/15% $ZrB_2$ composite extruded from the low-energy mixed powders is lower than that of the A6061/5% $ZrB_2$ composite obtained by the same processing route.

As the extrusion parameters (extrusion ratio, rate and temperature) are constant for the different materials tested, and the reinforcement particles do not undergo deformation while extruding, the higher the reinforcement content the smaller the volume fraction of the material that really is subjected to deformation during extrusion. It implies that a higher reinforcement content produces greater deformation of the matrix during extrusion. Unless the extruded material recrystallizes, the higher deformation produces a greater hardening effect. This explains the greater hardness of the composites in comparison with the unreinforced alloy, and the increase of hardness with the higher amount of reinforcement.

In spite of its not promoting the optimum composite powder characteristics, 1.5 h of high-energy milling is however sufficient to reduce the reinforcement clustering and, to a lower degree, to remove part of the defects present in the reinforcement particles. As a consequence, a short milling time, such as 1.5 h, can bring a small improvement in the composite tensile strength. Comparing values of tensile strength of the composites extruded from the low-energy mixed powders with those of 1.5 h mechanically alloyed composite powders, it is clear that A6061/15% $ZrB_2$ composites exhibit a higher proportional increase. This confirms that the enhancement of UTS is mainly due to the elimination of the clusters and particle defects.

On the other hand, the optimum milling time, which produces particles with equiaxed morphology and with better distribution of the reinforcement throughout the matrix, brings a considerable improvement in the composite strength. In this case, it is not only the optimisation of composite parameters that explains this improvement. Other reasons are attributed to the metallurgical phenomena promoted by mechanical alloying in the matrix, such as grain refinement, oxide and carbide dispersion and high dislocation density imposed by the cold working, even though a significant part of this is eliminated by the hot extrusion.

As reported in a previous work [19], the presence of a hard phase improves the deformation imposed by the mechanical alloying on the ductile aluminium. This partially explains the higher value of UTS of A6061/15% $ZrB_2$ composite milled for 10 h in comparison with A6061/5% $ZrB_2$ milled for 12.5 h. The higher deformation imposed on the matrix by the extrusion, due the higher reinforcement content, as stated before, also contributes to the higher UTS and hardness values of the 15% $ZrB_2$ reinforced material.

## 4. Conclusions

Mechanical alloying can produce composite powders with homogeneous distribution of the reinforcement phase throughout the particle, and the extrusion process is able to produce practically full-density composite materials.

In the case of composites obtained by low-energy mixing, the incorporation of $ZrB_2$ particles produces a small increase in the material hardness and a small decrease in the UTS.

Mechanical alloying breaks particle clusters, eliminates most of the weak points present in the reinforcement particles, decreases the reinforcement particle size and improves the homogeneity of reinforcement distribution in the matrix.

The enhancement of the composite structure as well as the metallurgical phenomena promoted in the matrix by mechanical alloying brings around 100% improvement in the composite UTS and hardness, compared with the composites obtained by conventional low-energy mixing process.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