

# Effect of molybdenum addition to ZA22 grain refined by titanium in the cast and after pressing by ECAP

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**Abstract.** Zinc aluminum alloys are versatile materials which are widely used in manufacturing many industrial and engineering parts due to their attractive properties. The ZA22 has the extra advantage of possessing super plastic behavior within the temperature range from 350 to 375°C. The equal channel angular pressing, ECAP is a relatively recent manufacturing process by which heavy plastic deformation can be produced in materials resulting in grain refinement of its microstructure. It is, therefore, anticipated that if the ECAP process is applied to the ZA22 alloy after being grain refined by certain grain refiners may produce super plastic behavior in this alloy at room temperature, by this eliminating the heating process and its costs, hence widening its applications rendering it to be cost effective. In this paper, the effect of molybdenum addition at a rate of 0.1 % wt. to ZA22 grain refined by Ti on its metallurgical and mechanical characteristics in the cast condition and after applying the ECAP process is investigated. It was found that addition of Mo to ZA22 either in the non-refined or the refined by Ti resulted in refining its structure being more refined in the latter. The ECAP process resulted in further refinement of its structure of the ZA22-Ti, ZA22-Mo and the ZA22-Ti-Mo alloys. Regarding the mechanical behavior, it was found that addition of Mo to ZA22 resulted in pronounced reduction of its mechanical strength presented by the following values of the flow stress at 20% strain: from 451 MPa to 346 MPa, whereas pronounced increase in case of Ti addition i.e. by 22.22% and only increase of 1.1% when Mo is added in the presence of Ti. However the Vickers hardness HV was increased by 5% in case of Ti addition and 2.5% increase in case of Mo addition. Finally it was concluded that super plastic behavior was obtained at room temperature by the addition of Mo and the ECAP process.

## 1. Introduction

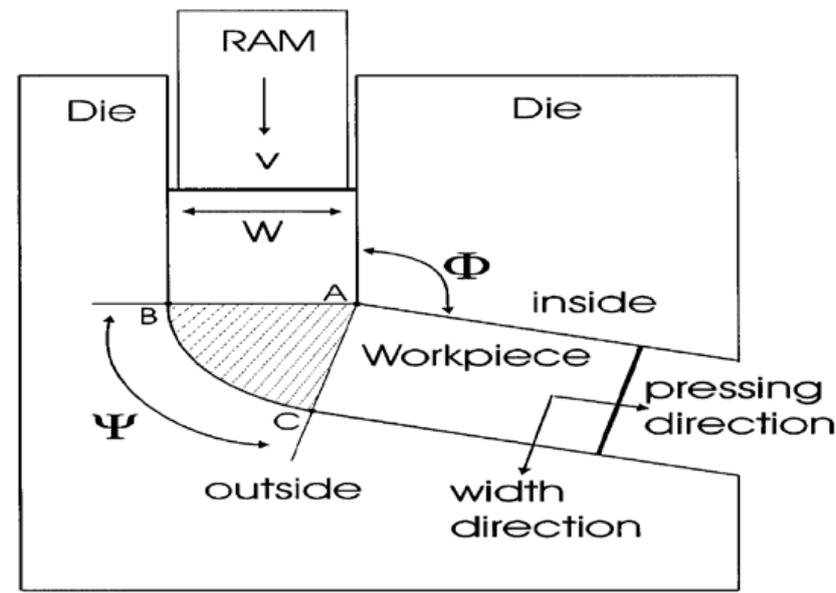
Zinc- aluminum alloys, in general are versatile materials which are widely used in a wide variety of engineering and industrial applications due to their attractive properties such as strength, toughness, rigidity, bearing load capacity, economical and clean cast ability. In many aspects they are superior to aluminum, magnesium, and copper alloys. Zinc aluminum die casting alloys are widely used in the automobile and air craft industries in manufacturing many mechanical parts such as carburetor bodies, fuel pumps bodies, wind-shield wiper parts, control panels, horns and parts of the hydraulic brakes. Furthermore, zinc-aluminum alloys are used in structural and decorative parts which include radiators, steering wheels, hubs and instrument panels, [1-2]. Other applications include electrical, electronic and



appliance industries. Building hardware padlocks and toys are major areas of applications of these alloys,[3]. Recently, Ridge Tool Company has replaced its bearing gear covers from bronze into Zn-27% Al because they found that this alloy has many of the desirable characteristics of bronze like easy finishing, corrosion resistance and good wear resistance in addition that the Zn-27%Al cuts material cost by 50% and reduces weight by 43%beside the most important advantage that it has longer service life. A newly developed “nanometer-crystalline” in Japan, zinc-aluminum alloy with a molecular elongation of more than 100 percent is said to be so resilient as to make possible an earth-quake resistant damper that can protect buildings. Shutter mechanisms in cameras, and many other electrical and electronics consumer applications, [4]. For aeronautical industry where alloys are subject to multidirectional service requests, they must provide an optimal combination of mechanical strength, plasticity, toughness, fatigue resistance and good resistance to stress corrosion. Moreover, the mechanical properties of zinc-based alloys make them attractive substitutes for cast iron and copper alloys in many structural and pressure-tight applications. These zinc-based alloys have a distinct cost advantage over copper-based alloys [4]. The major advancement in the zinc industry over the past years has been the development of zinc alloys with higher aluminum contents. These new zinc–aluminum based alloys have high strength and hardness, improved creep and wear resistance and lower density, and, although developed originally for sand and gravity casting, they are now being used in growing amounts for pressure die casting. These alloys, which possess excellent casting and mechanical properties, have been increasingly used to replace traditional alloys such as aluminum, bronze, brass and cast iron in many industrial applications, [5]. Against these advantages of zinc-aluminum alloys they have the disadvantages of low creep resistance and solidification with dendritic structures of large grain size which tends to deteriorate their mechanical properties, specially the impact strength. Therefore, It is essential to grain refine their microstructure by some grain refining by some rare earth elements, e.g. Ti or Ti+B. This has engaged many researchers in the last six decades, when it was found that the presence of Ti in Al resulted in grain refinement of its structure from large columnar structure with large grain size into equi-axed refined structure with small grains which caused enhancement in its mechanical behavior and surface quality, [6-7]. The literature on grain refinement of Al and its alloys and zinc aluminum alloys is voluminous, [8-15]. Review of the grain refinement of Al and its alloys and zinc-aluminum alloys are given and discussed [8] and [9-10] respectively.

Another method of grain refinement beside the refinement by some rare earth elements is the severe plastic deformation, SPD, processes, which have engaged some researchers in the last two decades many studies have been directed towards material processing by applying severe plastic deformation, referred to later as SPD. The main function of SPD is imposing extremely large plastic strains on materials which in turn will result in achieving fine grain size structure in the material that is subjected to. The reduction of grain size to a micrometer level results in enhancement of the mechanical properties such as very high strength and hardness without loss of ductility, which may also be accompanied by low temperature super-plasticity. Significant grain refinement may be achieved in bulk polycrystalline metals through the application of SPD. In the early eighties Segal et al at Minsk in the former USSR originated the method of equal channel angular pressing referred to later as ECAP which involves subjecting massive billets to pure severe plastic shear strains without change in their cross sectional areas. Their objective, at that time, was to develop a metal forming process with a high strain rate, [16]. In the early nineties the method was further developed and applied as an SPD method for processing of structures with submicron and Nano metric grain sizes. ECAP can apply a high shear strain to materials through a specially designed die having two equally sized channels connected at a finite angle. The technique has been proven to be very useful in improving mechanical properties of metals and alloys, [17]. The technique is a viable forming procedure to extrude materials by use of specially designed channel dies without substantially changing the geometry by imposing severe shear plastic deformation. This technique has the potential for high strain rate super-plasticity by effective grain refinement to the level of the submicron-scale or even Nano scale, [16, 18]. Severe plastic deformation (SPD) is a new discipline of metal forming

technology used to produce a very fine grained structure in metals and their alloys in order to improve their mechanical and physical properties (Fang, et al., 2006). In recent years, ultra-fine grained materials are currently of great scientific interest due to important mechanical and physical properties, increased fatigue life and high damage tolerances. Investigations of the mechanics of severe plastic deformation help engineers to come up with better designs for processes as well as better prediction of the results of processes. ECAP process is the most welcome process because of its nearly homogenous and effective mode of straining (simple shear). During deformation, the sample undergoes simple shear while there is no change in the cross-section geometry. In the ECAP process, a well lubricated billet of a square or round cross section of some length is pressed throughout a die of some angle,  $\Phi$ , with a die relief angle,  $\Psi$ , as shown in Figure 1. ECAP is a useful tool for achieving exceptional grain refinement in bulk metallic alloys, and the grain sizes produced through ECAP are in the sub-micron range. Recently, several analytical studies reported that the magnitude of shear strain imposed to the sample is determined by the channel angle  $\Phi$  and the angle associated with the arc of curvature  $\psi$ , [16-18].



**Figure 1.** Equal channel angular process

## 2. Materials, equipment and experimental procedures

### 2.1 Materials

Pure granular Zinc, High purity molybdenum, titanium and high purity aluminum were used in manufacturing main alloy ZA22 and the following binary master alloys: Al-Mo and Al-Ti, from which the different microalloys were made. Their chemical compositions were determined using Scanning Electron Microscope, SEM. Pure graphite crucibles were used in the melting process and graphite rods were used for stirring. The details of their manufacturing are given in [9].

### 2.2 Experimental procedure.

The experimental procedure started by designing manufacturing the ECAP die from H-13 and heat treated in accordance with the specified treatment cycle by the suppliers. Figure 2 shows a photograph of the designed and manufactured ECAP die.



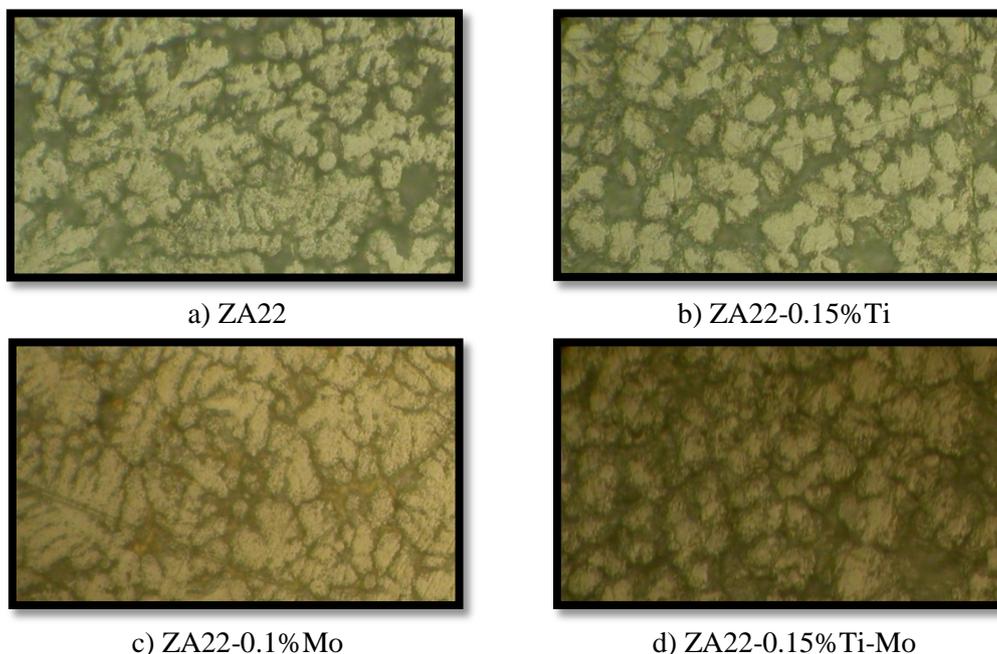
**Figure 2.** ECAP die

### 3. Results and discussion

In this chapter, the results obtained through this investigation will be presented and discussed. As ZA22 alloy is industrially grain refined by either titanium, Ti, or titanium and boron, Ti-B, the obtained results will be dealt with under the following headings: Effect of molybdenum addition at a weight percentage of 0.1% on the grain size, microstructure, hardness, and mechanical behavior illustrated by the representative true stress, representative true strain, ZA22 grain refined by Ti and ZA22 grain refined by Ti+B. Finally, comparison is made between the effect of Mo addition at a rate of 0.1 % weight percentage to ZA22 alloy grain refined by Ti and ZA22 grain refined by Ti+B.

#### 3.1 Effect of Addition of molybdenum on the Metallurgical and Mechanical Characteristics of ZA22 alloy Grain Refined by Ti

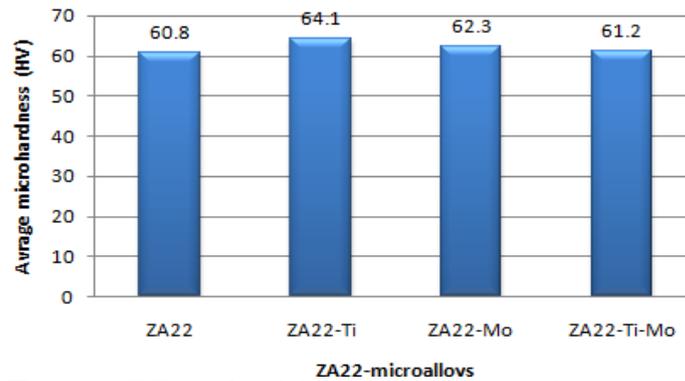
The effect of addition of Ti or Mo alone or together on the microstructure is explicitly shown in the photomicrographs of Figures 3 (a),(b),(c) and (d) for ZA22, ZA22-Ti, ZA22-Mo and ZA221-Ti-Mo, respectively.



**Figure 3.** Photomicrographs of ZA22 and its micro alloys: (a) ZA22, (b) ZA22-Ti, (c) ZA22-Mo, (d)ZA221-Ti-Mo, in the as cast conditions, X 500

### 3.2 Effect of Mo Addition on the Hardness of ZA22 and ZA22 grain refined by Ti

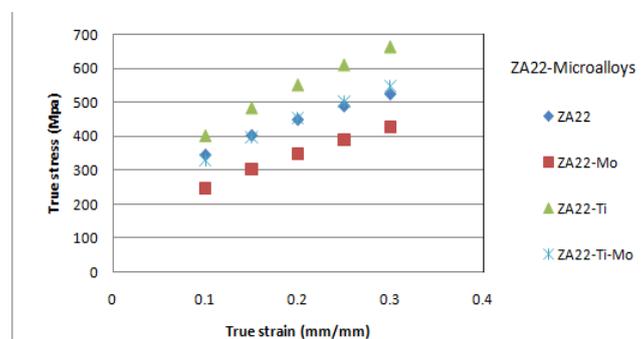
It can be seen from the histogram of Figure 4 that addition of either Ti or Mo alone or both together resulted in enhancement of the hardness. The maximum increase is at Ti addition being 5.4 % followed by Mo addition (2.5 %) and the least little achievement is when both are added together, (0.7 %).



**Figure 4.** Effect of molybdenum addition on the average Vickers' smicro-hardness of ZA22 and ZA22 grain refined by Ti in the as cast condition

### 3.3 Effect of Mo Addition on the Mechanical Characteristics of ZA22 and ZA22 grain refined by Ti

Figure 5 shows the effect of Mo addition on the general mechanical behavior of ZA22 and the ZA22 grain refined by Mo and Ti micro-alloys represented by the true stress versus true strain curve of each of them. It can be seen from these curves that addition of Mo to ZA22 resulted in deterioration of its general mechanical behavior, e.g. a reduction in flow stress at 20% strain from 451 MPa to 349 MPa has occurred, whereas addition of Ti either alone or in the presence of Mo resulted in enhancement of its mechanical behavior. The enhancement is being more pronounced in the case of addition of Ti alone. These are explicitly illustrated from the results shown in Table 6 where the strength coefficient of the ZA22 has decreased from 836.4 MPa to 774.5 MPa in case of Mo addition but increased to 1150.8 MPa by adding Ti alone and to 933 by adding Ti+Mo. Regarding the work hardening index it can also be seen from Table 6: that it has increased from 0.364 of the ZA22 to 0.456, 0.495 and 0.458 in case of Ti, Mo, and Ti+Mo additions respectively. This may be attributed to the secondary interphases formed within the main matrix of the ZA22 alloy.

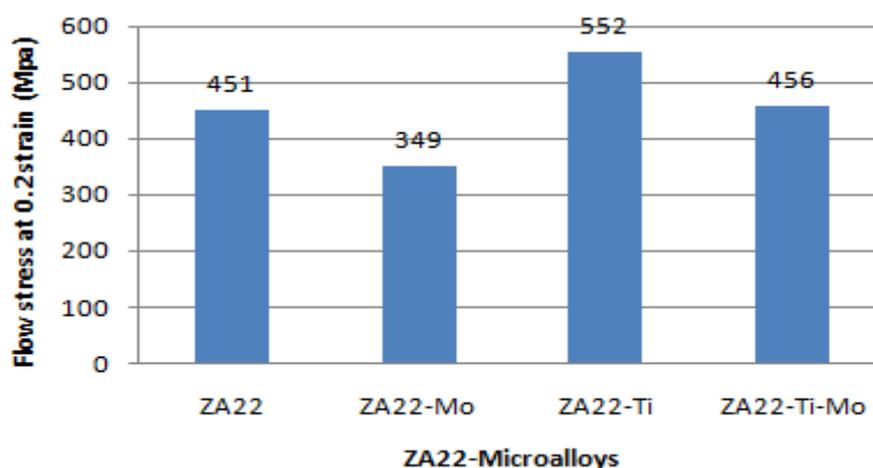


**Figure 5.** Effect of molybdenum addition on the True Stress true Strain of ZA22 and ZA22 grain refined by Ti in the as cast condition

**Table1.** Mechanical characteristics of ZA22 and its different micro-alloys in cast condition

Micro Alloys	Flow stress (MPa) at strain= 20 %	Strain hardening index (n)	Strength coefficient (K) MPa	General equation of mechanical behavior
ZA22	451	0.384	836.4	$\bar{\sigma} = 836.4\bar{\epsilon}^{0.384}$
ZA22-Ti	552	0.456	1150.8	$\bar{\sigma} = 1150.8\bar{\epsilon}^{0.456}$
ZA22- Mo	349	0.495	774.5	$\bar{\sigma} = 774.5\bar{\epsilon}^{0.495}$
ZA22-Ti-Mo	456	0.458	953	$\bar{\sigma} = 953\bar{\epsilon}^{0.458}$

Addition of Ti alone resulted in increase of its flow stress at 20 % strain as an increase of 22.4 % was achieved; also addition Ti+Mo resulted in a little achievement by (1%). However, addition of Mo alone resulted in decrease by (22.6 %). but addition of Mo alone or with Ti resulted in decrease of its flow stress at 20 % strain. as shown on Figure 6.

**Figure 6.** Histogram of the flow stress at 0.2 strain of ZA22 and ZA22

#### 4. Conclusions

Addition of Mo to ZA22 resulted in the following:

- a).** In the as cast condition:
  - i). Modifying its metallurgical structure by reducing its grains size.
  - ii). Increase of its micro hardness, enhancing its mechanical behavior and increase of its strain hardening index, n, hence improves formability
- b).** After pressing by the ECAP process:
  - i). Further refinement of the grain size of ZA22 and its microalloys.
  - ii). Decrease in the microhardness and the flow stress but resulted in increase of the strength factor and increase of the strain hardening index, n, of ZA22 and its microalloys.
  - iii). Reduction in the extrusion force and work.
  - iv). The addition of Ti and Mo to ZA22 and its micro alloys indicated that they have gained some superplastic behavior at room temperature. This renders the process cost effective

#### 5. Acknowledgment

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