On the Development of an Al4.8 wt% Cu Alloy Obtained from Recycled Aluminum Cans Designed for Thixoforming Process

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This work has focused on the development of a new aluminum alloy containing 4.8 wt% of Cu alloy obtained from recycled aluminium cans designed for thixoforming process. After the step of melting and solidification of the alloy in a metallic permanent mold, samples were solution heat treated at 525°C for times ranging from 2h to 48h, quenched in water and followed by natural aging. Results have shown the evolution of hardness so from them solubilization solution heat treatment was chosen for 24h. The best condition for aging was 190°C during 3h. With this data pieces were thixoforged at 580°C and 615°C corresponding, respectively, to solid fraction (f_s) of 0.8 and 0.6. The optimized T6 temper was applied and tensile tests were performed. The mechanical properties obtained are compatible with those obtained for consolidated alloys processed in semisolid state (SS) and after T6 temper hardness increases from 95 HB to 122 HB and the best results were a tensile strength of 324MPa ± 10MPa, yield strength of 257MPa ± 18MPa, and a elongation of 7.1% ± 1%. For alloys designed for thixoforming process, these results are in accordance with what was expected whereas globular microstructure, high ductility, and good performance under cyclic conditions are desirable.

1. Introduction

The automotive industries are seeking for new technologies to reduce fuel consumption in vehicles; therefore, the demand for lighter and stronger materials is increasing. Aluminum alloys are an alternative to replace many mechanical components because they bring weight reduction associated with good resistance. The search for chemical compositions and processes that ensure adequate mechanical properties is the explanation for several studies done in recent decades [1–8]. Among these alternatives, the thixoforging process for aluminum alloys is a good choice since pieces produced by this way can be subjected to T6 temper. Some works had demonstrated the better mechanical properties of thixo-forged products than those produced by cast or die casting process [9–13]. The T6 temper aims to promote the formation of thin precipitates dispersed and maximizing the mechanical strength of the alloy. The production of alloys such as A356 and 2024 have their origin from raw materials with a high purity, therefore having a high cost. This is a problem since those alloys can not be obtained from recycled alloys with high content of harmful elements such as Fe. Usually the Fe is an undesired element in aluminum alloys and by economically feasible way it cannot be removed leaving only the dilution as an option when you want to reduce its concentration. The aluminum alloy cans are made of 3004 and 5182 alloys that come from the lid and body of can, respectively, and some residual elements are present too. The recycle process is economically viable; however the mix obtained cannot be applied directly to produce useful products and additions are always necessary as, for example, commercial pure aluminum (99.7%) or alloy elements.
The aim of this work was to establish parameters to determine the time and temperature to optimize the mechanical properties of a new recycled aluminum alloy containing 4.8 wt% Cu.

2. Experimental

The first step of this work was to produce a recycled alloy from beverage aluminum cans and the detailed steps were the same as described in a recent work developed by Reis et al. [4]. The recycled alloy was poured into a permanent mold and ingots with around 0.4 kg were produced. The chemical analysis was performed on optical emission spectrometer WAS-Oxford Model Foundry Master Pro and in wt% as follows: Si = 0.28; Fe = 0.61; Cu = 0.23; Mn = 1.03; Mg = 1.91; Cr = 0.03; Zn = 0.25; Ti = 0.03; residual = 0.15 with maximum of 0.05 for each and Al balance.

In order to produce an alloy adequate to the semisolid process a gap in semisolid state (SS) is needful sufficiently large to turn the control of the solid fraction ($f_s$) doable and the usual gap must be at least 40°C. Therefore, the prime alloy is not in condition to be used in SS process and to start it was used to produce several samples with Cu content ranging from 0 wt% to 8 wt%. Each alloy produced was analyzed using a Differential Thermal Analysis (DTA) module by Shimadzu DTA-50. For example, for the first alloy with only 0.23% of Cu the beginning of the fusion starts at approximately 637°C and ends at 650°C as shown in Figure 1(a). This is an example of short gap that is not adequate to the semisolid process. Throughout the use of other compositions, it was possible to create a pseudobinary diagram as function of the Cu content as shown in Figure 1(b) indicated by dotted lines since the continuous lines indicate the binary diagram for the Al-Cu. Therefore, these data allowed establishing the composition range where the gap of temperature is at least 40°C with coexistence of liquid and solid. What is more is a better control of the solid fraction as function of temperature. From Figure 1(b) the content of 4.8 wt% of Cu was a typical composition that would allow an expressive semisolid (SS) field and it was chosen.

In the second step of this work, the prime ingots were melted again at 690°C and the alloy was submitted to a degassing process using a mix containing 97% of Ar and 3% of Cl₂ during 5 min. This procedure aimed to remove oxides present in the alloy and also the dissolved hydrogen. After this procedure the dross was removed and finally metallic Cu was added aiming at a content of 4.8 wt%. Moreover, 0.5 wt% of TiB₂Al (Al5%Ti1%B) was added to promote the refining of grains. The alloy obtained was poured into a permanent mold with dimensions of 4.5 × 15 × 20 cm. Table 1 shows the final chemical composition of the new alloy with 4.8 wt% of Cu.

2.1. Establishing Best Conditions for T6 Tempering. Throughout the investigation the minimum time for maximum solubilization of the all precipitates was defined. Using the data obtained in Figure 1(b) the 525°C for this step was chosen. Therefore, to determine the time for optimizing solution heat treatment, samples were heated at 525°C.

![Figure 1: DTA results. (a) Example of the result obtained for the alloy with 0.23 wt% of Cu and (b) pseudobinary phase diagram of Al alloy recycled with Cu addition.](image-url)
The samples were solubilized during 2, 6, 24, and 48 h and quenched in water and after that they were naturally aged. The efficiency of the heat treatment was evaluated by Vickers Hardness measurements. After this step the best time and temperature were investigated for the artificial aging (T6). The maximum temperature to be studied was determined by a complementary study using a differential scanning calorimetric (DSC) brand Netzsch Jupiter® DSC 404 F3 with argon atmosphere a heating rate fixed at 10°C/min until 500°C and signs related to precipitation as function of time and temperature were collected throughout the variation of energy during the heating. The resulting peaks represent the energy involved in the precipitation process and the onset of the them has indicated the higher temperature that alloy would be submitted in the precipitation heat treatment.

2.2. Thixoforging Process. From the plate produced in second step, thixoforged parts were made. Thixoforging four pieces at 580°C and 615°C was decided, respectively, corresponding to solid fractions of \( f_s = 0.8 \) and 0.6. In this case again Figure 1 has helped to choose those temperatures. The heating rate was around 20°C/min and the chosen temperatures were sufficiently higher to afford a good condition for the forming process. Furthermore, the resting time of 20 min and 30 min was necessary to ensure the formation of the typical globular microstructure of thixoforged parts in semisolid process. A resting time too much short can restrain the conformation and on the other hand if it would be too much long an excess of hydrogen from atmosphere could be introduced causing some porosity. The best choice is a time as short as possible since the conformation and globular structure are guaranteed. Also, thixoforged parts were submitted at more T6 promising temper studied. The parts obtained have been used for preparation of specimens to perform tensile tests.

The matrix used for the thixoforging process was made by AISI H13 steel which can withstand high operating temperatures. The shape of the thixoforged parts was very simple since the main focus of this work was not studying flow conditions. The mounting of the thixoforged equipment basically consists of a conventional press, a base for stamping, the matrix, a punch, and a furnace for heating the alloy. The forming force was maintained at about 15t and Figure 2(a) shows a schematic of the apparatus used.

The preconditioning used to produce the characteristic globular microstructure in SS was the thermomechanical heat treatment (THT) similar to a well-known thermomechanical method, the strain-induced melt-activation (SIMA) [15]. The preconditioned raw material was used to produce the parts as follow: samples were placed in an electric furnace and when the alloy in the SS has reached the resting time desired it was removed from the furnace and placed into the matrix permitting the conformation and four pieces were obtained with dimensions of 80 × 50 mm and a thickness between 20 and 30 mm. Figure 2(b) shows a thixoforged piece. The matrix before being used was heated with a propane torch (LPG). This procedure besides improving the flow conditions has avoided possible liquid metal projections due to vaporization of humidity.

Finally, the thixoforged pieces were submitted to the T6 temper and tensile test was made from them. The results allowed evaluating the mechanical properties for the new alloy reaching correlations with its microstructure. For each experiment at least 3 tensile specimens were made. Figure 3 shows the dimensions of the machined test specimens. All mechanical tests were performed in a universal machine tensile testing brand EMIC model DL10000.

2.3. Microstructural Characterization. The microstructure of the samples was examined by optical microscopy. The preparation process went through a roughing by sanding
Table 2: Results of the tensile tests.

<table>
<thead>
<tr>
<th></th>
<th>2024 [14] (T6)</th>
<th>Can alloy (°F)</th>
<th>Al4.8 wt% Cu (°F)</th>
<th>Thixoformed – Al4.8 wt% Cu T6</th>
<th>f_y = 0.6, 615°C (°F)</th>
<th>f_y = 0.8, 580°C (°F)</th>
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<tr>
<td></td>
<td></td>
<td></td>
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<td></td>
<td>20 min</td>
<td>30 min</td>
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<tr>
<td>Y_s (MPa)</td>
<td>345</td>
<td>111</td>
<td>207 ± 30</td>
<td>257 ± 18</td>
<td>202 ± 18</td>
<td>200 ± 12</td>
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<tr>
<td>σ_s (MPa)</td>
<td>425</td>
<td>151</td>
<td>307 ± 19</td>
<td>324 ± 10</td>
<td>282 ± 9</td>
<td>283 ± 6</td>
</tr>
<tr>
<td>ε (%)</td>
<td>10</td>
<td>6.2</td>
<td>4.5 ± 1</td>
<td>7.1 ± 1</td>
<td>9.0 ± 1</td>
<td>5.3 ± 2</td>
</tr>
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1Yield strength. 2Ultimate strength. 3Elongation. °F (as cast). °F T6 (solutionizing during 24 h at 525°C and aging during 3 h at 190°C).

3. Results and Discussion

Hardness curves for the different samples submitted to the solution heat treatment during different times and naturally aged are presented in Figure 4. The best result was obtained for 48 h but the treatment during 24 reached almost the same result. Although the results of this study have shown that the time of 48 h is the best condition, however, due to the slight increase in hardness it was chosen to perform solution heat treatment during 24 h.

In Figure 5 the micrographs are presented as cast and after the solution heat treatment at 525°C during 48 h. The micrographs suggest clearly that there is reduction in the volume fraction of precipitates in the solutionized sample. The solution heat treatment also increases the grain size. As expected a lot of amount of precipitates that are mainly in the grain boundaries were dissolved in the aluminum bulk of the grains. The main purpose after this step is to perform T6 temper to form new precipitates with coherent interface that will produce an alloy with higher resistance [16, 17].

Usually the aging step is performed under temperatures from 130°C up to 280°C. Figure 6 compares calorimetric differential results obtained for samples solutionized under different times and it is possible to identify that the temperature of approximately 240°C is the maximum feasible to perform artificial age. Although Figure 7 shows clearly that 2 h is probably sufficient to a good solubilization it was chosen 24 h to ensure higher hardness and strength. After the process of precipitation, the samples were heated again and the precipitation peaks disappeared completely. From this result to make studies for the artificial aging was decided at temperatures of 190°C and 230°C.

From samples solutionized during 24 h the studies were performed under artificial aging and results are in Figure 7. The maximum hardness occurs around 3 h under a temperature of 190°C reaching a hardness of 121 HB and at 230°C the hardness reached was 112 HB. Therefore, for thixoformed parts T6 temper was chosen at 190°C during 3 h.

The results obtained in Figures 6 and 7 have been used to establish the condition for the heat treatment in thixoformed parts using the new alloy Al4.8 wt% Cu. In Table 2 all results of tensile tests summarized are presented. Usually the mechanical properties of the alloys processed in SS are higher than those produced in conventional casting process. However, Table 1 compares the results obtained with a commercial alloy 2024 and the conclusion is that properties obtained for the new alloy processed in SS are limited. But the processing for 2024 alloy was the extrusion, and higher performance is expected for alloys mechanically processed. For alloys processed in the SS was expected a yield strength between 257 and 280 MPa, ultimate strength

![Figure 3: Specimen dimensions for tensile test in mm.](image)

![Figure 4: Evolution of hardness to the natural aging of the new alloy Al4.8 wt% Cu solution heat treatment under different times.](image)
Figure 5: Microstructure of Al4.8 wt% Cu. (a) As cast. (b) after soaking for 24 h at 525 °C. Samples were etched with 0.5% HCl solution during 5 min.

Figure 6: Differential scanning calorimetry of solutionized samples Al4.8 wt% Cu. Peaks show precipitation in the recycled aluminum alloy.

Figure 7: Curves for T6 temper for new alloy recycled Al4.8 wt% Cu.

of 318–344 MPa, and a minimum of elongation of 6% [13]. Some samples reached those limits and others do not; however in all examples was obtained higher performance for thixoforged parts when likened with the same alloy nonprocessed in SS. An important aspect that must be pointed is the improvement of the elongation which can indicate a likely better behavior of the part when it is applied under cyclic conditions; this is a very important aspect for automotive industry. The ultimate tensile strength decreases with the resting time for lower solid fraction \((f_s = 0.6)\) and the opposite occurs for higher solid fraction \((f_s = 0.8)\) and the same behavior for the yield strength was obtained. The results have shown that prolonged resting time associated with lower solid fraction results in higher elongation.

In Figure 8 are presented some examples of tensile tests curves. The increase of the resistance of the alloy may be associated mainly due to the formation of the precipitates such as \(\text{Al}_2\text{Cu}\) and in 2011 a very interesting study was published showing the precipitation mechanism of an alloy with chemical composition similar to this study by Birol [14] and it was demonstrated that under the artificial aging there is a significant gain in hardness.

In Figure 9 are presented the microstructures obtained for the parts thixoforged. In both solid fractions it is possible to confirm sine increase of the globular grain as function of the time. The microstructural evolution probably followed the well-known Ostwald Ripening model adapted for systems in SS [18]. For all samples were observed particles with globular morphology which has considerable importance for ensuring higher fatigue resistance. Some dark regions appear to be high porosity but actually those are due to the etching of the samples with HCl for prolonged times to reveal the globular microstructure and Figure 9(e) is a typical example of a nonetched sample that exemplifies the low level of porosity of the samples.
It is very difficult to correlate the mechanical properties with the final result of the microstructure, since the alloy is maintained longer in the SS, as consequence particles grow; besides hydrogen is absorbed by liquid phase and some precipitates are dissolved in the liquid. The growth of particles probably promotes lower resistance as the example presented by Zoqui et al. in 1998 [19]. The presence of hydrogen could lead to reduction of the strength due to formation of bubbles in a subsequent heat treatment such as solutionizing followed by T6 temper. Finally, the dissolution of precipitates can promote better properties due to the reduction of coarse type. Moreover, unknown factors may also operate and therefore to establish rules that allows us to know clearly how each of these factors are contributing to improve or spoil the final mechanical properties is a challenge. In summary, it was highlighted that the thixoformed process of the new alloy has shown a good way to obtain adequate properties and the typical globular microstructure used in SS process. The use of recycled cans can be a promising way for large scale production of mechanical components that can be applied in the automotive industry. Some complementary studies related with fatigue are necessary to finally prove the feasibility of the use of this alloy commercially for production of parts.

4. Conclusion

In this work an innovative way to recycle aluminium can scraps has been proposed and it has demonstrated the feasibility of its use with copper addition to produce a raw material to be used in thixoforming process producing parts with properties required by the automotive industry. Therefore, thixoforming process of this new alloy at temperatures between 580°C and 615°C and for resting time in SS from 20 min to 30 min is feasible.

The solution heat treatment which gives higher hardness for the recycled Al4.8 wt% Cu alloy was that one performed during 48 h at 525°C. However, results have shown that 24 h of treatment is also adequate to promote some solutionizing. In the differential scanning calorimetric analysis, it was stablishing that total precipitation occurs for temperatures higher than around 240°C. Therefore, the previous studies have shown that the best treatment to maximize the strength of the new alloy should be a T6 temper during 3 h at 190°C.

The mechanical properties obtained for the thixoformed parts using the raw material Al4.8 wt% Cu are in accordance with that one expected for pieces produced using conventional raw materials for semisolid processing. A yield strength, ultimate strength, and elongation up to, respectively, 257 MPa, 331 MPa, and 9% were reached. These values are consistent with other references.

Parts thixoforming have resulted in an integrate material with typical globular microstructure designed for SS process. This result indicates that the recycled alloy may have a high performance when submitted to the fatigue applications. Some complementary studies are necessary.

The mechanical properties of Al4.8 wt% Cu is very sensitive to the resting time and temperature. The results suggest that under a fixed temperature there is a resting time that maximize mechanical properties. For example, for higher solid fraction higher resting time is necessary to obtain better results.

Competing Interests

The authors declare that there are no competing interests regarding the publication of this paper.
Figure 9: Microstructure of samples thixoformed of the Al4.8 wt% Cu alloy (a) $f_s = 0.6$ and resting time 20 min, (b) $f_s = 0.6$ and resting time 30 min, (c) $f_s = 0.8$ and resting time 20 min, (d) $f_s = 0.8$ and resting time 30 min, and (e) $f_s = 0.6$ and resting time 20 min without etching.

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