

# Effect of Mo Addition to ZA22 Alloy Grain Refined by Ti+B on its Metallurgical and Mechanical Characteristics after Pressing by the ECAP Process

Adnan I. O. Zaid, Safwan M. A. Al-qawabah, Ahmad O. Mostafa

**Abstract**— Zinc aluminum alloys in general and ZA22 in particular exhibit attractive physical and mechanical properties combined with high tensile strength, hardness, very good wear and corrosion resistances, making it a bearing alloy as a replacement of their conventional counterparts like aluminum cast alloys, copper-based alloys and cast iron in various engineering applications. However against these attractive properties they have the disadvantage of solidifying in dendritic structure which affects their mechanical properties. To meet the growing demands for the application of these alloys, further investigations on their properties is required. In this paper, the effect of addition of two refiners namely Ti-B and Mo to ZA22 on its metallurgical and mechanical characteristics after pressing by the equal channel angular pressing, ECAP, is investigated. ) The ECAP process resulted in grain refining of ZA22 and ZA22 grain refined by Ti or Ti-B as was illustrated in the micrographics perviously assessed.

**Index Terms**— ECAP, Equal channel angular pressing, Grain refinement, Mechanical characteristics, Metallurgical, Molybdenum, ZA22, Zinc aluminum alloy.

## 1 INTRODUCTION

With newly developed materials being produced for their superior properties e.g. high ductility, high strength - to- weight - ratio, near net shape 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. Therefore, there is a great need for research on these newly developed materials to form and shape them into their final dimensions, hence particular research is typically required for this purpose. A new series of hyper-eutectic zinc-aluminum based alloys were first developed in North America in 1970s [1]. The aluminum content was selected as about 8%, 12%, 22%, 27% (mass fraction) and the copper content was up to 3% (mass fraction). They were named after their aluminum content as ZA8, ZA12, ZA22 and ZA27, respectively [2-8]. Of these alloys, ZA27 alloy exhibits attractive physical and mechanical properties combined with high tensile strength and wear resistance properties, making it a bearing alloy as a replacement of their conventional counterparts like aluminum cast alloys, copper-based alloys and cast iron in several engineering applications [9-12]. However, some properties of this

alloy which must be taken into account are comparatively poor ductility and its dimensional instability, as a result, its extensive applications in industry are seriously limited [13-14]. Zinc-aluminum alloys 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. These 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 they have the disadvantages of low creep resistance and the solidification in dendritic structure with large grains in the absence of grain refiners. This 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 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. refined by Ti or Ti-B resulted in grain refinement of their structures which in turn

- Adnan I. O. Zaid is currently a full professor in mechanical and industrial engineering in Applied Sciens Private University, Jordan, Amman 11931. E-mail: adnan\_kilani@yahoo.com
- Safwan M. A. Al-Qawabah is currently an associate professor in mechanical engineering in Tafila Technical University, Jordan, Amman. E-mail: safwan1q@gmail.com
- Ahmad O. Mostafa is currently a postdoctoral researcher in mechanical and materials engineering in Masdar Institute of Science and Technology, UAE, Abu Dhabi 52442. E-mail: amostafa@masdar.ac.ae

caused enhancement in their hardness but caused deterioration of their mechanical behavior. 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). 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.

Against these advantages of zinc-aluminum alloys they 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. Since Cibula (1950 and 1952) findings that the presence of titanium in the aluminum melt prior to solidification will refine the large grains columnar structure into equi-axial structure with fine grains. Ever since it became customary in the aluminum foundry to add Ti or Ti-B to the Al melt before solidification and the binary Al-Ti and the ternary Al-Ti-B master alloys were manufactured for this purpose which are now commercially available. Furthermore, it was found that addition of Mo at a rate of 0.1 wt. % to ZA22 and ZA22 grain 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.

In this paper, the effect of addition of molybdenum, Mo, to ZA22 and to ZA22 grain refined by Ti-B after pressing by the ECAP process on their metallurgical and mechanical aspects is investigated. Another method of grain refinement beside the SPD processes and has engaged many researchers in the last six decades.

## 2 MATERIALS, EQUIPMENT AND EXPERIMENTAL PROCEDURES

### 2.1 Materials

Pure aluminum and pure granular zinc of the chemical compositions shown in Tables 1 and 2 respectively, were used in manufacturing the main zinc- 22% aluminum alloy ,referred to later as 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 Aluminum Industry (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 graphite rods were used in manufache main alloy ZA22, master alloys and the different ZA22 micro-alloys, and pure graphite rods were used for stirring.

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   |

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 and other contaminations.

Tool steel H13 of the composition shown in Table 3 was used in manufacturing the equal channel angular pressing die, ECAP. It was heat treated following the treatment cycle recommended by the suppliers, hardened and tempered to obtain a final hardness of 52 RC.

TABLE 2  
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 Preparation of the Master Alloys

Three master alloys were used to obtain the different micro alloys namely: the ternary Al-5%Ti-1%B This alloy is used in aluminum factories as a grain refiner of commercially pure aluminum. It was obtained from ARAL (Arab Aluminum factory in Amman) in the form of rod about 10 mm diameter. The chemical composition of this alloy shown in Table 4.

TABLE 3  
CHEMICAL COMPOSITION OF TOOL STEEL H13

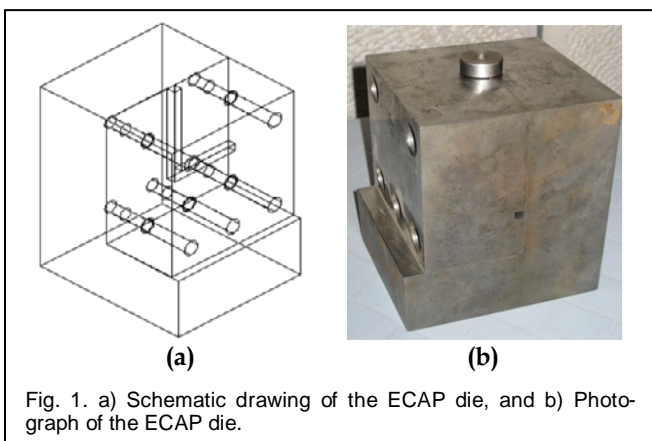
| Element | Wt%      |
|---------|----------|
| C       | 0.45     |
| Si      | 0.8      |
| Cr      | 5.5      |
| Ni      | 0.3      |
| Mo      | 1.7      |
| Cu      | 0.25     |
| V       | 1.2      |
| Mn      | 0.2      |
| Fe      | Reminder |

TABLE 4  
CHEMICAL COMPOSITION OF THE AL-4.9 %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( $\mu\text{m}$ ) | 179  |

## 2.3 Equipment and Experimental Procedures

The experimental procedure started by designing and manufacturing the ECAP die shown in figure 1.

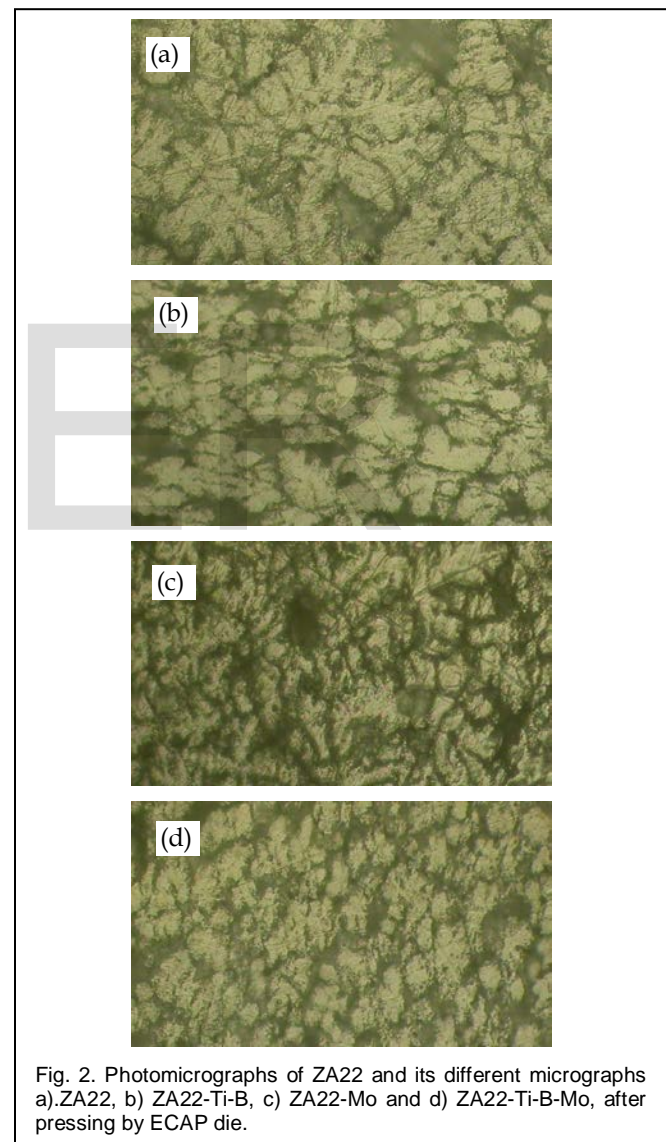


## 3 RESULTS AND DISCUSSION

### 3.1 Effect of Mo addition on the metallurgical aspects

### of ZA22 grains refined by Ti +B after pressing by the ECAP process

Zinc aluminum alloys normally solidify in dendritic structure with large grain size which tends to affect their mechanical strength, toughness and surface equality. The addition of Mo to ZA22 has changed its structure from dendritic large grains structure into equ-axial with smaller grains .Its effect and the effect of Ti-B are explicitly shown in the photomicrographs of figure 2 (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. 2.b. Furthermore, it can be seen from figure 2c that the grains has gathered in colonies whereas in addition of both Mo and Ti+B petal like.



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

Regarding the effect of these additions on hardness it can be seen from the histogram of figure 3 that addition of either Ti-B or Mo alone or both together resulted in decrease of its micro

hardness. The maximum decrease is at the addition of Mo being 12.7 % followed by Ti-B-Mo addition with reduction of 7.29 % whereas addition of Ti-B alone resulted in increase of its Vickers micro hardness by 2.37 %. This is due to softening which has taken place as will be discussed later.

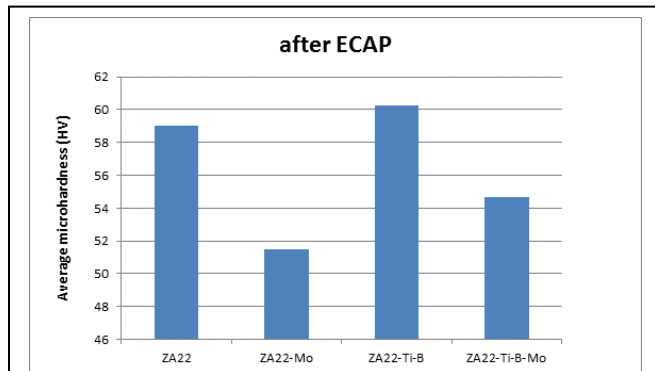


Fig. 3. Effect of Mo addition on the Vickers micro hardness of ZA22 after ECAP.

### 3.3 Effect of Mo Addition to ZA22 on its Mechanical behavior

Figure 4 gives comparison between the mechanical behavior of ZA22 and its micro alloys namely ZA22- Mo, ZA22-Ti-B and ZA22-Ti-B after ECAP process. It can be explicitly seen from this figure that the addition of either Mo or Ti-B either alone or together to ZA22 resulted in decrease of its mechanical behavior which indicates that softening of the alloy has occurred. Comparing the values of the flow stress at 20 % strain; it can be concluded that the maximum decrease is 15.42 % when Mo-Ti-B is added to ZA22, followed by Mo addition by 8.24 % and the least is 3.99 % when Ti-b is added.

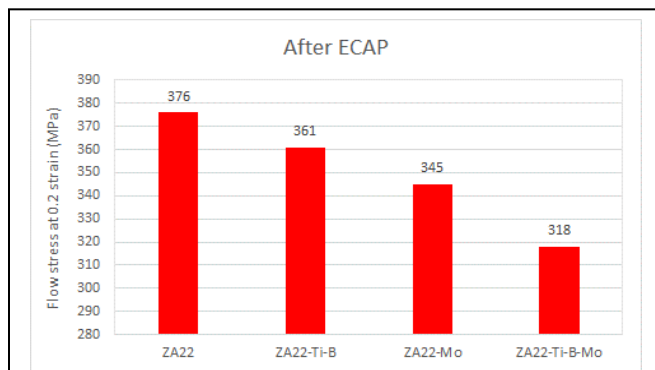


Fig. 4. Effect of the Mo addition to ZA22 grain refined by Ti or Ti-B on the maximum pressing force.

### 3.4 Effect of Mo Addition to ZA22 on the Maximum Pressing Force

It can be seen from figure 5 that addition of Mo and Ti-B either alone or together to ZA22 resulted in reduction of the maximum ECAP force. The maximum reduction was obtained when Mo was added alone being 55.49 % followed by Ti- B-Mo addition, 45 %. The least reduction is 35.76 when Ti-Mo is added. Similarly; the consumed work was reduced in the same trend where the reductions are: 58.93%, 43.57 % and 25 % in case of Mo, Ti-B and Ti-B-Mo respectively, as illustrat-

ed in figure 6. This is attributed to the refining of the grains as discussed in the metallurgical and the soft intermetallic phases within the matrix of the ZA22 alloy.

### 3.4.2 Effect of Mo addition on the work consumed in

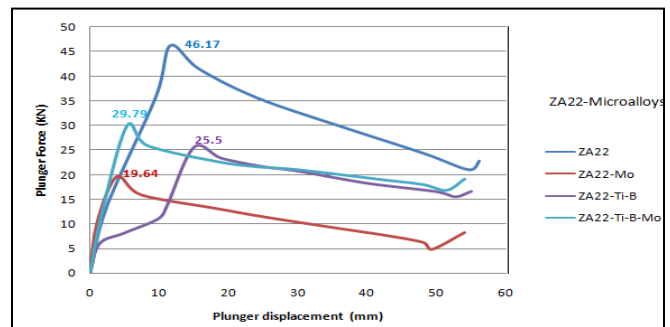


Fig. 5. Effect of the Mo addition to ZA22 on the maximum pressing force.

### the ECAP Process

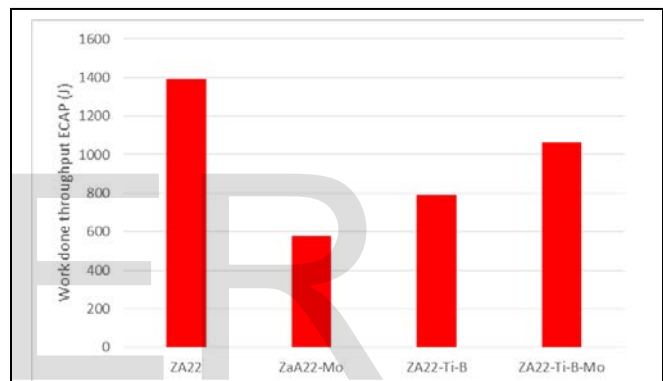


Fig. 6. Effect of Mo addition to ZA22 grain refined by Ti or Ti-B on the work consumed by the ECAP process.

## 4 CONCLUSIONS

The following points are concluded:

i). The ECAP process resulted in decrease of hardness and flow stress of ZA22 and its micro alloys but resulted in increase of their strength factor, K and work hardening index n, i.e. improvement of their formability and reducing the number of stages required for forming at strain beyond the plastic instability and all its investigated micro alloys.

ii). Addition of Mo or Ti-B either alone or together to ZA22 resulted in reduction of both the maximum pressing force and the consumed plastic work.

iii) The previous point gives an indication that superplastic behavior might have occurred in the ZA22 and its different micro alloys at room temperature. Usually this alloy and the ZA27 alloy do not exhibit superplastic behavior except at a temperature range between 300°C -40 0°C. Work is in progress to test this phenomenon. The results are promising and will be published in due course.



## ACKNOWLEDGMENT

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

## REFERENCES

- [1] Budinsk, K.G. (1992), *Engineering Materials Selection*, Fourth Edition, Prentice-Hall, Inc., New JERSEY.
- [2] Callister, W.D. (1994), *Materials Science and Engineering and Engineering: an Introduction*, Third Edition, John Wiley and Sons Inc., New York.
- [3] Nevison, D.C.H. (1998), *Zinc and Zinc Alloys*, American Society of Metals, ASM Handbook, Fourth Edition.
- [4] Kalpakjian, S. Schmid, S.R., (2003). *Manufacturing processes for engineering materials*, 4th edition, prentice Hall.
- [5] Cubberly, W. H, *Properties and metal selection: none ferrous alloys and pure metals*, Metals Handbook, ASM, V.2, 1994
- [6] Zaid, Adnan I .O, "Effect of Addition of Tantalum and Zirconium on the Mechanical Behaviour of Aluminum Grain Refined by Ti+ B". Accepted for Presentation at the 8th International Symposium on Advanced Materials, Islamabad-Pakistan. Sept. (2003).
- [7] "Effect of Addition of Zirconium on the Mechanical Strength and Fatigue Life of Zinc-Aluminum Alloy-5, AZ5, Grain Refined by Ti". Proceedings of the 8th International Symposium on Advanced Materials, Islamabad-Pakistan. Sept. (2003).
- [8] Zaid, Adnan I.O. Grain Refinement of Aluminum and Its Alloys". Proceedings of the seventh International Symposium on Advanced Materials, ISAM-7. Islamabad-Pakistan. Sept. 17th - 21st (2001).
- [9] Zaid, Adnan I .O. "Grain Refinement of Zn- Al Alloys", Proceedings of the Second International Conference on the Frontier of Advanced Engineering Materials, FAEM-2006, Lahore, Pakistan, (2006).
- [10] Abdel Hamid, A. A., (1985). On the mechanism of the grain refinement of aluminum by small addition of Ti and B, The Second Arab Aluminum Conference ARBAL, 85, Egypt, Oct. 1985.
- [11] Abdel Hamid, A.A. (1992), Structure Modification of the  $\alpha$ -Phase in Zn-Al Cast Alloys by Microalloying. *Metallkd*, V.83, pp.314-318.
- [12] Abdel-Hamid, A.A. and Zaid, A.I.O. (2000), "Poisoning of Grain Refinement of Some Aluminum Alloys", Seventh, Cairo Intern. Conference, Current Advances in Mechanical Design and Production, Cairo, Feb 2000, pp.331-338.
- [13] Arjuna A. Rao, Murty B.S., and Chakraborty M, (1997). Role of zirconium and impurities in the grain refinement of aluminum with Al-Ti-B, *Material Science and Technology*, 13, pp.769-777.
- [14] Assifa, M. M., (2011), Effectiveness of Naphthalene in Grain Refinement of Commercially Pure Aluminum and Zinc Ingot Castings, *Engineering & Technology Journal*, V-29, Issue 8, pp 1545-1553.
- [15] Azad, A. Bichler, L. and Elsayed, A. (2013), Effect of a Novel Al-SiC Grain Refiner on the Microstructure and Properties of AZ91EMagnesium Alloy, *International Journal of Metal casting*, V-7, Issue 4, pp 49-60.
- [16] Birch, M.E.J. and Fisher, P. (1986), "Grain Refining of Commercial Aluminum Alloys with Titanium Boron Alloys" *Aluminum Tech*, Institute of Metals, pp.117-142.
- [17] Pearson, J. and Birch, M. E. J. (1979), The Effect of the titanium Boron Concentrations on Aluminum Grain Refining Alloy. *Journal of Metals*, V. 31, No.11, pp.27-31.
- [18] Pollard, W.A. Pickwick, K. M. Jubb, J.T., and Packwood, R. L, (1974), The Grain Refinement of Zinc-Aluminum Alloys by Titanium, *Can. Metal. Soc.*V.13. No 4.
- [19] Cibula. A, *Journal Institute of Metals*, 1949-1950, V.76, pp.321-360.
- [20] Cibula. A, *Journal Institute of Metals*, 1951-1952, V.80, pp.1-15.
- [21] Elbaradie, Z.M., (1998), Grain Refining of Zn22%wt Al Superplastic Alloy. *Journal of Materials Processing Technology*, V.84, pp.73-78.
- [22] Tsan, C. L. Nakata, T. and Hayashi, T. (1976), Effect of Zirconium, Titanium, Manganese, and Nickel Additions on Dendrite Morphology of Zinc-Aluminum Alloys. *IMONO*, V. 3, pp. 167-174.
- [23] Tu'rk, A. Durman, M. and Kayali, E.S. (2007), the effect of manganese on the microstructure and mechanical properties of zinc-aluminium based ZA-8 alloy, *Journal Material of Science*, v-42, pp 8298-8305.