

# Effect of Mo Addition to ZA22 Grain Refined by Ti after ECAP Pressing

Adnan I. O. Zaid

**Abstract**— Zinc aluminum alloys, ZA, in general and ZA22 in particular are widely used materials in the automobile and air craft industries due to their required and favorable physical and mechanical properties. Against their favorable properties they have the disadvantage of solidifying in dendritic structure of large grain size unless the mode of solidification is carefully controlled. This tends to reduce their mechanical strength, toughness and surface quality. It is therefore crucial to grain refine their structure to overcome these discrepancies. Different methods are available such as addition of some grain refiners as Ti, Mo, V, or by subjecting the material to severe plastic deformation, SPD. In this paper, addition of 0.1 wt. Mo to zinc 22% aluminum, ZA22, and ZA22 grain refined by Ti and after that they were subjected to SPD using the equal channel angular pressing, ECAP, process. The effect on its metallurgical and mechanical characteristics is investigated and the obtained results are presented and discussed.

**Index Terms**— Grain refinement, Zinc aluminum 22% alloy, ZA22, Severe plastic deformation, Equal channel angular pressing, ECAP, Metallurgical, Mechanical characteristics.

## 1 INTRODUCTION

Zinc aluminum alloys are widely used in many industrial and engineering applications especially in the automobile and air craft industries due to their useful and attractive properties such as their strength to weight ratio, rigidity, toughness, bearing load capacity, good corrosion and wear resistances in addition to their ease and clean cast ability. They are used in manufacturing a wide variety of parts e.g., carburetors, fuel pumps bodies, wind shield wiper parts, control panels, horns, and parts of hydraulic. They are also used in structural and decorative parts. Other applications include electrical and electronic equipment, building hardware, padlocks and toys, [1-3]. 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, good corrosion and wear resistances, cuts material cost by 50% and reduces weight by 45% in addition to 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% is said to be so resilient as to make possible an earth-quake resistant damper that can protect buildings. Furthermore, Shutter mechanisms in cameras and many other electrical and electronic consumer applications are made from these alloys, [4]. The major advancements in the zinc industry over the past years has been the development of zinc alloys with higher aluminum contents. These new developed zinc aluminums based alloys have high strength and hardness, improved creep and wear resistances and lower density.

In the aeronautical industry the parts are subjected to multi-directional service requests, they must provide an optimal combination of several properties e.g. mechanical strength, plasticity,

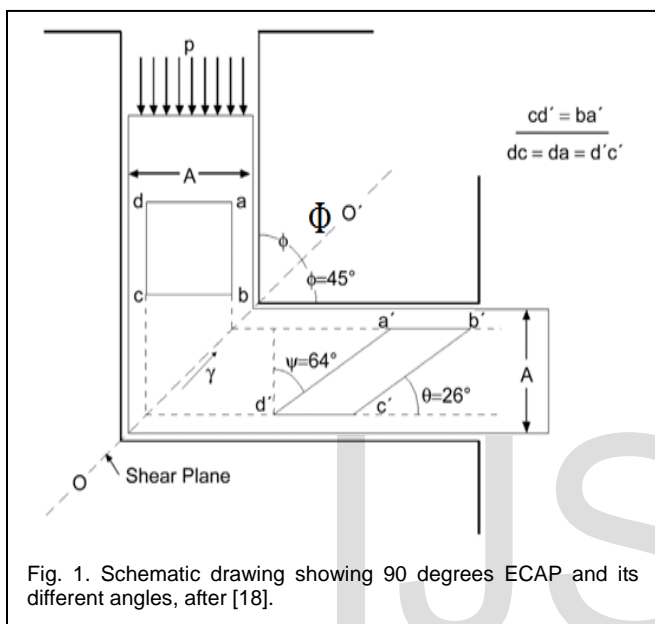
toughness, fatigue strength and good resistance to stress corrosion cracking which make these zinc aluminum alloys attractive substitutes for cast iron and copper alloys in many structural and pressure-tight applications. They have a distinct cost advantage over copper-based alloys, [4]. Although they have been developed originally for sand and gravity casting, they are now being used for pressure die casting. Also due to their easy and excellent clean casting and mechanical strength they have been increasingly used to replace the traditionally used alloys such as aluminum, copper, brass and bronze alloys, [5]. Against all these advantages they have the disadvantage of solidifying in dendritic structure with large grain size which adversely affects their mechanical strength, especially impact strength, toughness, creep resistance and surface quality. Therefore, it is essential to grain refine their structure to overcome these drawbacks. The grain refinement by the addition of rare earth elements is an old subject since 1950, when Cibula has published his first paper that if a very small amount of titanium is added to aluminum melt prior to solidification, it will cause appreciable reduction in the grain size and change its columnar structure into equiaxed one with small grain size, [6, 7]. It was after that when the researchers have engaged in grain refinement of Al and its alloys for the last seven decades and a large number of publications were reported on the subject, [8-12]. Although grain refinement of Al and its alloys started in early 1950s; it was not until mid seventies when it was applied to zinc aluminum alloys. The literature on grain refinement by rare earth elements is voluminous, and a comprehensive review on the grain refinement of aluminum and its alloys was published by the author in 2001, Ref., [14] and for zinc alloys in 2006, Ref., [15]. Recently grain refinement by rare elements on different metals and alloys is published in Ref., [16].

Grain refinement by severe plastic deformation, SPD, is relatively a new technique in the last two decades. The main function of SPD is imposing extremely large plastic strains on the material which in turn will result in achieving grain refinement of polycrystalline material structures resulting in

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enhancement of their physical and mechanical properties especially mechanical strength and hardness without loss of ductility. This may be also accompanied by lower temperature super plasticity, [17]. In the early eighties, Segal et al in Minsk of the former USSR originated a new process of SPD called it equal channel angular pressing, ECAP. In this process, the material is subjected to severe plastic shear strain without change in geometry or cross sectional area through a specially designed die having two equally sized channels connected at a finite angle aiming to obtain a forming process at high strain rate in the material, Fig.1, Ref.[18].

alloy, ZA22, and binary master alloys: Al-0.1%Mo and Al-10.7%Ti, from which the different microalloys were made. The chemical compositions of the pure granular zinc and aluminum as determined by the Scanning Electron Microscope, SEM are shown in Tables 1 and 2 respectively. Pure graphite crucibles were used in the melting process and graphite rods were used for stirring. The commercially pure aluminum was obtained from Jordan Electricity Authority in form of bundles of wires



The technique has proven to be very useful method in grain refinement and improvement of mechanical properties of metals and alloys, [17], (hunetti paper.). The technique is a viable forming procedure which presses the material through the die. In the early nineties, the method was further developed and applied as a method for processing of structures with submicron and Nano metric grain size, [18,19]. Although grain refinement of materials by rare earth elements and SPD have been in use for many years, however, the available literature reveals that applying the two methods simultaneously is very rare and only very few minor papers are published, [20-22]. This formed the main objective of this paper in which molybdenum is added to zinc 22% aluminum alloy at a rate of 0.1 wt. %, which corresponds to its peritectic point on the phase diagram of the zinc aluminum alloy, Fig. [2]. After that it is subjected to severe plastic deformation using the equal channel pressing, ECAP, process. Fig.2 The phase diagram of zinc aluminum alloys.

## 2 EXPERIMENTAL PROCEDURES

### 2.1 Materials

Pure granular Zinc, High purity molybdenum, high purity aluminum and titanium were used in manufacturing the base

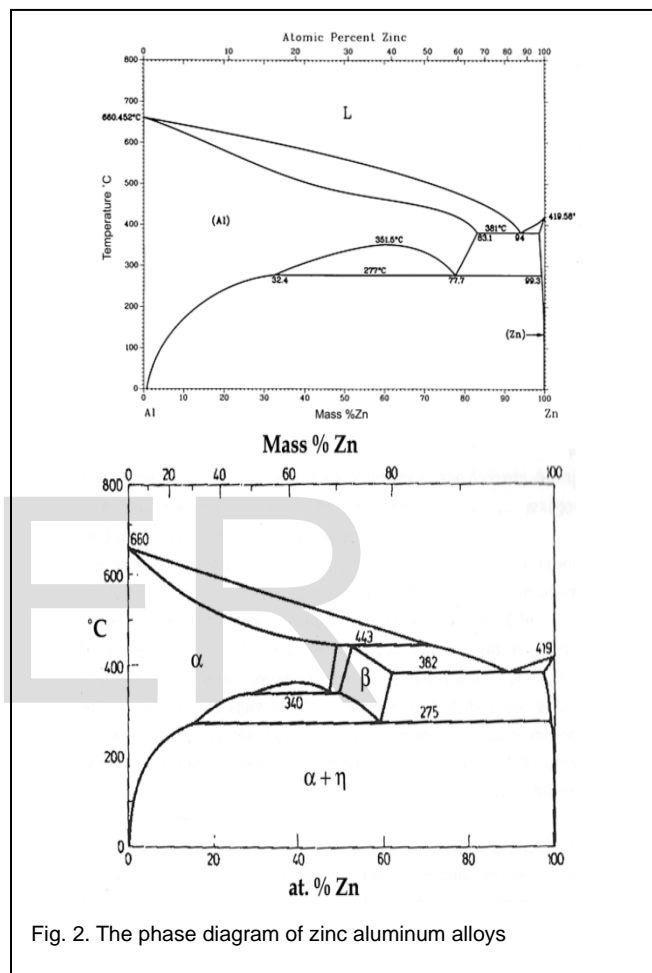


TABLE 1  
CHEMICAL COMPOSITION OF ZINC

Element	Wt %
Pb	0.003
Fe	0.002
Cu	0.004
Al	0.005
Sn	0.002
Cd	0.002
Zn	Bal

**TABLE 2**  
THE CHEMICAL COMPOSITION OF COMMERCIAL PURE ALUMINUM

Element	Wt %
Fe	0.09
Si	0.05
Cu	0.005
Mg	0.004
Ti	0.004
V	0.008
Zn	0.005
Mn	0.001
Na	0.005
Al	Bal.

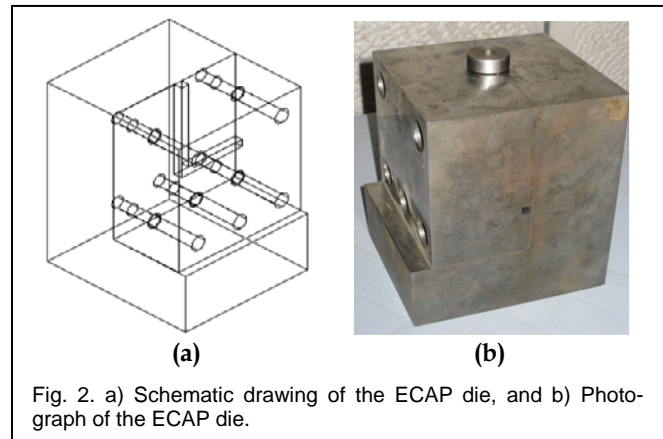
### 2.2 Experimental methods

The experimental procedure started by designing and manufacturing the ECAP die from tool steel H-13 of the chemical composition shown in Table 3. and heat treated in accordance with the specified treatment cycle by the suppliers. Fig.2 shows a photograph and schematic drawing of the designed and manufactured ECAP die and. followed by manufacturing the binary Al-10.7%Ti and Zn-6.47Al alloy which are used for preparation of the different microalloys namely ZA22-Ti, ZA22-Mo and ZA22-Ti-Mo in addition to the main ZA22 alloy. After the preparation, their chemical composition was determined using the scanning electron microscope, SEM. Followed by preparing the main basic alloy, ZA22 followed by manufacturing the master alloys which were then used in

**TABLE 3**  
CHEMICAL COMPOSITION OF TOOL STEEL H13

Element	Wt%
C	0.45
Si	0.8
Cr	5.5
Ni	0.3
Mo	1.7
Cu	0.25
V	1.2
Mn	0.2
Fe	Reminder

manufacturing the different microalloys. The following tests were carried out on specimens of appropriate dimensions: compression test, Vickers micro-hardness, HV, optical microscopic examination for determining the mechanical behavior and the Vickers micro-hardness, the grain size and the general microstructure of the base alloy, master alloys and each microalloy. The compression test was carried on the Instron Universal testing machine of 250 KN capacity at 10mm/minute cross head speed and the autographic records were used for determining the mechanical behavior.



### 2.3 Preparation of the ZA22 Base Alloy, Master Alloys and the Different microalloys

The predetermined amounts of aluminum and zinc having the chemical composition shown in Tables 2 and 3 respectively were melted in a graphite crucible inside an electric resistance furnace of 800 degrees Celsius. After melting, the mixture was poured to solidify and cool at room temperature in thick hollow brass dies of mm internal diameter and mm thickness.

### 2.4 Mechanical tests

The mechanical behavior of the base metal, ZA22, and all its microalloys. Cylindrical specimens of 10 mm diameter and height were machined from ZA22 and each micro alloy for determining their mechanical behavior using the autographic records of the compression tests which were carried out on the Instron Universal testing machine at cross head speed of 10 mm/ minute. The Vickers micro hardness tests were carried out using the digital micro hardness tester (model HWD-3). Ten readings were taken on the surface of each specimen from which the average HV micro hardness was determined.

### 2.5 Metallurgical examination

To determine the grain size and the general microstructure of ZA22 and its microalloys, cylindrical specimens of 10 mm diameter and 10 mm height were machined from each, mounted on araldite, then ground using successive grit numbers of Emery paper, (400, 600,800 and 1200), followed by polishing with one micron diamond paste, and finally etched using (5% HNO3 + 3% HCl+4% HF+88% H2O) solution for 20 seconds and the Metallurgical examination using was carried out using the optical microscope type (NIKON108). Finally the Photomicrograph of each specimen was obtained at a magnification of X500.

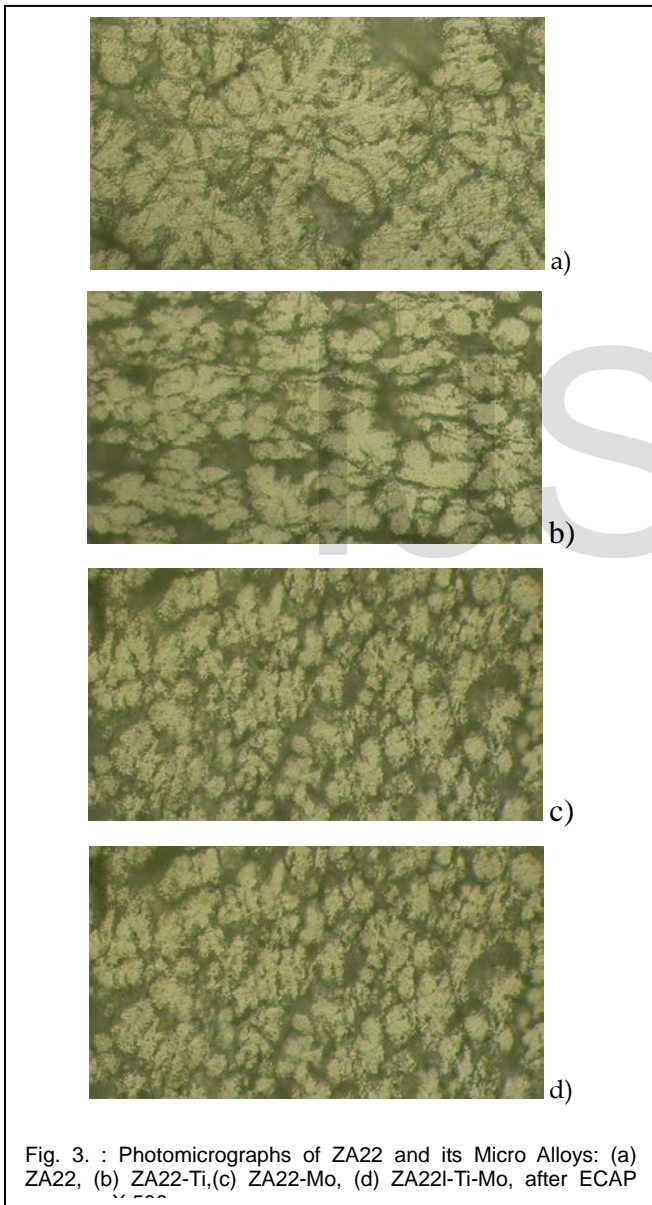
## 3 RESULTS AND DISCUSSION

Assessment of the effect of the addition of different grain refiners after the ECAP process is investigated through the autographic record of ZA22 and its microalloys, namely ZA22-Ti, ZA22-Mo, ZA22-Ti-Mo and ZA22-Ti-B-Mo, shown in Fig. .... Furthermore, specimens with the appropriate dimensions were machined from the ECAP pressed work pieces and in-

vestigated from the metallurgical aspects and mechanical characteristics.

### 3.1 Effect on grain size

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 ZA22-Ti-Mo, respectively. It can be seen from Fig.3 (b) that the addition of Ti as discussed in the addition of Ti to ZA22 structure and after ECAP it resulted in further refinement. Similar effect is produced by addition of Mo to the ZA22 after ECAP, Fig.3(c) Where further refinement was achieved by the ECAP process. The best refinement was achieved by addition of both of them Ti-Mo after ECAP process, Fig.3 (d).



### 3.2 Effect on mechanical behavior

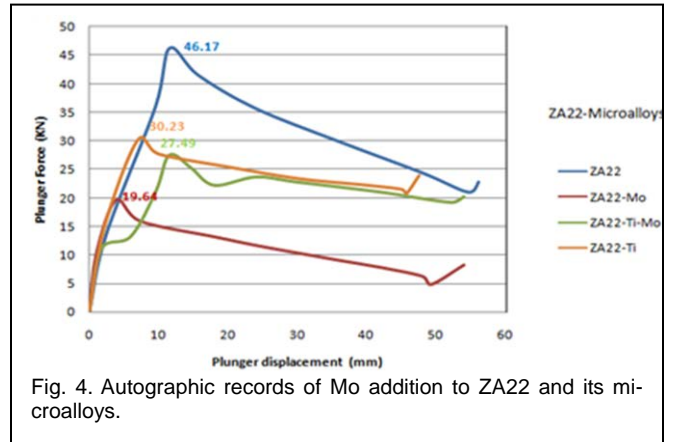
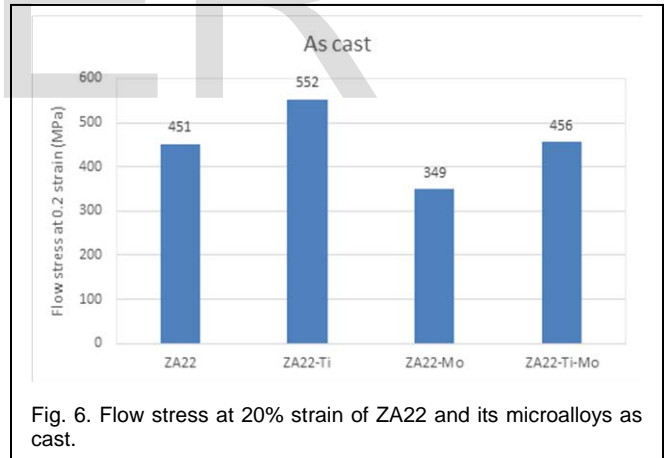
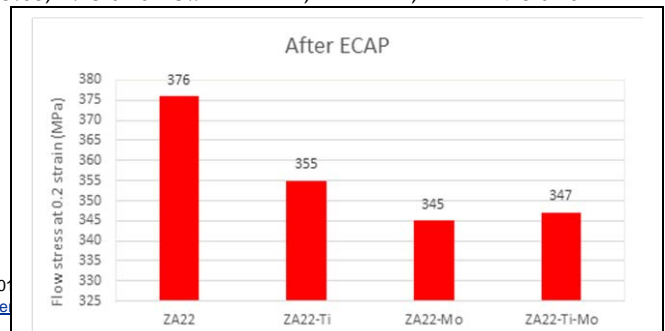


Figure 4 shows the autographic records, (punch load - punch displacement) of ZA22 and its microalloys. It can be seen from this figure that addition of Mo either alone or in the presence of any other element resulted in sudden decrease of the load after reaching its maximum value; the drop starts at different distances of the punch travel and at different rates. The earliest drop started in case of Mo addition to the base alloy followed by Ti addition and the latest delay in drop of the punch load is in case of Mo in the presence of Ti and the ZA22 base alloy. This is unlike what is expected that they all will increase in punch load due to strain hardening. The rate of drop in load



is maximum in case of Mo addition and minimum in case of base alloy. This is explicitly illustrated in Fig.5, which gives the values of the flow stress at 20% strain which shows the drop in flow stress as compared with the values in the cast condition, Fig.6. The drop percentages at 20% strain are: 16.63, 35.68, 1.15 and 23.9 in ZA22, ZA22-Ti, ZA22-Mo and ZA22-Ti-



Mo respectively. It is worth noting that the percentage drop in case of Mo is very small it was the most effective element in refinement of ZA22 reduced the flow stress at 20% strain from 451MPa into 349 MPa, i.e. by 22.62% compared to increase in case of Ti addition increase in flow stress by 22.39% which is due to the formation of the Titanium aluminate within the main matrix of the base alloy which is very hard. Hence it was suspected that this might be due to onset of superplastic behavior in them. Work is now in progress to find out the maximum elongation percentage from tensile tests on ZA22 and its microalloys and the obtained results are promising.

### 3.3 Effect on Hardness

The effect of the different elements on the Vickers microhardness after ECAP is shown in Fig. 7 which reveals that addition of Mo to ZA22 either alone or in the presence of Ti resulted in reduction of its Vickers microhardness by the following percentages: 2.96, 9.4, 17.5 and 13.1 9 in ZA22, ZA22-Ti, ZA22-Mo and ZA22-Ti-Mo respectively as compared to the cast condition, Fig.8. It is worth noting that the maximum reduction percentage is in case of Mo addition and the minimum is in the base alloy, ZA22. This is another indicator of softening due to the addition of Mo and Ti either alone or together.

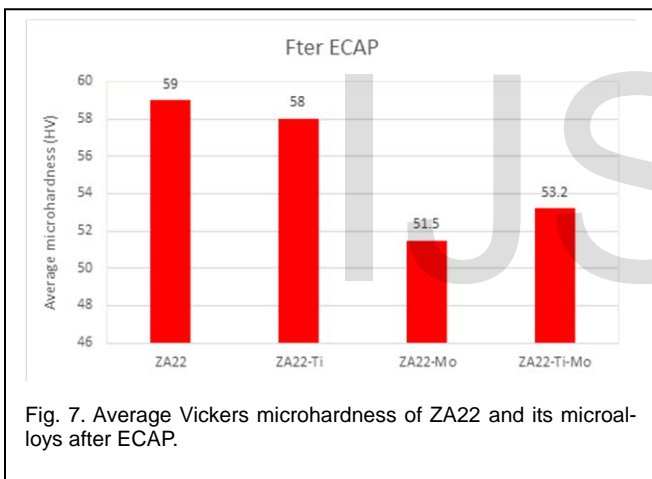


Fig. 7. Average Vickers microhardness of ZA22 and its microalloys after ECAP.

## 4 CONCLUSIONS

From the results obtained throughout this investigation the following points are concluded:

- i). Addition of molybdenum, Mo, to the ZA22 alloy, resulted in modifying its structure from dendritic into equiaxed one. Furthermore, it changed its general microstructure from dendritic structure into equiaxed one.
- ii) Addition of Mo to ZA22 grain refined by Ti resulted in increase of its microhardness in the cast condition, whereas the ECAP process resulted in reduction of its hardness with a maximum of 17.3% in case of Mo addition.
- iii) Addition of Ti, Mo either alone or together to ZA22 in as cast condition resulted in deterioration of its mechanical behavior represented by reduction of the maximum pressing force for geometrically similar specimens and in reduction of its flow stress at 20% strain with a maximum of % and 22.6% respectively in Mo addition. Furthermore, it caused increase of

its work hardening index,  $n$ , i.e. improvement of its formability and hence reduces the number of stages required for forming the alloy at large process strains in excess of the plastic instability strain in tension.

iv). The reduction in the pressing force and the softening caused by the ECAP gives an indication of superplastic behavior occurring in the ZA22 and its different microalloys at room temperature. Normally, this alloy and the ZA27 alloy could not attain superplastic behavior except at temperature between 300 and 400 °C. This makes forming the alloy cost effective.

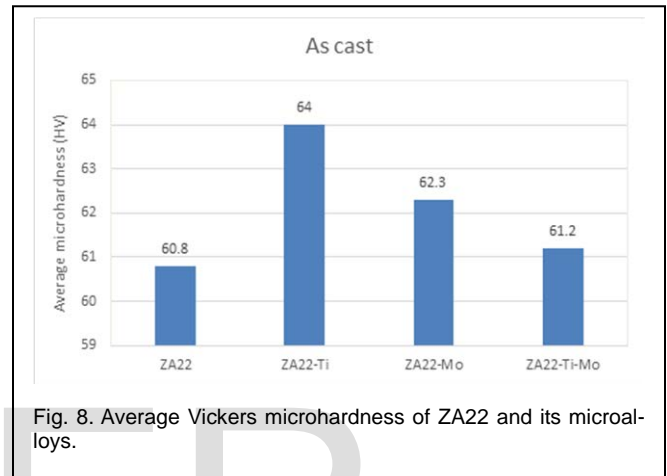


Fig. 8. Average Vickers microhardness of ZA22 and its microalloys.

## ACKNOWLEDGMENT

The author is grateful to the Applied Science Private University, Amman 11931 Jordan for the financial support granted to this research (Grant No. DRGS-2015).

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