

Consolidation of AA 7075-2 wt% ZrO₂ Composite Powders by Severe Plastic Deformation via ECAP

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Abstract The powders of the AA 7075-ZrO₂ were mixed by mechanical milling, but it was found that the system presents a few disadvantages when processed by conventional sintering and hot extrusion, since intermetallic phases between ZrO_2 particles and alloying elements were formed. Equal channel angular pressing (ECAP) processing was proposed as an alternative method to consolidate the composite where there is no intermetallic formation. The analysis of the ECAP process showed that the intermediate temperature (220 °C) produced a higher consolidation level than conventional sintering and hot extrusion (400 and 500 °C, respectively). This fact was supported by relative density analysis. In the case of the sintered and hot-extruded sample, the relative density exhibited a value of 0.95, while ECAP sample showed a value of 0.98. Hardness values show that microstructural refinement obtained during mechanical milling was preserved during ECAP processing even when it was carried out at 220 °C.

KEY WORDS: Metal matrix composites (MMCs); Powder consolidation; Severe plastic deformation (SPD)

1 Introduction

The relation between low-specific weight and high mechanical strength of aluminum-based composites has increased the interest for its development in the aeronautic industry. The highest mechanical strength can be achieved by dispersing hard ceramic particles through the matrix, promoting the so-called oxide dispersion strengthening

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(ODS materials) [1, 2]. There are several methods for composites production, but mechanical milling (MM) is one of the techniques that have showed higher efficiency to disperse ceramic particles since the process is held completely in solid state, contrary to liquid state methods where a difference in density between matrix and particles makes the dispersion of the reinforcement phase difficult [3, 4]. On the other hand, the equal channel angular pressing (ECAP) is one of the novel methods for powder consolidation, which has shown superior mechanical properties of the final consolidated material; moreover, a better dispersion of

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reinforcement can be achieved since the deformation process involves large strain [5–7]. One of the advantageous features of ECAP is that there is no reduction in the cross section of the sample [8]. In addition, ECAP requires lower pressure and temperature in comparison with conventional hot extrusion [6]. Often, further deformation processes are used in the production of aluminum-based composites to enhance dispersion and density of the composite [9–11].

Previous studies have used ZrO₂ as reinforcement with the aim of improving the mechanical properties of the aluminum alloys. Fuentes-Ramirez et al. [12] improved the wear resistance of pure Al using a surface treatment employing colloidal ZrO₂. Hemanth [13] used nanosized ZrO₂ to modify LM13 cast aluminum alloy, obtaining superior properties of hardness and tensile strength in comparison with the unreinforced alloy. In the same way, Abdizadeh et al. [14] produced an A365 aluminum alloy with partially yttria-stabilized zirconia particles as reinforcement by the vortex method. This composite reached a hardness of 70 HBN and the tensile strength of 240 MPa, while the unreinforced material exhibited values of 45 HBN and 45 MPA, respectively. Dutkiewicz et al. [15] used an aluminum alloy 7475 using ZrO2 nanoparticles with an average size of 20 nm, obtaining a compressive stress near to 990 MPa.

The aluminum alloy AA 7075 is considered a highstrength alloy, since its yield point is over 500 MPa [16, 17]. On the other hand, ZrO_2 is a hard ceramic [18, 19] which is used to promote superior mechanical properties of the alloy in comparison with the unreinforced one. Unfortunately, it is showed an undesirable reaction between ZrO₂ and the alloying elements at high temperatures, when the powders are consolidated by conventional powder metallurgy processes, such as sintering and hot extrusion (400 and 500 °C, respectively). Under this condition, intermetallic phases are formed leading to a solute depletion in the matrix, confirmed by the appearance of new intermetallic phases in the X-ray diffraction patterns and the calorimetry results. Hence, the alloy is not capable of displaying age hardening, since there is no solute to form η ' and η (MgZn₂) phases. Therefore, high-temperature process is no longer an advisable option to produce AA 7075 with ZrO₂ particles. Therefore, a low-temperature ECAP processing is proposed as an alternative powder consolidation process, which is used to strengthen the composite of the aluminum alloy 7075 reinforced with ZrO₂ nanoparticles.

2 Materials and Methods

The initial matrix powders were obtained from a commercial bar of AA-7075 supplied in T6 state, and the chemical composition of the alloy is given in Table 1. This

 Table 1
 Average composition of aluminum alloy 7075 (wt%)

Mg	Si	Cr	Fe	Cu	Zn	Al
3.53	0.15	0.41	0.48	2.16	6.58	Bal.

composition was determined by chemical analysis. The bar was annealed at 415 °C for 48 h with the purpose of removing the T6 treatment. The bar was grinded, and then the obtained burrs were sieved using -50 mesh size. The vttria-stabilized zirconia particles used in this research were previously milled in a planetary ball mill for 80 h using ZrO₂ balls as milling media with a ball-to-powder weight ratio of 20:1, and methanol as process control agent (PCA), reaching an average size of 110 nm. The ZrO₂ particles had an irregular shape and consisted of a mixture of 63 and 37 wt% of monoclinic and tetragonal structures, respectively, according to [20]. The composite was produced by blending the AA 7075 with 2 wt% of ZrO₂ particles. Then, they were mechanically milled in a Simoloyer horizontal attritor ball mill for 15 h. Stainless steel balls were employed as the milling media in a ball-to-powder ratio of 20:1, and 1.5 mL of methanol was used as process control agent. Milling was performed at 1000 rpm and more details of the process can be found elsewhere [21].

The composite powders were cold compacted inside of AA 6061 tubes by employing a Universal Testing Machine SHIMADZU AG-I. This process was performed in several steps until a load of 196 kN was reached. The tubes (with the powders inside) were subjected to ECAP process in order to get a fully consolidated material. For this purpose, an ECAP die with an inner and outer angle of 90° and of 37°, respectively, was used. The ram speed was 4 mm/min at room temperature and at 220 °C, in the same universal testing machine.

Additional studies were executed via cold compaction of the powders at 538 kN. After that, the powders were subjected to hot sintering at 400 °C for 3 h under Argon atmosphere, and finally, they were hot extruded at 500 °C with an extrusion ratio of 4:1. Unfortunately, these results were discouraging because it was found that the material was not able to response to age-hardening process, so that they are presented only for comparison purposes.

The microstructure of the composite was characterized by scanning electron microscope (SEM) operated at 20 kV, transmission electron microscope (TEM) operated at 100 kV and energy-dispersive spectroscopy (EDS). The phase identification was carried out by X-ray diffraction (XRD) in a Bruker D8 Advance DaVinci Design diffractometer, in the 2θ range of 25° - 85° , using Cu radiation K\alpha ($\lambda = 0.154$ nm), with a step size of 0.02° and speed of $1^\circ/$ min. Vickers hardness tests for the milled powders and consolidated materials were performed in accordance with ASTM E92 standard in a microhardness tester Shimadzu HMV-G21. The digital image analyzer software Sigma ScanPro 4.0 was used to quantify the remaining porosity of the consolidated material. Additionally, studies of differential scanning calorimetry (DSC) were carried out on the mechanically alloyed powders to understand the nature of phase transformations which takes place in the composite system. The DSC tests were performed from room temperature to 550 °C in a Seratam Labsys Evo, with a heating rate of 10 °C/min.

3 Results and Discussion

3.1 Consolidation by ECAP

The mechanism of powder consolidation by ECAP is believed to act in the following way: Initially, the applied load diminished the distance between powders promoting a closer contact (it is understood that this compaction is additional because the powders have been previously cold compacted). Then when the powders were passing through the shear plane in the ECAP die, the shear stresses broke the oxide layer on the surface of aluminum particles and a new fresh surface was exposed. As a consequence, these surfaces came in contact, and inter-particle welding occured due to applied load and stress, consolidating the powders into a bulk material [5, 6].

In order to fully understand the process of the powder consolidation inside the tubes, Fig. 1 presents the loaddisplacement curves obtained during the ECAP. According to [5], at the beginning, the load increases due to further compaction of the powders and also because of the friction



Fig. 1 Load–displacement curves of the AA 7075-2 wt% ZrO_2 consolidation process by single ECAP pass

between tube and die walls. The maximum load is reached when the yield point of the front part of the tube is achieved. Once this point is overpassed, the load decreases until a minimum as the tube and powder pass completely throughout the shear plane. This load decrement is expected since the load requirements are lower for deforming powder instead of bulk material. The load starts to increase again at 32 mm of displacement when the friction between the external wall of the tube and the exit channel becomes significant; furthermore, in this moment, the upper part of the tube (rear plug) starts its entrance to the shear plane.

One of the most important features in evaluating the ECAP process, when used as metal powder consolidation process, is the remaining porosity. The presence of a significant porosity in the material can lead in most cases to detrimental mechanical properties [22]. SEM micrographs of the consolidated powders of selected samples with different number of passes of ECAP and working temperatures are shown in Fig. 2. It can be notice that the use of high temperature reduces the porosity in the composite. The pores are higher in number and larger in size also when ECAP is conducted at room temperature even when it is subjected to three passes (Fig. 2a, c), while porosity is reduced when one pass of ECAP is performed at 220 °C as illustrated in Fig. 2b, d, respectively.

Porosity was evaluated at the most favorable condition by image analysis through Sigma ScanPro software, and results are listed in Table 2. In the case of the process carried out at room temperature, the best condition was find to be three ECAP passes which exhibited a remaining porosity value of 1.9%, while the powders consolidated at 220 °C by only one ECAP pass showed 0.1% of porosity. This finding can be explained by two facts. First, the heat generated by plastic deformation activates the inter-particle diffusion similar to conventional sintering but at a lower temperature and a shorter time. Second, the metallic powders of the composite being submitted at 220 °C in the ECAP process had a slight recovery, which could enhance the inter-particle bonding of the previously hard milled powders.

Another parameter to evaluate the consolidation process is the hardness. Accordingly, the Vickers hardness values of the unreinforced bulk alloy and the composite at different processing conditions are listed in Table 3. The first interesting finding is that the sample processed by ECAP at high temperature exhibits higher hardness than in the case of the unreinforced bulk aged alloy. In this way, it seems that the mechanical properties are enhanced by ECAP. The influence of the processing temperature is also visible on the composite material processed at room temperature by three ECAP passes since it exhibits 161 HVN which is below of the hardness peak of the bulk commercial aged



Fig. 2 SEM micrographs of AA 7075-2 wt% ZrO_2 composite **a** and **c** consolidated by three ECAP passes at room temperature, and **b** and **d** consolidated by a single ECAP pass at 220 °C

 Table 2
 Remaining porosity of the AA 7075 and the composite at different conditions evaluated by SEM

Condition	Remaining porosity (%)
AA 7075-2 wt% ZrO ₂ /3 pass—Room temperature	1.9
AA 7075 powder/1 pass—220 °C	0.4
AA 7075-2 wt% ZrO ₂ /1 pass—220 °C	0.1

 Table 3
 Average Vickers hardness of the AA 7075 and the composite in different conditions

Condition	Vickers hardness (HVN)
AA 7075 commercial supersaturated solid solution [25]	88
AA 7075 commercial hardness peak (aged condition T6) [25]	184
AA 7075 powders (after mechanical milling)	254
AA 7075-2 wt% ZrO2 powders (after mechanical milling)	281
AA 7075-2 wt% ZrO ₂ /3 pass ECAP at room temperature	161
AA 7075-2 wt% ZrO ₂ /single pass ECAP at 220 °C	257

alloy. When the composite processed by ECAP at 220 °C is compared with all other conditions, it is clearly seen that its hardness is the highest. This situation can be explained by the hypothesis made earlier, assuming that the particle bonding is promoted at high temperature. It can also be seen that the HVN value of the composite at the mechanical milled condition is higher than the value in the consolidated condition at room temperature. It can be associated with the presence of relatively large porosity in the latter sample.

TEM micrographs for the AA 7075-2 wt% ZrO₂ composite material consolidated by single ECAP pass process at 220 °C are shown in Fig. 3, where the ZrO_2 particles and the matrix crystallite zones can be noticed. Figure 3a, b shows bright and dark fields correspondingly (dark-field micrograph taken from arrowed point in the selected-area electron diffraction pattern). It can be noted that there is absence of reinforcement clusters in the matrix, and the distribution of reinforcement particles appears homogenous, supporting the statement made by Tan and Zhang [9] and Sabirov et al. [10, 11], who suggested that the high deformation imparted during ECAP leads to a better and homogenous dispersion of reinforcement. It can also be seen in Fig. 3b that the crystallites are visible to be small enough to declare them as nanosized, confirmed by the ring pattern on the selected-area electron diffraction pattern of



Fig. 3 TEM micrographs of the AA 7075-2 wt% ZrO2 mechanically milled and consolidated by ECAP at 220 °C

Fig. 3, which is in agreement with Horita et al. [23]. In this way, the high values of Vickers hardness corresponding to this sample are in agreement with the expected microstructure [24], since the grain refinement produced by severe plastic deformation is visible in Fig. 3.

3.2 Comparison between ECAP Consolidation and Sintering–Hot Extrusion Processes in the System AA 7075-ZrO₂

In this section, relevant arguments are given to explain why the ECAP process possess significant benefits for consolidation of AA 7075-ZrO₂ composite in contrast to the disadvantages showed by the sintering–hot extrusion at high temperatures (400 and 500 °C, respectively). First, Table 4 shows the density values of the composite consolidated by the two routes. It is evident from Table 4 that the consolidation process by sintering and hot extrusion shows similar results than the ECAP process, because the relative densities are 0,95 and 0.98, respectively, showing that the ECAP process has advantage over the conventional consolidation routes.

Other observed feature can be seen on the aging curves of the bulk AA 7075 (commercial) and the AA 7075-2 wt% ZrO₂ composite consolidated by sintering and hot extrusion (Fig. 4). It is evident that the response of the composite to the precipitation was negligible, and that effects on the properties of the composite was in a negative way, so this is the reason that a new way to consolidate the powders of the system AA 7075-ZrO₂ as tested.

This lack of hardening is proposed to be an adverse reaction between the ZrO_2 particles and the alloying elements of the matrix (majorly Zn). In this way, when the composite is processed at high temperature some new intermetallic phases are formed, leaving a depletion of solute in the matrix.

 Table 4
 Relative densities of the composite material consolidated by sintering and hot extrusion and by ECAP Process at 220 °C

Consolidation process	Relative density
Sintering and hot extrusion	0.95
ECAP at 220 °C	0.98



Fig. 4 Variation of hardness with aging time for commercial bulk AA 7075 [24] and the AA 7075-2 wt% ZrO_2 composite by sintering and hot extrusion

These detrimental phases were identified by XRD and are presented in Fig. 5, where the diffractogram of the composite powders in the as milled condition, and the one corresponding to sintering and hot extrusion are compared. It is apparent that the peaks of the MgZn₂ and ZrO₂ phases disappeared or lowered their intensity after sintering and hot extrusion. In addition, some new peaks are formed after this processing route. It is stated that these intermetallic



Fig. 5 X-ray diffraction patterns of AA 7075-2 wt% ZrO₂ composite powder in the as milled condition and after sintering and hot extrusion condition

Table 5 Intermetallic phases formed during high temperature processes in the composite system AA 7075-ZrO₂

Phase	Structure	JCPDS-card	
Zn _{0.865} Mg _{0.73} Al _{10.27} O ₁₇	Rombohedral	76-2464	
Zn ₂₂ Zr	Cubic	65-6202	
Al ₂ ZnZr	Cubic	65-4732	

phases (presented in Table 5) are responsible for solute depletion in the matrix.

Figure 6 presents a comparison between XRD patterns of the sintered and hot-extruded composite processed by ECAP at 220 °C. It is clear that there is no formation of new phases in the second case since there is no evidence of



Fig. 7 DSC thermograms of the powders of the mechanically milled AA 7075 powders, and the powders of the AA 7075-2 wt% ZrO_2 composite

diffraction peaks corresponding to new phases as in the case of hot-extruded sample. Furthermore, it is apparent that the peak intensity of the ECAP processed sample is lower than the extruded material, which is a consequence of the severe plastic deformation imposed to the composite.

In Fig. 7, the DSC thermograms of the mechanically milled powders of the AA 7075 with and without reinforcement are presented. It is evident that there is a clear difference between the curves corresponding to the alloy and the one regarding the composite powders. The main difference remains in the temperatures between 349 and 430 °C, where an exothermic peak is noticed in the case of the composite, which is not present in the unreinforced alloy curve. Also, there is another peak, endothermic in this case around 480 °C, which is not observed in the non-



Fig. 6 XRD patterns of 7075-2 wt% ZrO₂ composite processed by sintering and hot extrusion and single pass ECAP at 220 °C: **a** from 37° to 40° in 2 θ (deg.) and **b** from 76° to 84° in 2 θ (deg.)

reinforced sample curve. These mentioned peaks are believed to represent the different reactions of formation of the intermetallics phases presented in Table 4.

According to the precipitation reaction of the AA-7075 alloy and in agreement with [26-29], the peaks found between 100 and 150 °C are due to the dissolution of GP zones and formation of η '. It is worth to mention that these processes can be overlapped, i.e., a precipitation reaction is not already finished when another has begun (simultaneous reactions). For example, in the range between 150 and 250 °C, formation and growth of η ' take place, but also the formation of η phase. At higher temperatures than the mentioned range, n precipitates grow until its dissolution which begins at 300 °C and reaches its maximum rate at 380 °C. The precipitation reactions are not noticed in the thermogram curve of the composite, since reaction between ZrO_2 and alloying elements is taking place in the microstructure. According to these results, a useful working temperature below 300 °C can be recommended for a successful performance in subsequent processes.

4 Conclusions

- 1. It has been possible to obtain a full dense composite material based on an aluminum alloy 7075 reinforced with ZrO_2 nanoparticles by combining the plastic deformation imparted to powders by mechanical milling and severe plastic deformation process (ECAP at 220 °C).
- 2. The ECAP was carried out at lower temperature and with minor load requirements, in comparison with conventional sintering and hot extrusion processes, and thus, the temperature of the process is low enough to avoid reaction between reinforcement and the alloying elements.
- 3. The usage of relatively high temperature (220 °C) in the ECAP process enhanced the consolidation process, obtaining a lower value of remaining porosity percentage and a higher Vickers hardness than the composite processed at room temperature.
- 4. The microstructural refinement obtained during mechanical milling is completely preserved during the ECAP at 220 °C according to the hardness values and TEM observations. In addition, the hardness of the consolidated composite material by ECAP is higher than that of the commercial bulk aged AA-7075 alloy.

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