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Effect of Mo Addition to ZA22 Grain Refined by Ti+B on its Metallurgical and Mechanical Characteristics

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Abstract— Zinc- aluminum alloys, in general are versatile materials which are widely used in a wide variety of engineering and industrial applications due to their unique and attractive properties such as strength, toughness, rigidity, bearing load capacity, economical and clean cast ability. However, they solidify with large grain dendrites which form in the absence of grain refiners which tends to deteriorate their mechanical properties and surface quality. However, fine grain structure is achieved by the addition of small amounts of titanium (Ti) or titanium + boron, (Ti+B), into the melt prior to solidification or by subjecting the metal or alloy to severe plastic deformation, (SPD), or by combining both methods together. The ECAP, which is relatively a new method is the most common one among the SPD methods. It is an important and useful method in producing fine and ultra-fine grain size. Reviewing the available literature, it was concluded that most of the reported work, concerned with the grain refinement of the zinc-aluminum alloys, is either by addition of an individual grain refiner element alone or using heavy plastic deformation processes or combining the two methods together. Furthermore, it was found that addition of Mo at a rate of 0.1 wt. % to ZA22 and ZA22 grain refined by Ti or Ti+B resulted in grain refinement of their structures which in turn caused slight enhancement in their hardness but caused deterioration of their mechanical behavior.

Index Terms— Cast condition, Grain refinement, Mechanical characteristics, Metallurgical, Molybdenum, Zinc aluminum alloy, ZA22

1 Introduction

With newly developed materials being produced for their superior properties of high ductility, high strength, low weight, etc., a need for implementing them into practical use has arisen. Because of these features, many advanced materials show potential in engineering applications such as medical devices and aerospace structural components, but an adherent gap exists between the research and industrial fields to push these materials into usage. For newly produced materials to be shaped and formed into their final dimensions, further particular research is typically required (Morehead, 2007). Zinc- aluminum alloys, in general are versatile materials which are widely used in a wide variety of engineering and industrial application due to their attractive properties such as strength, toughness, rigidity, bearing load capacity, Zinc aluminum alloys in general and ZA22 in particular are in increasing demand because of their unique and useful properties, they are versatile materials which have wide applications in industrial and engineering applications especially in the automobile and aircraft industries due to their unique and 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, (Budinsk, 1992), (Callister, 1994), and (Nevison, 1998). Against these advantages of zinc-aluminum alloys have the disadvantages of low creep resistance and the solidification with dendritic structures of large grain size which tends to deteriorate their mechanical properties and surface quality, especially the impact strength. Therefore, it is anticipated that addition of some grain refiners to it might overcome these discrepancies. The literature on the grain refinement of metals and alloys is voluminous and its review by the two methods is beyond the scope of this paper. The reader is referred to Refs. [20-26]. In this paper, the effect of addition of molybdenum, Mo, to ZA22 and ZA22 grain refined by Ti+B on their metallurgical and mechanical aspects are investigated. 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, [3,4]. 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.Another method of grain refinement beside the SPD processes, which has engaged many researchers in the last six decades, is the addition of grain refiners from rare earth elements e.g. titanium or titanium+ boron. Since Cibula finding 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

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mechanical behavior and surface quality, [5,6], researchers started working on the phenomenon of grain refinement by rare earth elements. Since then the literature on grain refinement of Al and its alloys and zinc aluminum alloys became voluminous, [7-26]. Review of the grain refinement of Al and its alloys and the factors affecting it is given and discussed for Aluminum and its alloys and the zinc-aluminum alloys, [25,26].

2 Materials

Different materials were used throughout this work, namely pure aluminum and pure granular zinc of the chemical compositions shown in Tables 1 and 2 respectively, were used in manufacturing the zinc- 22% aluminum, ZA22, main alloy. High purity molybdenum, titanium and high purity aluminum were used in manufacturing the following binary master alloys: Al- Mo and Al-Ti. The ternary master alloy Al-Ti-B was commercially available and was supplied by the Arab Company for manufacturing aluminum (ARAL). These three master alloys were used as grain refiners for the ZA22 main alloy and for the manufacturing of the different ZA22 micro alloys. Pure graphite crucibles were used in manufacturing the main alloy ZA22, master alloys and the different ZA22 micro-alloys, and pure graphite rods were used for stirring purposes.

TABLE 1
Chemical composition of zinc

Element	Wt%
Pb	٠,٠٠٣
Fe	٠,٠٠٢
Cu	٠,٠٠٤
Al	٠,٠٠٥
Sn	٠,٠٠٢
Cd	٠,٠٠٢
Zn	Bal

TABLE 2
The chemical composition of 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.

The commercially pure aluminum was obtained from Jordan Electricity Authority in the form of bundles of wires. They were cut into small pieces and pickled by immersing them in 95% distilled water and 5% concentrated HCl to get rid of the oxide layer.

3 Master alloys

The binary master alloy ZA22-Mo was prepared from high purity metals to obtain the different micro alloys and the ternary Al-5%Ti-1% was obtained from ARAL (Arab Aluminum factory in Amman) in the form of rods about 10 mm diameter. The chemical composition of this alloy is shown in Table 4.

Pure granular Zinc, High purity molybdenum, titanium and high purity aluminum were used in manufacturing main alloy ZA22 and the following binary master alloy: Al- Mo and the ternary Al-Ti-B from which the different micro alloys were prepared. 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.

TABLE 3
Chemical composition of H13 alloy steel

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

TABLE 4
The Chemical composition of the Al-5%Ti-1%B ternary master alloy, wt. %.

Element	Wt%
Ti	4.9
B	0.99
Fe	0.12
Si	0.09
V	0.12
AL	Bal.
Grain Size(μm)	179

4 Experimental Procedures

The experimental procedure started by melting the predetermined amounts of aluminium and copper in a graphite crucible inside an electric resistance furnace of 1200 degrees C. After melting the mixture is poured to solidify and cool to room temperature in thick hollow steel dies of 40 mm thickness having an internal cross section of 160 mm length and 45 mm width and 6 mm depth.

The experimental procedure started by preparing the master alloys from which the different micro alloys were prepared; followed by preparing the specimens for the microstructure examination, hardness measurement and me Then the Vickers micro hardness, (HV), of each specimen was determined in the cast and after each pass condition, using the digital micro hardness tester (model HWDM-3). Ten readings were taken on the surface of each specimen from which the average HV micro hardness was determined. To determine

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the grain size and the general microstructure and the photomicrograph of each specimen, a small piece was cut off from each specimen mounted on araldite, then ground using successive grit numbers of Emery paper, (400, 600,800 and 1200), followed by polishing with1micron diamond paste, and finally etched using (5% HNO_3 + 3% HCl+4% HF+88% H_2O) solution for 20 seconds and a photomicrograph of each specimen under each specific condition was obtained using an optical Microscope type (NIKON108) at a magnification of X500. Finally, cylindrical specimens of 10 mm diameter and 10 mm height were machined from ZA22 and each micro alloy for determining their mechanical behaviour from the autographic records obtained from the compression test using the Universal testing machine at cross head speed of 10 mm /minute.

5 RESULTS AND DISCUSSION

5.1 Effect of Mo addition on the metallurgical aspects of ZA22

The effect of addition of Ti+B or Mo alone or together on the microstructure is explicitly shown in the photomicrographs of figure 1 (a), (b) , (c)and (d) for ZA22, ZA22-Ti-B, ZA22-Mo and ZA22l-Ti-B-Mo, respectively. In general, it can be seen that addition of either Mo or Ti+B or both together resulted in refining of the structure, being more pronounced in case of Ti+B addition Fig. 1.b. Furthermore, it can be seen from Fig.14.c that the grains has gathered in colonies whereas in addition of both Mo and Ti+B petal like structure.

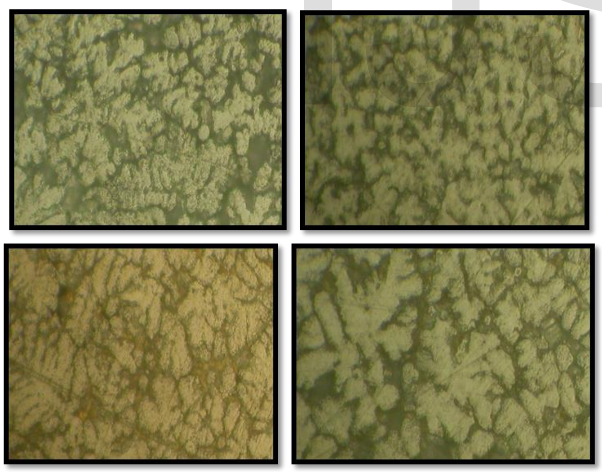

Fig. 1. Photomicrographs of ZA22 and its Micro Alloys: (a) ZA22, (b) ZA22-Ti-B, (c) ZA22-Mo, (d) ZA22l-Ti-B-Mo, in the as cast conditions, X 500.

5.2 Effect of Mo addition on the hardness of ZA22 Grain refined by Ti+B

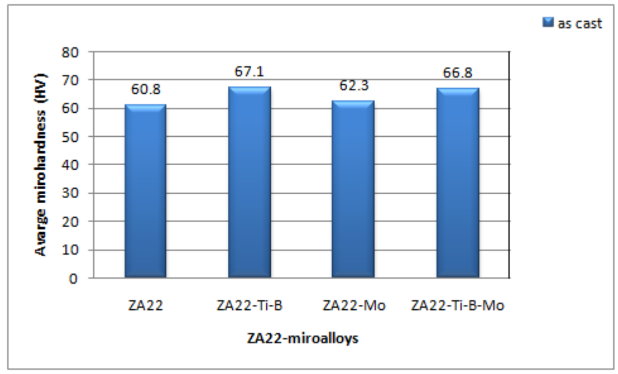

Fig. 2. Effect of molybdenum addition on the average Vickers micro hardness of ZA22 and ZA22 grain refined by Ti+B in the as cast condition

Regarding the effect of thE additions on hardness, It can be seen from the histogram of figure 2 that addition of either Ti+B or Mo alone or both together resulted in increase of its micro hardness. The maximum increase is at Ti+B addition being 10.4 % followed by Ti+B+Mo addition (10%) and the least increase is when Mo is added alone, (2.5%).

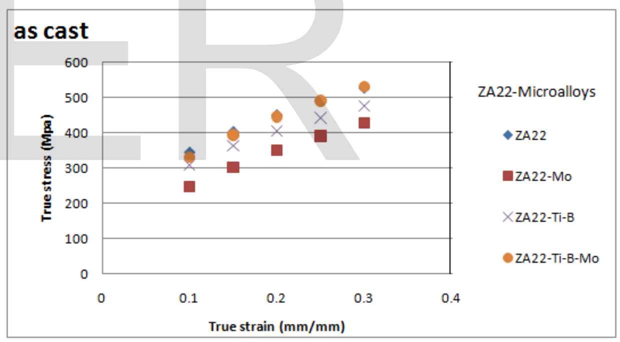

Fig. 3. True Stress – True Strain of ZA22 and ZA22 grain refined by Ti+B

5.2 Effect of Mo addition on the hardness of ZA22 Grain refined by Ti+B

It can be seen from figure 3 that the addition of Mo, Ti+B and Ti+B+Mo to ZA22 resulted in deterioration of its mechanical behavior, e.g. The deterioration is being more pronounced in the case of addition of Mo alone where a reduction of 22.6% in flow stress at 20% strain had occurred. Also addition of Ti+B either alone or in the presence of Mo resulted in deterioration of its mechanical behavior.

The mechanical characteristic of ZA22, ZA22-Ti-B, ZA22-Mo and ZA22-Ti- Mo are shown in Table (7) which shows that the strength factor, K, increases in case of Ti+B+Mo addition by 7%, and decrease in cases of Ti+B, and Mo addition. Regarding strain hardening index, n, it increased with addition of either Ti+B or Mo alone or both together, indicating that the formability of ZA22 is improved i.e. less preforms and stages are needed when large strains are involved in a forming pro-

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cess, hence it becomes less costly in manufacturing by the addition of these elements. The best is being by Mo addition. Table (5): gives the mechanical characteristics of ZA22 and its different micro alloys.

The effect of addition of either Ti+B or Mo alone or both together on the flow stress at 0.2 strain of ZA22 is shown in figure 4. which shows an decrease of its value by 10.2 % in case of Ti+B addition and slight decrease of about 0.9 % in case of Ti+B+Mo addition and a pronounced decrease of 22.6 % in case of Mo addition

TABLE 5
THE MECHANICAL CHARACTERISTICS OF ZA22 AND ITS DIFFERENT MICRO ALLOYS

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	$\bar{\sigma}=836.4\ \varepsilon^{-0.348}$
ZA22-Ti-B	405	0.394	763.84	$\bar{\sigma}=763.8\ \varepsilon^{-0.394}$
ZA22-Mo	349	0.495	774.5	$\bar{\sigma}=774.5\ \varepsilon^{-0.495}$
ZA22-Ti-B-Mo	447	0.432	895.4	$\bar{\sigma}=895.4\ \varepsilon^{-0.432}$

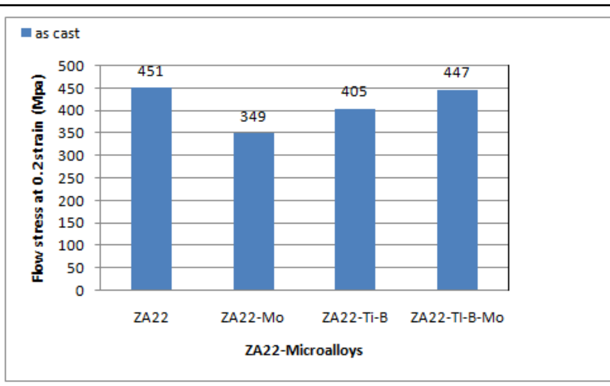

Fig. 4. Effect of molybdenum addition on the flow stress at 0.2 strain on ZA22

Conclusion

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

i). Addition of molybdenum, Mo, or Ti+B, alone or together to the ZA22 alloy resulted in reduction of its grain size.

ii). Addition of Mo to ZA22 grain refined by Ti+B resulted in slight increase of its micro hardness in the cast condition.

iii) Addition of Mo to ZA22 grain refined by Ti+B in as cast condition resulted in pronounced deterioration of its mechanical behavior i.e. it reduced the true stress-true strain (σ-ε) curve, flow stress where decreased by 22.6% at 20% strain was achieved in Mo addition, whereas it improved its work hardening index, n, and its ductility, i.e. improves formability and hence reduces the number of stages required for forming the alloy at large process strains in excess of the plastic instability strain.

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