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EFFECT OF ANNEALING AND SILVER CONTENT ON THE MECHANICAL PROPERTIES OF Zn-Al-Ag ALLOYS

Through the powder metallurgy technique, alloys of the eutectic composition of the Zn-Al system were manufactured (22.3 wt.%Al), reinforced with Ag additions (0.5, 1, 2.5, 5 wt.%), with subsequent annealing heat treatment at three different temperatures; 100, 150 and 200°C for 1 hr. X-ray diffraction, optical microscopy and mechanical tests were performed on the resulting samples. The addition of Ag favors the formation of alpha and beta compounds with Al and Zn respectively, which improves the compressive strength of the alloy. However, with the presence of Ag the hardness is decreased. On the other hand, the application of an annealing heat treatment, shows no significant effect on the evaluated properties of the alloy. The microstructure of the alloys resulted in the presence of very small grains smaller than 1 mm and with rounded morphology.

Keywords: Zn-Al-Ag; Powder metallurgy; Mechanical properties; Silver; Annealing

1. Introduction

Today, innovation in lightweight alloys, such as Al and Mg alloys, has opened the door to their potential application in the ground transportation and aeronautical industries. Within light alloys, zinc-aluminum system alloys have been in demand in a wide variety of applications [1]. Because they are good candidates to replace ferrous and non-ferrous alloys, due to their good mechanical properties at room temperature. However, a major problem is that Zn-Al alloys exhibit lower mechanical properties when they are exposed to operating temperatures above 100°C [2]. One of the solutions to this problem has been the incorporation of thermally stable particles (ceramics) such as alumina [3], silica [4], silicon carbide [5], graphite [6], etc. Nevertheless, this procedure presents the problem of low adhesion between the reinforcing particles and the matrix, since the main production method of these alloys is by casting. Other methods have been the application of heat treatments focused on precipitating secondary phases that harden the alloy [7], since the microstructure of eutectic Zn-Al alloys can be modified by heat treatments [8]. On the other hand, there is also the option of modifying the alloy composition by adding alloying elements such as Cu, Si and Mn, which produce dispersed compounds within the matrix [9]. In his doctoral thesis Cosalco [10] studied the effect of silver additions in the eutectoid Zn-Al alloy, where he found that the silver additions refine the grain, which is reflected in a considerable increase of the mechanical properties of the alloy, as well as he observed a superplastic behavior of the alloy. On the superplasticity property of the latter alloy, some authors [11,12] delved into the subject, finding that indeed the grain refinement caused by the silver in the alloy is what allows this behavior. Likewise, there are different works in which the relationships between silver content-microstructure-mechanical properties in alloys of the Zn-Al-Ag system have been analyzed [13-15], finding that silver has a strong influence on the final composition of the phases present, which causes microstructure refinement together with an increase in mechanical properties. Finally, Sevik [16] analyzed the effect of different silver additions in Zn-Al alloy on the microstructure, hardness and wear properties of the alloy, it was observed that the addition of silver to the alloy effectively improves the hardness and wear properties. However, in this study it was reported that corrosion resistance decreased with increasing silver content. From this review it can be seen that the addition of silver in the alloys of the Zn-Al system constitutes the refinement of the alloy grain [10]. Although, the optimum amount of Ag to achieve the finest grain size has not been established. Additionally, the different manufacturing procedures involving heat treatments help to develop different characteristics in the alloy, but without sufficiently altering the microstructural core. From the literature review, the production method of the alloys has been the traditional casting method, with the consequent problems of chemical segregation

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of elements and abnormal grain growth during solidification, which leads to the failure to obtain homogeneous mechanical properties. Thus, powder metallurgy can offer a wide panorama in the efficiency of material transformations compared to conventional techniques, since the raw materials are powders that are more manageable than liquids and the energy requirement for the transformations is much lower. Therefore, it is interesting to study the physicochemical and mechanical properties of Zn-Al-Ag alloys processed by powder metallurgy, which is the objective of this work.

2. Experimental

Through powder metallurgy, the 77.7 wt.% Zn-22.3 wt.% Al-XAg alloy (X = 0 wt.%, 0.5 wt.%, 1 wt.%, 2.5 wt.%, 5 wt.%) was fabricated. Five samples of each composition were made and the results reported are the average of the measurements on each sample. The powders were subjected to a grinding process in a high energy planetary mill (Retsch, PM 100, Germany). The grinding parameters used in the 5 mixtures were as follows: grinding for 1.5 hours at 250 rpm, using isopropyl alcohol as a control agent and managing a ball weight to powder weight ratio of 10:1. Once the powders were ground, they were pressed to form cylindrical pellets with an average diameter and height of 10.5 mm and 3 mm respectively, using a tool grade steel die. Compaction of these samples was carried out at room temperature by unixial pressing using a pressure of 250 Kg/cm^2 in a hydraulic press (Montequipo, LAB-30T, México). Afterwards, all the pellets were sintered in an electric furnace. (Carbolite RHF 17/3E, England) at 380°C for 1h, with a heating rate of 10°C/min. The furnace was set up with a protective argon atmosphere to prevent oxidation of the metals. In order to determine the effect of different annealing heat treatments on the mechanical properties of the alloys, 3 heat treatments were carried out at 100, 175 and 250°C for 1 hour each, on the already sintered samples. After the grinding stage, the particle size distribution and the specific surface area were determined using a Mastersizer 2000 equipment of English origin. Finally, the study samples were characterized in order to determine the mechanical properties. The mechanical properties evaluated were as follows: The ultrasonic method determined Young's modulus, following ASTM standards [18], using a Grindosonic A-360 Japanese manufacturing equipment. Microhardness was evaluated in agreement with the ASTM E384–16 standard [19]. In this case, twelve measurements were performed at different sample locations and the average value of the indentations is reported; these measurements were performed with a microhardness tester (Wilson Instruments Model S400, USA). The compressive strength was evaluated at a Universal Material Tester WP 300 Gunt. Densification degree by the Archimedes method [17], microstructural analysis to determine shape and grain size using an optical microscope (Nikon Eclipse Ma200, Japan) and structural analysis to determine the crystalline phases present in the resulting alloys, using a Siemens diffractometer, D-5000, Germany.

3. Results and discussion

3.1. Particle size distribution

Fig. 1. shows the particle distributions for each of the manufactured samples. In this figure it can be seen that with silver additions of 2.5 wt.% and principally 5 wt.% very large particle sizes are achieved. The opposite case occurs at low concentrations of silver, where although the size distribution is smaller, the particle size is also smaller in where there are particles below 5 microns, while for largest quantities of silver, are reached particles of up to 25 microns. The main reason for this is that silver, being a very ductile metal, deforms a lot during milling and certainly not only does not fracture, but it can join by welding with the other two metals (aluminum and zinc) causing the generation of large agglomerates. In the case of silver additions of 0.5 and 1 wt.%, the particle distribution is very good since the particle sizes range from 2 to 4 microns approximately, which can be beneficial during sintering. On the other hand, for the sample with 2.5 wt.% the distribution is much wider, since here we have sizes ranging from 2 microns to just over 10 microns. This can generate pores of a few microns during compaction that are difficult to remove during the sintering stage.

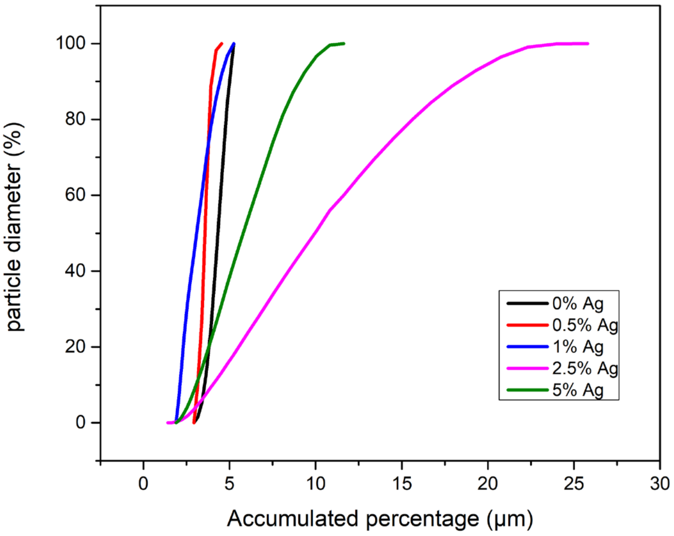

Fig. 1. Particle size distribution of samples with different silver contents and ground at 250 rpm for 1.5 h

3.2. Density

The results of the densification measurements on all samples obtained through the Archimedes principle indicate that the density of all samples was, in the order of 90% of the relative density of the alloy. Formation of some agglomerates between the 3 metals during the milling stage, caused the generation of some large pores, which prevented the achievement of higher densities in the alloys. In order to improve the densification of the products, it will be necessary to experiment with other processing conditions such as increasing grinding times, compaction pressures and sintering temperature, as well as using a control agent that helps to avoid the formation of agglomerates during grinding.

3.3. Phase analysis

In the X-ray diffraction analysis, it can be seen in Fig. 2. the elements found and the phases of the samples, where Zn is the element that is observed in greater quantity. Likewise, there are peaks corresponding to aluminum. The spectrum shows alpha and beta phases corresponding to different compounds formed by silver with aluminum and zinc respectively, which is an indication that silver goes into solution in the alloy. The structure is predominantly compact hexagonal because zinc is the main component of the alloy. However, there are also traces of a face-centered cubic structure due to the presence of aluminum and silver in the alloy.

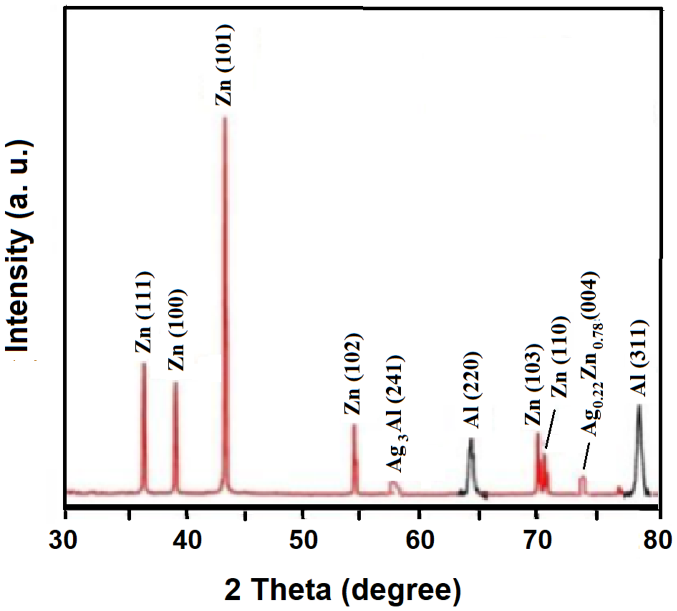

Fig. 2. Diffraction pattern of the 5%Ag sintered sample at 380°C for 1 h

3.4. Microstructure

The microstructure of each studied composition is shown in Fig. 3. Only the microstructures of each composition after the sintering stage are presented, because after the heat treatments performed on them, no significant changes in the microstructural characteristics were observed. In general, the microstructures are very fine and homogeneous, with rounded grains due to the milling process. In the micrographs with 0 and 0.5% Ag, some pores can be observed (black points). As the silver content in the alloy increases, the amount of pores decreases considerably. What helps densification in this case is precisely the presence of silver, which is a metal with a high thermal conductivity and to the extent that it is found in higher contents in the alloy, it favors the diffusion processes to improve the densification of the alloys. Flores-Ramos in his work on phase transformations in the Zn-Al-Cu system with silver additions [20], comments that the presence of silver inhibits the formation of different phases between the components of the system, which is reflected in the refinement of the grain. It was also documented that the Zn-Al-Ag alloy [13] exhibits superplastic properties due to grain refinement caused by the presence of silver in the alloy. From this it can be commented that the silver present in the alloys studied here is the direct cause of obtaining such

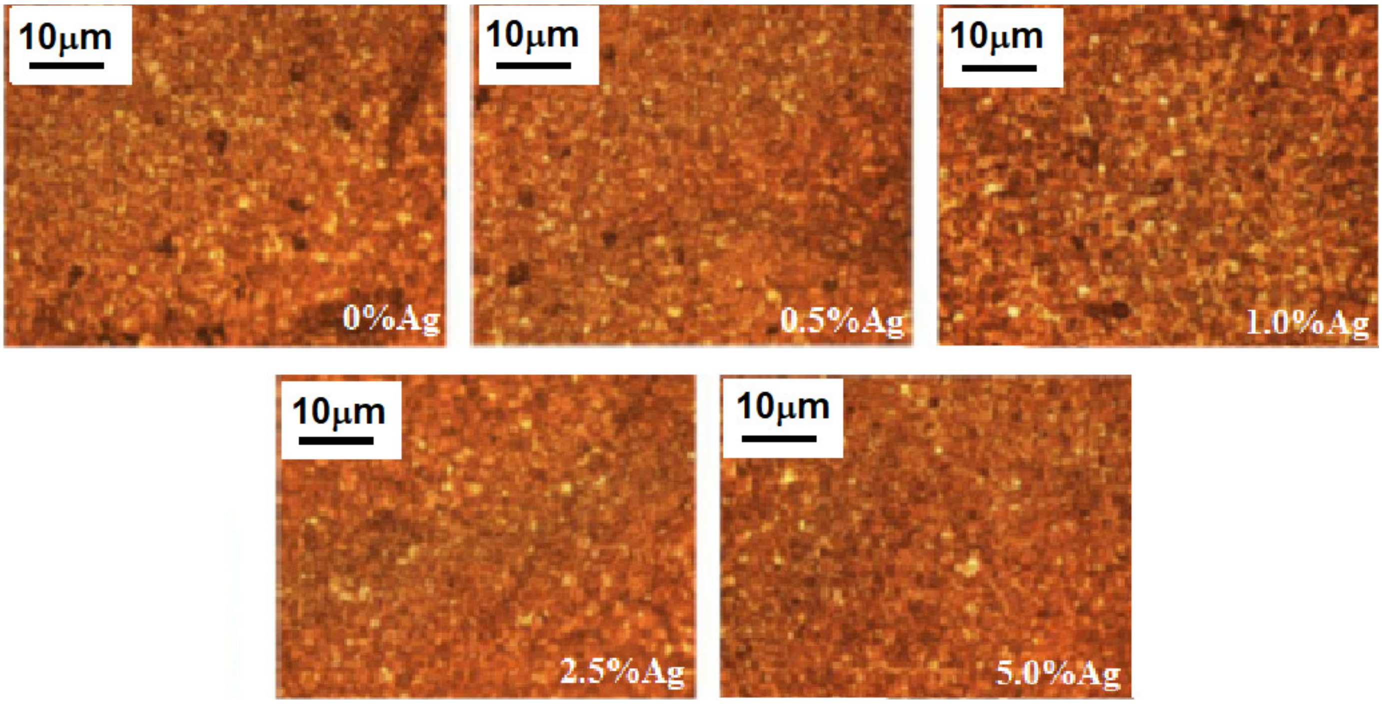

Fig. 3. Microstructure of the alloys with different Ag contents after sintering

fine microstructures, which can allow high deformations before fracture when subjected to stresses.

3.5. Mechanical properties

3.5.1. Hardness

Comparatively, Fig. 4. shows the hardness of un-annealed and annealed alloys at different temperatures as a function of silver added to the alloy. In general, what can be observed in the figure is that with increases of silver in the alloy with or without annealing, the hardness tends to decrease considerably, which is an effect of the high ductility of silver associated with its face-centered cubic crystalline structure like that of aluminum. From these results it is not observed that the annealing temperature has a significant effect on the final hardness of the alloy. On the other hand, this figure shows that the sample with 5 wt.% Ag annealed at 250°C presents a significant increase in hardness compared to the other alloys annealed at lower temperatures and with lower silver content. This behavior is somewhat strange and further experimentation at these conditions will be necessary to corroborate the result or to understand what phenomenon is occurring here that causes such an increase in hardness.

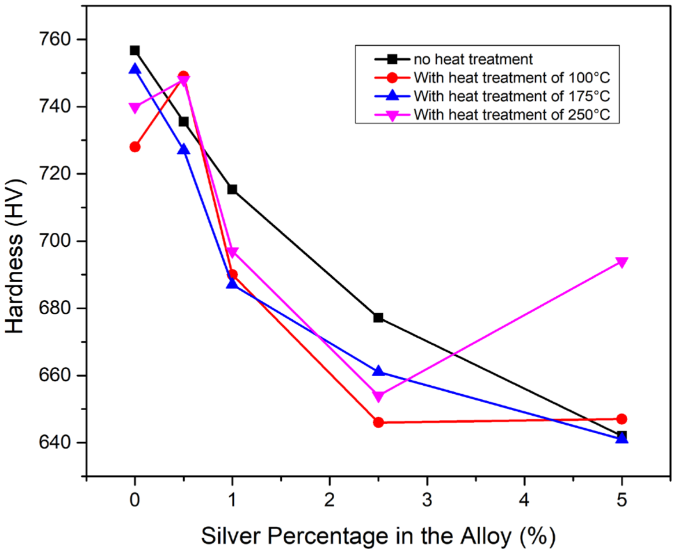

Fig. 4. Hardness values of the alloys at different annealing temperatures and as a function of the silver content in the alloys

3.5.2. Elastic modulus

The elastic modulus of the samples shows a different behavior from the correlation of hardness and density, as shown in Fig. 5. In which it can be observed that at low silver contents the elastic modulus is lower, increasing for the 2 higher silver contents. However, the variation in the magnitudes of the elastic modulus for the different samples is not significant. Therefore, silver additions cannot be considered to have a very large effect on the final value of the elastic modulus of this alloy.

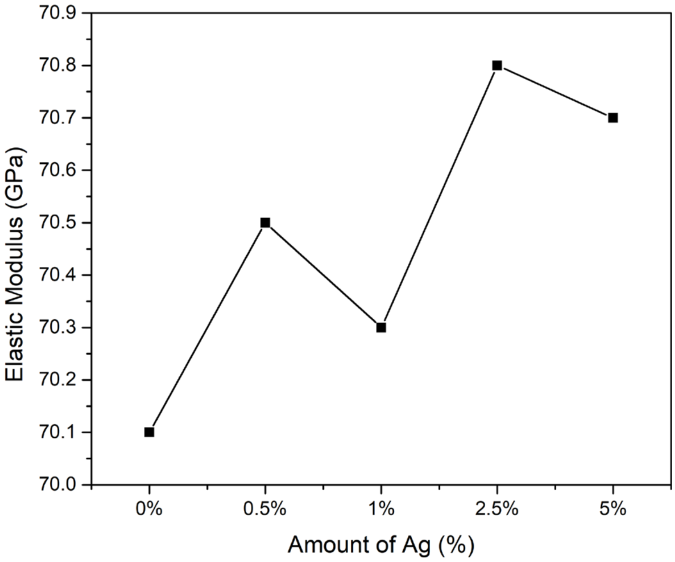

Fig. 5. Values of the elastic modulus of alloys at different annealing temperatures and as a function of the silver content of the alloys

3.5.3. Compressive strength

From the compressive strength results for alloys annealed at different temperatures and as a function of silver content, it is found that in general the compressive strength of the alloys increases with both increases in annealing temperature and increases in silver content, up to a certain limit because for 5 wt.% Ag the strength decreases. To corroborate this, the stress-strain curve for the sample annealed at 250°C is presented in Fig. 6.

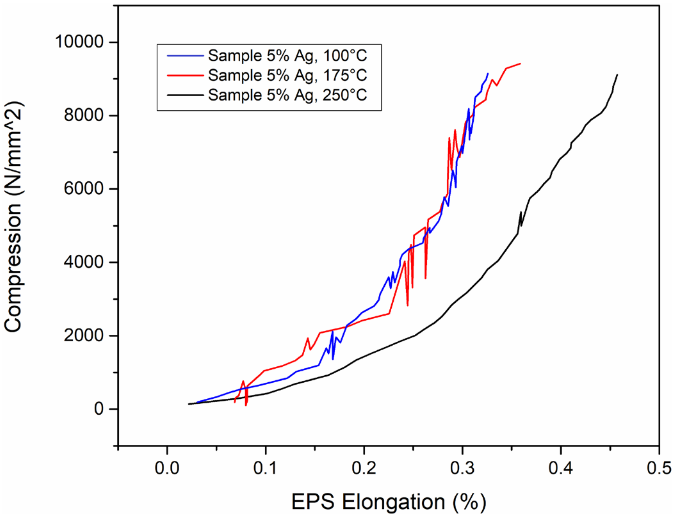

Fig. 6. Compressive strength values for different annealing temperatures and as a function of the silver content therein

TABLE 1 shows the results obtained from the compressive strength test for the samples annealed at 250°C, which were the ones that reported the best results. From the results of this table, it is observed that there are no significant differences in the yield strength for all the study compositions. However, with respect to the maximum stress achieved by each sample, it is found that it increases as the silver content in the alloy increases Being the sample with 2.5 wt.% Ag the one that reached the highest strength. Regarding the percentage of deformation obtained by each sample, again the behavior is repeated in the sense that the deformation is higher for higher silver contents, reaching a maximum for the sample with 2.5 wt.% Ag. The % strain obtained by the latter sample corresponds to approximately 70% higher than that of the sample without silver. Analyzing these results in detail, it can be seen that increases in silver in the alloy considerably improve the compressive strength and strain of the alloys, this is in total agreement with the results of hardness where it was observed that this property decreased, so it was expected increases in the strength of the alloy. These results are also in agreement with those obtained by Robles Casolco [2] in his study in which he suggests that the addition of silver to the Al-Zn alloy will give it plastic characteristics, i.e., it will be able to deform quite a lot without fracturing. This increase in the strength and strain percentage of the alloy is due to the grain refinement caused by the silver present in the alloy.

TABLE 1

Properties evaluated from the compressive strength test

Wt.% Ag	Yield point (N/mm^2)	Maximum strength (N/mm^2)	Strain (%)
0.0	1987	7868	0.34
0.5	2018	8341	0.43
1.0	2082	8268	0.53
2.5	2054	8951	0.57
5.0	2063	8434	0.46

4. Conclusions

Through the proposed powder metallurgy route it was feasible to manufacture Zn-Al-Ag alloys. The effect of mechanical milling is reflected in the obtaining of particles smaller than 4 microns, which also results in homogeneous microstructures with fine grains of a few microns in size and rounded shape. Additions of 2.5 wt.% Ag in the alloy enhance the elastic-plastic properties of the alloy because silver favors major strain, due to the refinement of the grain in the microstructure. XRD analysis confirms the presence of the original metallic phases after the sintering stage, in addition to the formation of silver compounds with aluminum and zinc respectively. Finally, it can be commented that due to the microstructural characteristics, the low density and the mechanical properties obtained in the alloys under study, these can have application in the manufacture of different parts for the automotive and aeronautical industries.

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