

Effect of Heat Treatment on the Mechanical and **Electrical Properties of Al-Co-Mn Alloys**

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Abstract

Al-Co-Mn alloys with different atomic percent were synthetized by induction melting technique. Controlled annealing treatment was applied to the resultant alloys under He atmosphere. Different microstructures were produced as a function of the Mn and Co content producing different grain morphologies. Hardness results indicate an increment in approximately 30 percent (150 kg/mm²) in samples with low cobalt and high aluminum; while fracture toughness evaluations present a noticeable increment for these samples of 50 MPa·m^{1/2} which represents an improvement of approximately five times more than sample with higher aluminum content. Electrical conductivity value, higher than 61.8% IACS was obtained in sample with high Co and low Al content. Electrical characterization was developed to observe the alloy performance as anodic element in a primary battery. Results are interpreted considering mainly a substitutional mechanism.

Keywords

Aluminum Alloys, Microstructure, Mechanical Properties, Electrical Properties, Energy

1. Introduction

Investigations of elements additions in Aluminum systems have been of great interest because of the multiple properties that can be generated on the alloys; specifically energy generation is one of the leading topics in the Al technological applications [1] [2]. Hence, research of commercial batteries is focused principally to decrease the environmental impact of toxic waste without efficiency affectation [3]-[5]. It is well known that in aluminum alloys, atoms can be introduced in the crystal structure in substitutional way or interstitially and the original properties can be modified due to such elements combining their own properties with the original properties of the element in the alloy [6] [7]. Previous studies demonstrated that if Co or Mn atoms are introduced in the Al lattice, these can maintain the structure stability at a relatively high operation temperature (~600°C) [8]. Also, it has been reported that the melting point of aluminum-based alloys increases due to the influence of Co or Mn [9]. Similarly, Co and Mn can improve the oxidation resistance, when the fcc/hcp martensitic transformation structure is obtained [9] [10]. Also, other investigations of Al-Co-Mn system, have been focused on memory shape properties [11]-[13]. Energy generation using anodes of pure or alloyed Aluminum in electrochemical arrangements has been limitedly studied, looking for a minimum self-corrosion and high efficiency energy production [14]-[16]. Thus, it is important to take into account the correlation between elements additions with the microstructure and their physical properties [17]. It has been reported that Co presence in alloys may promote a decrement in Mn solubility, which makes the formation of ternary compounds less probable, while, binary compounds are more easily to precipitate with Al [18] [19]. Because electrical conductors are exposed to a different kind of stresses, then, it is necessary to have a material with enough hardness and toughness to avoid structural failure, hence due to the limited information related about microstructure, and mechanical properties of Al-Co-Mn ternary alloys were carried out, therefore, a complete study has been developed in this investigation focusing the relevance of aluminum content to obtain a light alloy but with good mechanical resistance. Also in this work, the best alloy composition to work as anode in a primary electrochemical cell is reported.

2. Experimental Procedures

Several Al-Mn-Co alloys with different element content (using high-purity elements 99.99%) were synthetized. **Table 1** shows the nominal composition for each alloy using for melting process, a quartz crucible which was introduced in a vacuum chamber (~10⁻³ Torr) connected to a High Frequency Induction Unit. From the resultant alloys, two groups of alloys were heat treated under He atmosphere, namely at 600°C, and 1100°C, for a time of 30 minutes and then furnace cooled. Metallographic preparation was carried out by grinding the surfaces sample with paper sanding up to 600 grade, and after that, samples were polished with alumina up to 0.5 µm, according to ASTM E3-01 standard. Alloys were chemically etched with a Kroll reactant (80 ml H₂O, 10 ml HNO₃, 6 ml HF) during 5 s. Surfaces images analyses were carried out by using an Olympus LTD GX71F Optical Microscope (OM) as well in a LEO 1450 VP Scanning Electron Microscope (SEM). In order to determine the obtained phases a X-Ray Diffractrometer (XRD) Bruker equipment with a Cu-K*a* radiation ($\lambda = 1.541$ Å). Micro-hardness test were carried out with a bolding

time of 15 s. Fracture toughness tests were carried out under ASTM E399-90 standard using samples with a cross section of 4×3 mm and 20 mm length, with a notch of 2 mm in the middle of the sample.

Sample Designation	Elemental chemical content [at. %]			
	Al	Co	Mn	
M-1	70	10	20	
M-2	65	20	15	
M-3	60	35	5	
M-4	58	16	26	
M-5	40	30	30	

 Table 1. Alloys nominal composition diminishing the aluminum concentration.

Electrical evaluations were performed on samples polished up to alumina 0.05 μ m, with dimensions of 2.5 × 50 mm and 5 mm width, the tests were performed using the double bridge method and the measurements were carried out using a micro-ohmmeter AEMC 6250 equipment developing a statistical analysis for each sample. For the electrical test performance, prototype cells were built, using the obtained alloys as anode while graphite bars were employed as cathode.

3. Results and Discussion

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3.1. Microstructure

Figure 1(a)-(e) show the microstructures obtained of the alloys. In the images, it can be observed mainly the presence of two phases in the specimens. M-1 and M-2 specimens are composed of *a*-phase with well-defined enlarged crystals (Figure 1(a), Figure 1(b)), while in M-3 to M-5 samples are observed dendritic zones (Figure 1(c)-(e) respectively). In these images, the matrix corresponds to the β -phase. This occurs because the precipitation of the eutectic phase is produced due to a controlled cooling rate during the solidification process, *i.e.* when α phase has precipitated, then, the solution remained enhanced the β phase formation to keep the chemical equilibrium, therefore, while Al at.% decreases in the alloys, also the grain size presents a significant reduction. Area fraction analyses developed in M-1 alloy shown enlarged grains, occupying about 80% of total area, being the average grain size in this sample of 50 µm. In M-2 alloy also are observed enlarged grains, which grew up to 1 mm length approximately, this effect is produced mainly in aluminum alloys due to the absence of some type of barriers that can inhibit the grain growth [19]. For the specific case of M-3 and M-5 alloys which possesses less amount of Al but more Co and Mn, it is observed that α -phase is present in dendritic zones surrounded by the β -phase (Figure 1(e)). The amount of area fraction of α -phase was calculated and it decreases proportionally with the decrement of aluminum content, being the averages values of area fraction of 78, 65 and 52 percent for samples M-3, M-4 and M-5 respectively.



Figure 1. Images of the Microstructure of heat treated samples. (a) Image by OM and (b) Image by SEM, showing enlarged grains of samples M-1 and M-2 respectively; (c)-(e) Images by SEM, shown transformation from dendritic to eutectic structure corresponds to M-3, M-4 and M-5 samples.

Figure 2 shows the representative chemical analyses by SEM-EDS for each alloy. It can be observed that matrix (β -phase) is composed principally by Al, similar Co and Mn amounts coexists, whereas second phase (α -phase) is Mn rich principally and it contain Al in lower quantity than cobalt, so that, it is clear to observe in the plot the composition ratio of Mn peak in comparison with Al and Co of this phase. The variation in composition is the result of the Al amount and the substitutional Co in each sample after melting-casting-solidification processes and combined with the applied thermal treatment, therefore, it is highly probable that evaporation process can be developed mainly due to the presence of the high amount of aluminum in the alloy during the melting process. According to the area fraction calculations for each phase present in the alloy, the matrix phase is approximately 63% less than eutectic phase.



Figure 2. Chemical analyses obtained by SEM-EDS in (a) matrix and (b) eutectic phase; chemical compositions are given in wt.%.

Figure 3 presents the X-ray Diffraction (XRD) patterns of the alloys with heat treatment in which the chemical species identified for each alloy are observed. The phases (with high intensity) that were identified are principally MnAl₆ and MnAl₄, while the identified compounds based aluminum cobalt are CoAl and Co₂Al₅. It is observed that the heat treatment (mainly at 1100°C) tends to break the bonds of the MnAl₆ and therefore a tendency to lose crystallinity is produced, acquiring some texture structure [18]. Also the presence of Co₂Al₉ was identified; this phase correlates with the chemical analysis of **Figure 2** which correspond with the grains with columnar morphology (**Figure 1(b)**) which grew up to 100 μ m after the heat treatment. Then, due to transition metals often exhibit succession with well-defined stoichiometry when these elements are melted in correct proportions, then the successions that can occur in the proposed system Al-Co-Mn are: with cobalt: Co₂Al₉, Co₄Al1₃, CoAl₃ and CoAl₅ with manganese: MnAl₆, MnAl₄ and MnAl₃ [20].



Figure 3. X-Ray diffraction patterns of heat treated samples at different temperatures.

3.2. Hardness Test

Figure 4(a) shows the hardness value obtained for the alloys treated at different temperatures. Indentations were placed on the matrix and on the second phases. **Figure 4(b)** shows the difference in the microhardness values for both phases, being matrix phase 46% harder than eutectic phase, possibly as a result of a higher

Co concentration in this phase which possesses a higher hardness in comparison with Al and Mn phases. This fact may promotes the highest hardness values observed in M-3 specimen, which contain mainly the presence of Co₂Al₅ therefore, second phase formation can be considered as the main operative mechanism that produces hardening in the alloys, specifically for M-2 to M-4 samples, resulting in a 3.8% increment respect of M1samples. On the other hand, hardness increment obtained is related with the inhibition of dislocations mobility due to a lattice distortion, being the most common way of hardening in aluminum alloys by the production of precipitates or also the incorporation of element addition with different atomic radii [8]. Besides, it can be considered that the gap in atomic radii between the aluminum and manganese is 0.8103 Å, such difference in atomic sizes makes that the possibility to generate a lattice distortion increases and therefore a reduction in plastic deformation *i.e.* planes misalignment generating agglomeration of dislocation networks [8] [9].



Figure 4. (a) Vickers hardness of as cast and heat treated alloys; (b) Vickers hardness for each phase found in the alloys.

3.3. Fracture Toughness

Figure 5 shows the plot of the fracture toughness evaluation of samples treated at different temperatures, where it is noticeable that the most resistant alloys to be fractured are the M-2 and M-3 samples no-treated with high Co content and moderate aluminum in the alloy. This result is expected because sample with moderate Al content *i.e.* M3 can be the most susceptible to inhibit the micro-cracks nucleation due to the presence of aluminum rich phase (which is the softest material in the alloy), then the combination of a soft phase with a hard phase produces restriction or difficulty for crack nucleation-propagation [9]. In the same way, toughness increases notoriously for M-3 samples heat treated, attributed to an ordering-disordering in the crystal structure which stop the crack propagation. However for samples M-4 and M-5 the toughness decreases notoriously approximately 40 MPa \cdot m^{1/2} as a result of micro cracks generation during the load application. The cracks nucleation and interaction with these defects (dislocations)

may explain this detrimental effect, where is highly probable the low cohesion between grains, also can be produced by a manganese excess in the alloy (as can be observed in chemical analyses of **Figure 2(b)**) producing the crack propagation. Therefore, after these considerations it is established that low manganese concentration together with moderate aluminum in the alloy may result favorable to obtain an improved toughening.



Figure 5. Fracture toughness values for samples in cast and heat treated condition.

3.4. Electrical Evaluation

Figure 6(a) and **Figure 6(b)** present the plots of voltage open circuit (V_{OC}) and direct current (DC) tests respectively from samples with different heat treatment, also, inset in graphics, an image of the prototypes cells and the connecting array in a circuit a 1.5 V Led are shown. In both tests M-1 sample shows the higher values of V_{OC} and DC, nevertheless gradually the values diminishes, this behavior is generalized and observed in all samples due to the small area of the anode and electrode when the current circulate through Led, which is turn on after the circuit was connected. Then, the proposed material working as anode can generate voltage and therefore electric current via the product of a reversible chemical reactions between the electrolyte-ions and the electrodes superficial atoms, accumulating chemical species on the electrode surface by giving up or absorbing electrons, inducing in this way electric current.

On the other hand in **Figure 7** are shown the values of electric resistance for samples as a function of the heat treatment, where it is observed that samples with low aluminum in the alloy does not present a remarkable affectation, being it the samples with the lower resistance values, this behavior has been reported with anteriority and it is attributed to an extensive lattice array with a considerable absence of internal defects [16] [21], also, it is important to note that heat treatment

have remarkable influence on the resistivity values, due to heat treatment produces a rearrangement of the crystalline planes diminishing for consequence the electrical resistance. Nevertheless, M-2 sample shows a different tendency, keeping a constant low value, probably because the microstructure of this sample did not suffer a notorious change due to the treatments conditions. For the other samples it can be observed that an increment in the annealing temperature results in a decrement in the electrical resistance due to decrease in the dislocation density after annealing treatment [21], *i.e.* the electrical conductivity it is improved by making easier the electron pathway to circulate the electric impulse.



Figure 6. (a) Open Circuit Voltage graphic, inset of electric array scheme of the prototype cell; (b) Direct Current graphic, inset showing a led connection in the electric array.

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Figure 7. Electric resistance of samples as a function of the heat treatment.

	Electrical Conductivity IACS [%]		
Sample	As-cast	Annealed at 600°C	Annealed at 1100°C
M-1	56.4	56.5	57.6
M-2	59.5	60.0	59.6
M-3	59.4	58.04	59.6
M-4	61.8	61.7	57.6
M-5	58.6	60.1	61.8

Table 2. Average values of the electrical conductivity of samples with different Co and Mn additions annealed at 600°C and 1100°C.

Table 2 presents the numerical values obtained from the measurements of the electrical conductivity for samples as a function of the heat treatment and the element composition.

It can be observed sample M-5 with high aluminum content and low cobalt additions present the higher value of electrical conductivity in annealed condition at 1100°C close to 61.8% IACS, which means that the dislocation production by the interaction of cobalt and manganese it is low, hence the electron transit become easier across the alloy; however for the alloys with higher cobalt and manganese the electrical conductivity decreases towards values close of 59.9% IACS (average), which is not surprising since atomic radii for Co and Mn are higher 0.647 and 0.8147 Å respectively in comparison with atomic radii of Al (1.3697 Å), so it is difficult the free transit of electrons through the bulk alloy due to the presence of dislocations networks distributed inner the bulk material. These results present a good correlation with the resistivity values obtained in heat treated samples.

5. Conclusion

Al-Co-Mn alloys with different atomic percent were obtained by induction electromagnetic technique; microstructures obtained have shown different morphologies as a function of cobalt and manganese content from eutectic structures to equiaxed grains. Mechanical properties evaluation reveals that cobalt addition improves the fracture toughness by approximately five times (65 MPa·m^{1/2}), and increases hardness by 150 kg/mm² in comparison with sample with high aluminum concentration. The sample with a high cobalt and low manganese content exhibits the best performance. Electrical evaluations indicated that alloys treated at 1100°C possess the lowest electrical resistance value and an average electrical conductivity of 61.8% IACS. The present results suggest that the combination of the above mechanical-electrical properties of Al-Co-Mn alloy makes it a promising material in energy conduction applications.

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Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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