Assessment of the Aging Response of a Nanocomposite AA 7075 – ZrO$_2$

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Abstract: A metal matrix composite has been produced by mechanical milling, in an horizontal attritor, using powders of the commercial aluminum alloy 7075 (Al-Zn-Mg) as the matrix of the composite, and nanosized particles of ZrO$_2$ were use as reinforcement. The composite was sintered and hot extruded, in order to consolidate the powders of the composite, and submitted to a heat treatment with the aim of age harden it. The Vickers hardness test was discouraging, due to there was no positive response to the aging treatment. This situation was attributed to the reaction in the process carried out at high temperature (sintering and extrusion) between the ZrO$_2$ and the alloying elements Zn and Mg, since intermetallic compounds were found in the X-ray diffraction patterns of the composite. In this way, the matrix was depleted of Zn and Mg, leaving the matrix out of elements in solution in order to precipitate nanoparticles, which could improve the mechanical properties of the alloy, contrary situation found in the composite material.

Keywords: Aluminum metal matrix composite, age hardening, mechanical properties.

Introduction

Composite materials have taken a great importance in the last years due to the enhanced mechanical properties, reached by combining two materials of different nature, as metallic alloys and ceramics of different nature that could be oxides, borides, nitrides, carbon nanotubes and many others materials that can be used as reinforcements [1-4]. The usage of aluminum alloys as matrix has a special interest due to its low specific weight, which is the reason they are very popular in the aeronautic and aerospace industry. The 2XXX, 6XXX and 7XXX series can be thermal treated in order to obtain nanosized second phase precipitates (age hardening), which enhance the strength of the alloy. Between the mentioned alloys, the 7XXX series, whose main alloying elements are Zn and Mg, exhibit the greater response to the precipitation hardening, thus, the AA 7075 is considered a high strength alloy, because its yield strength is above 500 MPa in the optimal aging conditions. The precipitation reaction is:

\[ \alpha'_{ssss} \rightarrow \text{GP I zones} \rightarrow \text{GP II zones} \rightarrow \eta' \rightarrow \eta_{\text{precursor}} \rightarrow \eta \]

where $\alpha'$ is the supersaturated solid solution, the GP zones are Zn/Mg solute rich clusters with spherical morphology, the $\eta'$ precipitate is the metastable phase with hexagonal structure and
stoichiometry MgZn, along with the η precursor (stoichiometry MgZn₂ and hexagonal structure), they are the main phases found in the aging peak condition. The stable phase η is found in the overaged condition, and has the same stoichiometry and structure as its precursor [5,6]. Previous studies have used ZrO₂ as a reinforcement, with the aim of improving the properties of the alloy. R. Fuentes-Ramirez et al. [7] improved the wear resistance of the aluminium by a surface treatment with colloidal ZrO₂. J. Hemanth et al. [8] used nanosize ZrO₂ to modify the LM13 cast aluminum alloy, obtaining superior properties of hardness and tensile strength in comparison to the unreinforced alloy. In the same way, H. Abdizadeh et al. [9] have reinforced an A365 aluminum alloy with partially yttria-stabilized zirconia by the vortex method, reaching a hardness of 70 HBN and tensile strength of 240 MPa, in comparison of the unreinforced material which exhibited 45 HBN and 45 MPa, respectively. There are no reports of using a high strength aluminum alloy reinforced with ZrO₂, so, the main purpose of this paper is to obtain a composite material with superior mechanical properties, by dispersing partially yttria stabilized zirconia into the AA 7075 matrix.

**Experimental Procedure**

The powders of the alloy were obtained by grinding a bar of commercial aluminum alloy the AA 7075, the nominal composition of the alloy is summarized in Table I. The ZrO₂ used as reinforcement has an average particle size of 110 nm (Figure 1a), and it is composed of two structures, monoclinic and tetragonal, with 62,83 and 37,16 wt.% respectively. The composite was produced mixing the powders of the matrix and the reinforcement with two different contents of ZrO₂ (2 and 5 wt.%), and they were mechanically milled in a Simoloyer horizontal attritor mill at 1000 RPM by 15 h, using methanol as process control agent (PCA) and zirconia balls as milling media, with a ball-to-powder weight ratio of 20:1, in order to disperse the particles of the reinforcement trough the metal matrix, the morphology of the composite powders is showed in Figures 1b) and c). The powders of the composite were compacted at 750 MPa, and then sintered at 400 °C by 3 h, in argon atmosphere, with the objective to avoid excessive oxidation. After sintering, the composites were processed by inverse extrusion at 500 °C with an extrusion relation of rₓ=12,56 (diameter form 40 mm to 10 mm). The obtained bars were segmented and heat treated at 415 °C in order to solubilize the alloying elements (Zn, Mg, Cu), and immediately quenched in an iced brine bath at 0 °C, the aging heat treatment was carried out at 120 °C at several times, and Vickers hardness test was performed to assess the influence of aging heat treatment on the mechanical properties of the composites. The composites were characterized by electron microscopy in a Scanning Electron Microscopy (SEM) Phillips XL-30 operated at 25 kV and using the X-Ray Energy Dispersion Spectroscopy (EDS) technique with the aim of quantify the element weight percentage in the composites. To observe the morphology of the composite by Transmission Electron Microscopy (TEM), the composite was electropolished with a twin jet electropolisher with an intensity current of 30 mA and using a solution of 30 % HNO₃ and 70 % methanol as electrolyte. The characterization was carried out in a Transmission Electron Microscope JEOL 1230 operated at 100 kV. The structural features and phase presence were determined via X-Ray Diffraction (XRD) in a Rigaku diffractometer, in the 2θ range of 25-85°, using Cu radiation Kα (λ = 0,154 nm), with a step-size of 0.02° and speed of 1°/min, for the composites in powder condition and after inverse extrusion.

**Table I. Average composition of aluminum alloy 7075.**

<table>
<thead>
<tr>
<th>Element</th>
<th>Mg</th>
<th>Si</th>
<th>Cr</th>
<th>Fe</th>
<th>Cu</th>
<th>Zn</th>
<th>Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>wt. %</td>
<td>3,5</td>
<td>0,1</td>
<td>0,4</td>
<td>0,4</td>
<td>2,1</td>
<td>6,5</td>
<td>Bal.</td>
</tr>
</tbody>
</table>
Results and discussion

In Figure 2 is shown the results of the aging treatment of the unreinforced alloy and the composites with 2 and 5 wt.% of ZrO₂. It can be spotted that in the very beginning of the process, i.e., in the supersaturated solid solution condition (time 0 s), there is an improvement of the hardness of the composites, in comparison with the unreinforced alloy. The grade of enhancement of the Vickers hardness is dependant of the percentage of reinforcement in the composite, since the AA 7075–5wt.%ZrO₂ composite shows a higher Vickers hardness than the AA 7075–2wt.%ZrO₂ composite through all the process. As the aging time passes by, the hardness of the composites remains practically the same, and there is almost no response of the composite to the aging treatment in comparison with the unreinforced alloy, which higher value is 184,32 Vickers hardness number (HVN) in the aging peak condition (time 604800 s), and the higher value for a composite is 125,79 HVN for the AA7075–5wt.%ZrO₂. It could be stated that there is no precipitation hardening reaction acting on the composite, since there is no increase in hardness, and the mechanical properties were not as expected.

To determine the causes of the lack of precipitation reaction in the composites, various tests were performed. In Figure 3 is presented a comparison between an overaged unreinforced AA 7075 and an extruded AA 7075-5wt.% ZrO₂ composite. It can be seen the precipitates ƞ (MgZn2) as white spots on the micrograph, and the same is expected in the micrograph in Figure 3b where the composite AA 7075 5wt.% ZrO₂ in the extruded condition is shown, with the exception that some white spots have a different composition, determined by the EDS microanalysis, which showed a high percentage of Zr (Figure 3c).

This is due to the presence of ZrO₂ microclusters on the matrix. The element weight percentage determined by EDS of the all alloying elements of the composites is not much different from the unreinforced alloy (except for the Zr addition), so, a depletion of low melting point element zinc by melting is discarded, and the levels of oxygen in the composites are not that...
high for talking about an excessive oxidation of aluminum, zinc or magnesium.

Figure 3. SEM micrographs of a) overaged AA 7075, b) as extruded AA 7075-5wt.\%ZrO$_2$, and c) EDS spectrum of punctual microanalysis of white spots of 7075-5wt.\%ZrO$_2$ in extruded condition.

A possible recombination of the elements in the system can be expected as possible cause of lack of precipitation kinetics, and the answer can lie on the x-ray diffraction patterns, by comparing the diffractograms of the composite powders and in the condition as extruded.

Figure 4. X-ray diffraction pattern of AA 7075-5wt.\% ZrO$_2$ composite in the condition of powder (lower line) and after extrusion (upper line).

In Figure 4 the diffraction patterns are presented for the AA 7075-5wt.\%ZrO$_2$ composite for the two mentioned conditions. It can be seen that the main peak (around 28° in 2θ) of the monoclinic structure of ZrO$_2$ completely disapears in the upper diffractogram, which belongs to the consolidated composite, and a similar situation for the main peak (around 31° in 2θ) of the tetragonal structure of ZrO$_2$ can be spotted, with the difference that this peak does not completely dissapear from the diffractogram, it just decreased its intensity. That is a almost identical case for the main peaks of the η precipitates (MgZn$_2$) around 40.5 and 41.5° in 2θ. It can be seen that there is the formation of a phase (Zn$_{0.865}$Mg$_{0.73}$Al$_{10.27}$O$_{17}$) not visible in the composite in the powder condition.

In the Figure 5 the x-ray diffraction patterns show the apparition of the intermetallic Al$_2$ZnZr in the extruded composite, intermetallic not seen in the powder condition. The apparition of these phases is produced by the reaction of the low melting point element zinc with the zirconium contained in the reinforcement ZrO$_2$, and the oxygen from the reinforcement reacts with the aluminum of the alloy, forming these new phases in the composite. This feature of recombination of the elements in the system is promoted by the heat of the thermal treatment where the composites were submitted, as sintering (400 °C) and extrusion (500 °C), that is the reason why these phases are not seen in the powder condition of the composite.
The identification of the intermetallics found in the composite are summarized in Table II. This situation explains the behaviour of the metal matrix respect to the aging treatment, because when the zinc reacts to form more stable phases, there is no solute left in the matrix for producing precipitates to harden the material, since the matrix remains out of solute. This undesirable situation needs to be avoided to successfully produce a high strength aluminum alloy composite reinforced with ZrO$_2$, and a possible way to achieve this objective, is consolidating the powders of the composite at room temperature.

Table II. Phases formed during the sintering and extrusion process of consolidation of the AA 7075-ZrO$_2$ composites.

<table>
<thead>
<tr>
<th>Phase</th>
<th>Structure</th>
<th>JCPDS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn$<em>{0.865}$Mg$</em>{0.73}$Al$<em>{10.27}$O$</em>{17}$</td>
<td>Rhombohedral</td>
<td>76-2464</td>
</tr>
<tr>
<td>Zn$_2$Zr</td>
<td>Cubic</td>
<td>65-6202</td>
</tr>
<tr>
<td>Al$_2$ZnZr</td>
<td>Cubic</td>
<td>65-4732</td>
</tr>
</tbody>
</table>

In the Figure 6 is presented a TEM micrograph of the composite material with 5 wt.% of ZrO$_2$ in the as extruded condition, where two ZrO$_2$ particles are presented, one with a expected morphology as reported by [10], and other which seems to be reacting with a $\eta$ precipitate with bar morphology. The difference between these two ZrO$_2$ particles remains specifically in the morphology that they present, one particle seems to be morphologically complete, on the other hand, the nearest particle to the $\eta$ precipitate seems to be disaggregating. It has to be pointed out that the source of zinc in the system in this conditions are the $\eta$ precipitates.

Figure 6. TEM micrograph of the AA 7075-5wt.%ZrO$_2$ composite, showing two ZrO$_2$ particle, one of them reacting with a $\eta$ precipitate.

In order to produce an AA 7075 – ZrO$_2$ composite with superior mechanical properties obtained by mixing the precipitation hardening and oxide dispersion strengthening in the system could be achieved by processing the material by Equal Channel Angular Pressing (ECAP), method.
which has been successfully employed to consolidate powders at room temperature [11].

Conclusions and future work

- The improvement of the mechanical properties of the composites was visible just in the supersaturated solid solution condition, compared to the unreinforced alloy. As the aging time was greater, there was not a response of the composites to precipitation.
- The reason to have cero influence of aging treatment on the extruded composites, is that high temperature process like sintering (400 °C) and extrusion (500 °C), causes that the low melting point alloying element Zn reacts with the Zr from the reinforcement ZrO$_2$ to form several intermetallics (mainly Al$_2$ZnZr), in this way, there were no alloying elements left in the matrix to form nanosized precipitates to improve the mechanical properties of the composites.
- To confront this situation, is proposed to use the ECAP process to consolidate the powders of the composites at room temperature or another temperature which doesn’t promote the intermetallics formation, hence, a positive response of the composites to the aging treatment will be expected.

References