Grain refinement of cast Zamak 5 alloy by 0.1, 0.2 and 0.5 wt.% Mn

Ahmad Mostafa[1,a*], Ubeidallah Al-Qawabeh[1,b], Audai Al-Akailah[1,c]

[1] Mechanical Engineering Department, Tafila Technical University, Tafila 66110, Jordan
[a,*] a.omar@ttu.edu.jo, [b] ubeid1@yahoo.com, [c]audai.akailah@ttu.edu.jo

ABSTRACT In this work, the effect of 0.1, 0.2, and 0.5 wt.% Mn additives on the grain size and microhardness number of Zamak 5 alloy was investigated. The Mn concentration was controlled by microalloying process. The master alloy composed of Al-10Mn wt.% was diluted to produce three microalloys. Microstructural investigation was carried out using an optical microscope and the Vickers hardness number was acquired using a microhardness tester. The grain size measurements were performed using ASTM standard test method and confirmed using the attached lens with the microhardness tester. The yield strength, strength coefficient and strain-hardening exponents were calculated from the true stress-true strain diagrams. The results showed that addition of 0.1, 0.2 and 0.5 wt.% Mn to Zamak 5 transformed the dendritic structure into more equiaxed structure with 15.5, 26.7 and 101.3 µm equivalent diameters, respectively. Furthermore, the microhardness number improved by 16.6%, 44.4% and 33.3% for the three microalloys, respectively. The calculated yield strengths and strength coefficients were consistent with the microhardness results. This improvement is an indication for property enhancing of Zamak 5 by small Mn additives. From the current study, the optimum Mn concentration that may significantly enhance the mechanical properties of Zamak 5 was 0.2 wt.%.

Keywords: Grain refinement, master alloy, microalloying, Zamak 5 alloy, strength coefficient, strain hardening exponent.

1. Introduction

Zinc and zinc alloys are normally used in the form of coatings, castings, rolled sheets, drawn wires, forgings and extrusions for functional and decorative applications. Cast Zamak alloys, a family of zinc-aluminum alloys, are mainly prepared by die casting, sand casting and permanent mold casting owing to their low melting points, clean castability, resistance to atmospheric corrosion, close tolerances and recyclability [1]. Zamak castings possess excellent combination of good strength, impact resistance, ductility, good finishing characteristics, good corrosion and creep resistance at room temperature in addition to their relatively low cost [2]. Despite these advantages, Zamak casting microstructure is not favorable. It consists of random grain size distribution from surface to core. Furthermore, the formation of large dendrites during solidification tends to deteriorate their mechanical properties [3] due to several internal defects, such as residual stresses, voids and dislocations [4]. Grain refinement has been widely used to achieve a homogenized grain structure [5] and to improve the mechanical properties of cast/wrought metals and alloys [6]. The main role of the grain refiners is to develop fine equiaxed grains in the cast structure either by increasing the number of nucleation sites or by grain multiplications [2]. Generally, Zamak alloys are grain refined by adding small amounts of rare earth elements [7], transition metals (Co, Ni [8] and Mn [9]) and binary alloys (Ti+B) [10]. To the authors' knowledge, no or very little data on the effect of Mn inclusions on the microstructure and mechanical behavior of Zamak 5 alloy could be found in the literature. Türk et al. [9] investigated the effect of 0.01-0.53 wt.% Mn on microstructure and mechanical properties of Zamak 8 alloy. It is worth mentioning that Zamak 5 and 8 belong to the zinc-aluminum alloys family; however, their chemical composition is different. According to Türk et al. [9], yield, tensile and impact strengths were not influenced by Mn addition up to 0.045 wt.%. However, they deteriorated by further Mn addition. A continuous improvement in creep resistance with increase in Mn up to 0.53 wt.% was noticed due to the change in phase morphologies and formation of new intermetallics. It was also reported that addition of Mn to Zamak 8 altered the dendritic microstructure and formed finer eutectic in the matrix owing to its ability to from complex intermetallic compounds [9]. In view to the aforementioned introduction, this work aims at investigating the influence of Mn micro inclusions, i.e. 0.1, 0.2 and 0.5 wt.% on the microstructure, grain size and mechanical behavior of Zamak 5 alloy.

2. Experimental procedure

The starting materials for this research are Zamak 5 cast ingot, commercially pure aluminum of 99.8 wt.% purity and manganese of 99.98 wt.% purity. Pure Al and Mn were used to prepare Al-10Mn wt.% master alloy. According to the Al-Mn binary phase diagram [11], the maximum solid solubility of Mn in Al at atmospheric pressure is about 1.35 wt.%. However, master alloy was designed in the Al_FCC+$Al_{12}Mn$ two phase field in order to reduce Al concentration upon microalloy preparation. In other words, higher Mn concentration reduces the master alloy mass needed for microalloy preparation. The chemical compositions of the Zamak 5 cast ingot according to ASTM B86-18 [12] and commercially pure aluminum are listed in Table 1.

Table 1: Chemical compositions of Zamak 5 cast ingot and commercially pure Al

	Zamak 5 casting	Commercially pure Al
Al	3.5-4.3	Bal.
B	-	0.0005
Cu	0.75-1.25	-
Fe	0-0.1	0.11
Mg	0.03-0.06	0.004
Si	-	0. 05
Ti	-	0.004
V	-	0.008
Zn	Bal.	0.005
Others*	0-0.012	0.015

The Al-10Mn wt.% master alloy was prepared by melting equivalent Al and Mn masses with CaF_2 flux to prevent oxidation at 800°C in an alumina crucible. The melting process was carried out in an electric resistance furnace. The melt was taken out of the furnace, stirred using a silica rod and then returned to the furnace. The furnace temperature was raised to about 850°C for 10 minutes to enhance the solubility of Mn in liquid Al. The furnace temperature was then lowered to 750°C to minimize evaporation and kept for another 5 minutes. The melt was stirred for 30 seconds and allowed to solidify inside the crucible outside the furnace as described in [2,13]. Three Zamak 5+Mn microalloys were prepared with 0.1, 0.2 and 0.5 wt.% Mn concentrations by diluting the master alloy in Zamak 5 melt. The microalloys were prepared by melting the calculated masses of Zamak 5 and Al-10Mn master alloy at 650°C for 15 minutes. The melt was stirred for 30 seconds and poured into a preheated copper cylindrical die to avoid undesired microstructure.

Zamak 5 ingot and microalloys were sliced using a slow cutting machine in order to minimize heat generated during cutting process and to prevent any microstructural changes. The cut specimens were mounted in hot epoxy blocks, ground gradually from 240 up to 1200 grit using SiC sand papers and polished using 1µm diamond paste. The polished Zamak 5 and microalloys were chemically etched using a solution of 5 ml HCl and 100 ml distilled water for 90 seconds. Phase analysis was carried out using FactSage thermochemical data system [14] and phase assemblage diagrams were plotted. Microhardness tests were carried out using a Highwood HWDM-3 Vickers hardness tester with 100 g load. Three different values were taken at different locations on each specimen, from which the average HV number for each alloy was determined. The grain sizes were measured using a scaled magnification lens attached to the microhardness tester, which gave opportunity to take several size measurements on the same grain. Both strength coefficient and strain hardening exponent for all specimens were calculated from the true stress-true strain graphs obtained by compression test. The compression test was carried out using the ‘’WANCE’’ universal testing machine at a crosshead speed of 2 mm/min. The load-deflection data was acquired using the machine software and then converted into true stress-true strain curves for further analysis.

3. Results and Discussion

3.1. Effect of Mn on the microstructure of Zamak 5

The typical microstructure of cast Zamak 5 alloy is shown in Figure 1 (a). Heterogeneous microstructure with large dendrites could be observed. Generally, the primary dendrites are the unstable β phase below 275°C, while the matrix is the lamellar α+η fine eutectic-like [9,15]. The effect of 0.1, 0.2 and 0.5 wt.% Mn additions on the microstructure of Zamak 5 alloy is illustrated in Figure 1 (b-d), respectively. The presence of Mn in Zamak 5 alloy modified its cast structure by breaking down the large dendritic structure into equiaxed grains with various sizes based on Mn wt.%. The alteration of Zamak 5 microstructure by Mn addition could be due to formation of $Al_{12}Mn$ fine precipitates, which dispersed into Zamak 5 matrix and created new nucleation cites. When 0.1 and 0.2 wt.% Mn are added, the amount of $Al_{12}Mn$ precipitates in the matrix increases and thus the number of grains increases as shown in Figure 1 (b) and (c). At higher Mn concentration (0.5 wt.%), larger grains were observed as shown in Figure 1 (d). It could be due to the formation of ζ-intermetallic compound of the $MnZn_{13}$ type [16], which results in forming a different microstructure with an angular morphology [9].

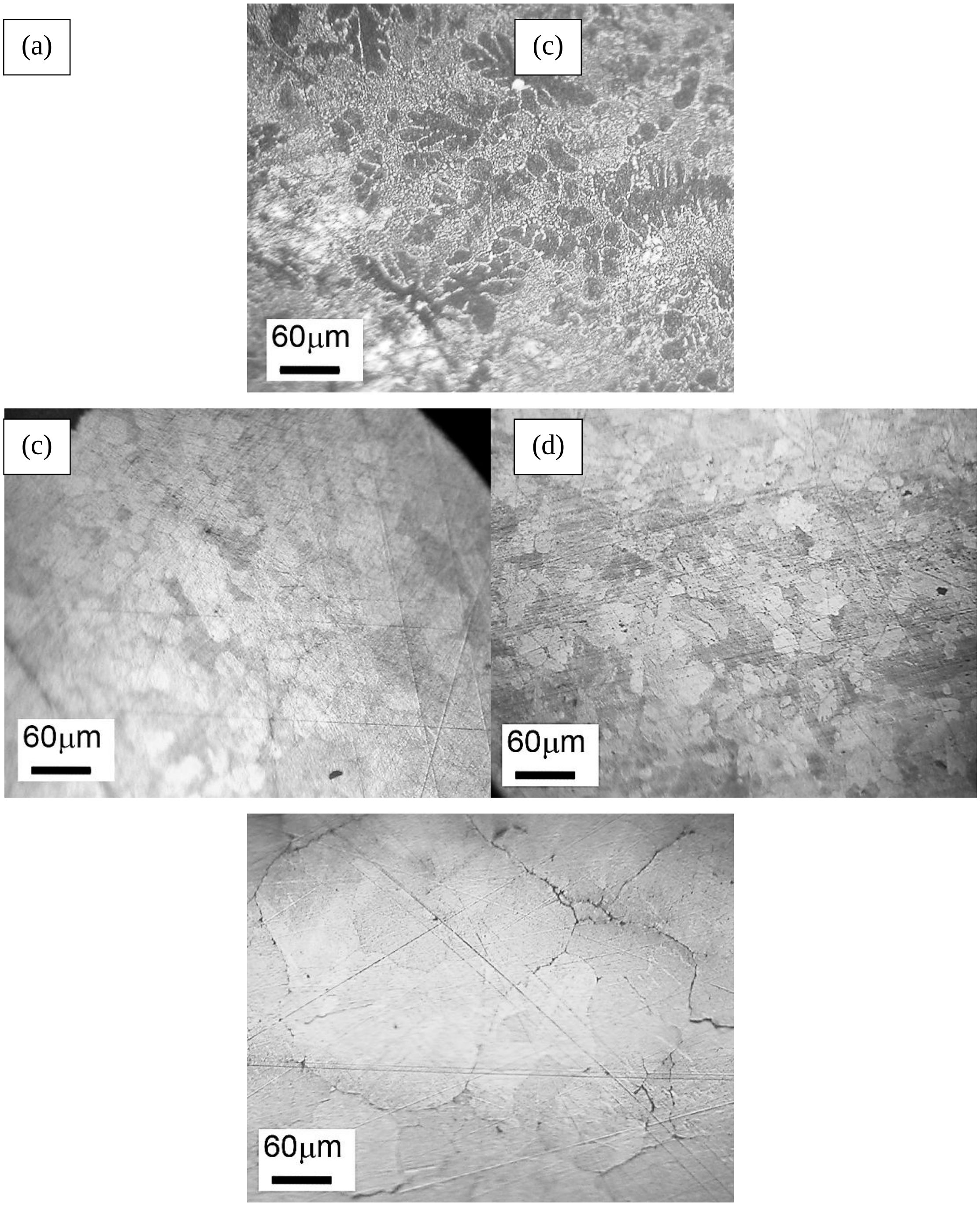


Figure 1: Optical micrographs of (a) Zamak 5, (b) 0.1 wt.% Mn, (c) 0.2 wt.% Mn and (d) 0.5 wt.% Mn

It is reported that the maximum solid solubility of Mn in Zn is about 0.8 wt.% at the eutectic temperature 416°C and drops down to 0.02 wt.% at 200°C [16]. Therefore, it is most probably that $MnZn_{13}$ intermetallic compound was formed in the 0.05 wt.% Mn microalloy only, which increased the average grain size significantly. It is important to mention that Zamak 5+Mn is a multicomponent alloy system and not only binaries. However, the phase relation knowledge using thermodynamic calculations in FactSage® thermochemical database system [14] helped in understanding the results. The average grain size of refined Zamak 5 alloy by 0.1, 0.2 and 0.5 wt.% Mn is given in Figure 2. Grain size of cast Zamak 5 was not included in Figure 2, because it was difficult to measure the grain size of a dendritic structure.

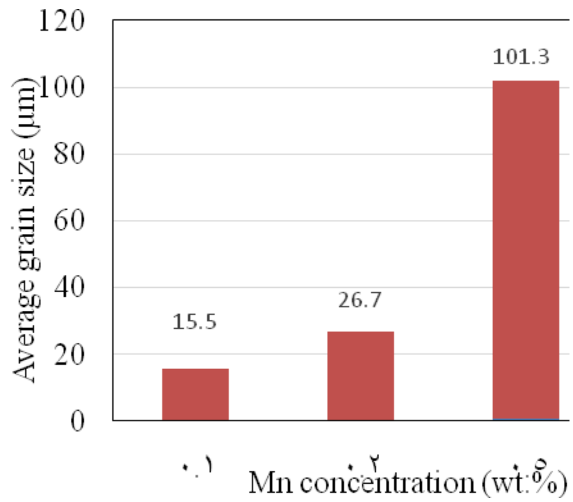


Figure 2: Average grain size of grain refined Zamak 5 by 0.1, 0.2 and 0.5 wt.% Mn

The grain refinement mechanism by manganese can be vary from one study to another according to the investigated alloy composition. However, knowing the cooling conditions of the master alloy can be of high importance [17]. In this work, the Al-10Mn wt.% master alloy was allowed to solidify in the crucible and outside the furnace, which can be considered as inequilibrium cooling condition. Under such a condition, several complex metastable intermetallic compounds of different characteristics may form. Upon microalloy preparation, the intermetallic compounds from master alloy splatter and their particles are released to act as nucleation sites for Zn during subsequent solidification. Microalloys were let to cool down inside a preheated metallic die and thus the alloy system can be said to solidify slowly under equilibrium conditions. Therefore, more stable phases will form, such as HCP-Zn, FCC-Al, Mg_2Zn_{11}, AlMgZn and $Al_{12}Mn$. It is important to mention that HCP-Zn and FCC-Al are solid solutions of Zn and Al, respectively. Phase assemblage diagrams are used to calculated the amount percentages of equilibrated phases as a function of temperature. Figure 3 illustrates the phase assemblage diagram for the microalloys calculated using FactSage® thermochemical database system [14]. The only difference between the three microalloys is the amount of $Al_{12}Mn$, which increases with increase in Mn concentration. Table 2 lists the amounts of phases in wt.% for all microalloys at room temperature.

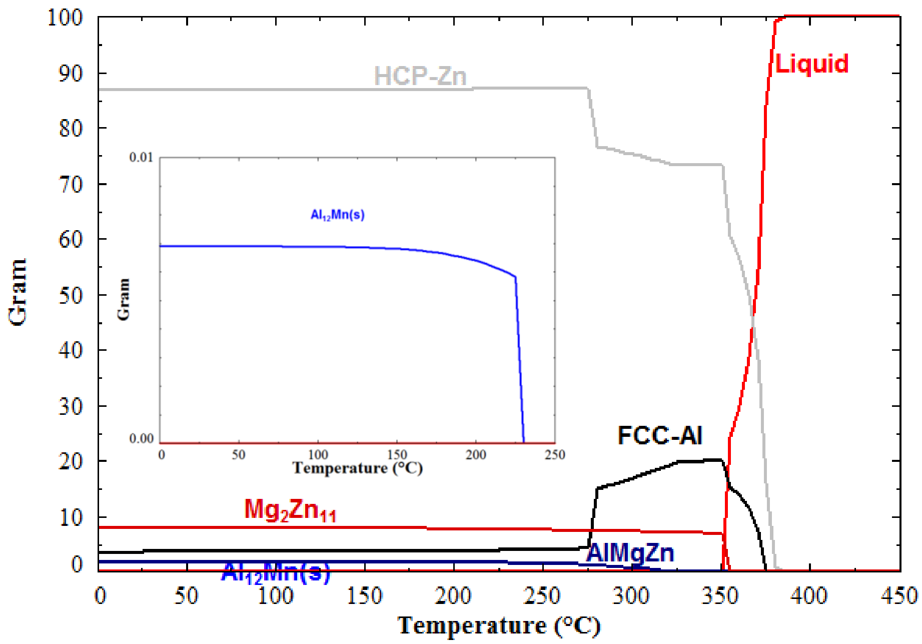


Figure 3: Phase assemblage diagrams for Zamak 5+Mn microalloys. The inset is a magnified portion shows the related information to $Al_{12}Mn$ formation

Table 2: The phase contents (wt.%) of Zamak 5+Mn microalloys at room temperature

Microalloy	HCP-Zn	FCC-Al	Mg_2Zn_{11}	AlMgZn	$Al_{12}Mn$
0.1 wt.% Mn	86.788	3.52	7.90	1.78	0.00689
0.2 wt.% Mn	86.787	3.51	7.90	1.78	0.01378
0.5 wt.% Mn	86.784	3.50	7.90	1.78	0.03446

It could be concluded that the average grain size of Zamak 5+ Mn microalloys is influenced by the amount $Al_{12}Mn$. The finer grains were found in 0.1 wt.% Mn microalloy, which has the least $Al_{12}Mn$ amount at room temperature. On the other hand, the grain size in 0.5 wt.% Mn increased significantly when $Al_{12}Mn$ increased. The increased grain size is an indication of the grain refining effect fade away or even disappear as a result of $Al_{12}Mn$ phase formation under equilibrium state. Similar observation was reported by Cao et al. [17] when they refined AZ31 alloy with Mn.

According to these authors the metastable ε-AlMn transformed to the stable Al_8Mn_5 phase at equilibrium.

3.2. Effect of Mn on the microhardness number of Zamak 5

Figure 4 represents the microhardness number of Zamak 5 alloy as a function of Mn concentration. The microhardness number has improved from 90 HV for Zamak 5 to 105 and 130 HV for the 0.1 and 0.2 microalloys, respectively. While, in the 0.5 wt.% Mn microalloy the microhardness went down to 120 HV below the number obtained in the o.2 wt.% Mn microalloy.

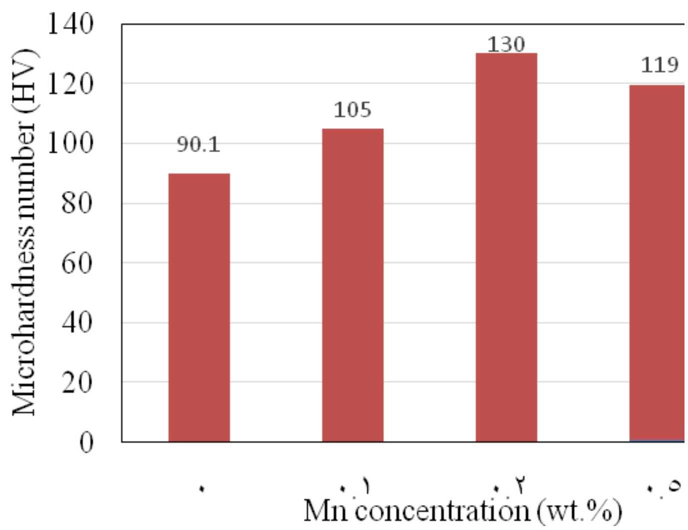


Figure 4: Average microhardness number of Zamak 5 and microalloys

The improved microhardness number can be attributed to the large grain boundary area associated with the fine structure of the microalloy. The hardening effect stems from the ability of the fine grained structure to resist atomic sliding upon loading, since the grain boundaries act as pinning points that block the dislocation motion. Because the lattice structure of adjacent grains differs in orientation, the dislocations require more energy to move from one direction to another. Hence, the yield strength and microhardness characteristics improve. The relationships will be reversed in case of large-grained structures and thus a drop in microhardness number happened when Zamak 5 alloy was refined with 0.5 wt.% Mn. However, the microhardness number drop was not lower than that in Zamak 5 alloy, because the formation of several intermetallic compounds (HCP-Zn, FCC-Al, Mg_2Zn_{11}, AlMgZn and $Al_{12}Mn$) as discussed in the previous section.

3.3. Effect of Mn on the mechanical behaviour of Zamak 5

Figure 5 shows the effect of Mn concentration on the mechanical behavior of Zamak 5 alloy obtained by compression test. The yield strength has improved from 185 MPa for Zamak 5 alloy to 250 and 320 Mpa for the 0.1 and 0.2 microalloys, respectively. Furthermore, the yield strength has slightly improved to 205 MPa for the 0.5 wt.% Mn microalloy as illustrated in Figure 6. The improved mechanical properties could be due to the increase of $Al_{12}Mn$ precipitates up to 0.2wt.% Mn. However, the drop in the mechanical behavior at 0.5 wt.% Mn could be due to the competition between the enhancement resulted from the increased $Al_{12}Mn$ precipitates and the behavior deterioration resulted from the increased grain size.

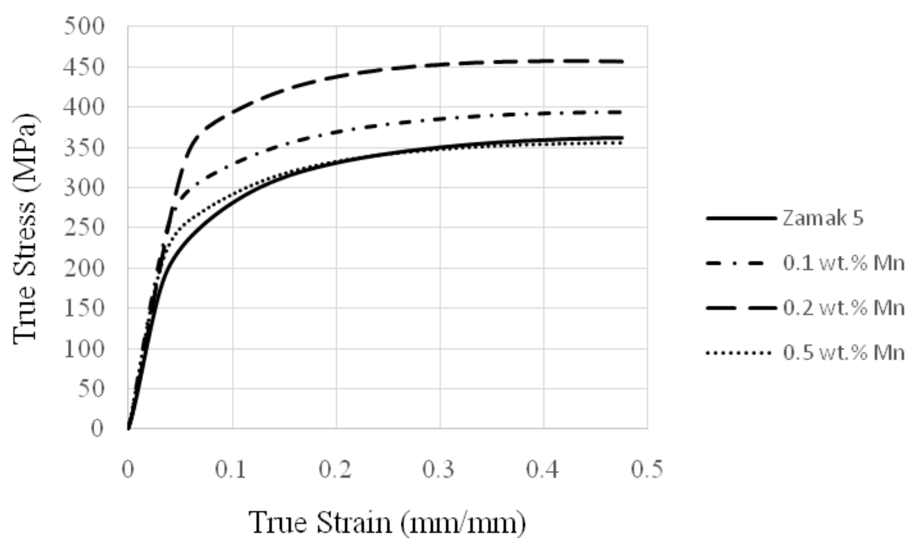
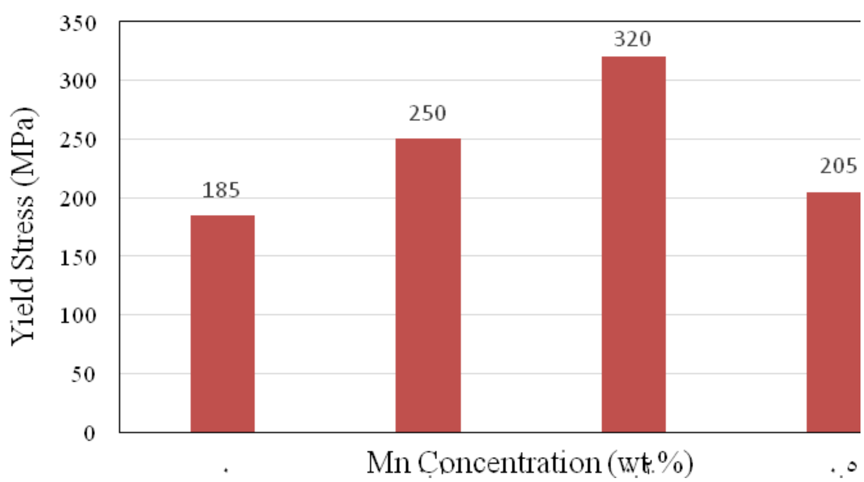


Figure 5: True stress-true strain diagrams for Zamak 5 alloy and 0.1, 0.2 and 0.5 wt.% Mn microalloys

Equally, the strength coefficient, *K*, given in Figure 7 (a), showed compatible trends to the yield strength values with 416.63 MPa for the Zamak 5 alloy and 465.12, 576.11, and 468.67 MPa for the 0.1, 0.2, and 0.5 wt.% Mn microalloys, respectively. The stress analyses results were found in the same trend as that obtained from microhardness results where the 0.2 wt.% Mn microalloy possessed the highest values for both data sets.

The strain hardening exponent, *n*, has significantly enhanced with increasing the Mn concentration as shown in Figure 7 (b). For instance, the value of *n* for Zamak 5 alloy was 0.1421, whereas for the 0.1, 0.2, and 0.5 wt.% Mn microalloys the value became 0.1433, 0.1654, and 0.2029, respectively. The improved strain hardening exponent values for all microalloys could be attributed to the increased grain size, where the mean free path (MFP) is higher than that for refined structures [18]. The value of *n* indicates the capability to uniformly distribute the deformation. In other words, *n* evaluates the strain-hardening capability of the material



[19].

Figure 6: The variation of yield strength with Mn wt.% in Zamak 5 alloy

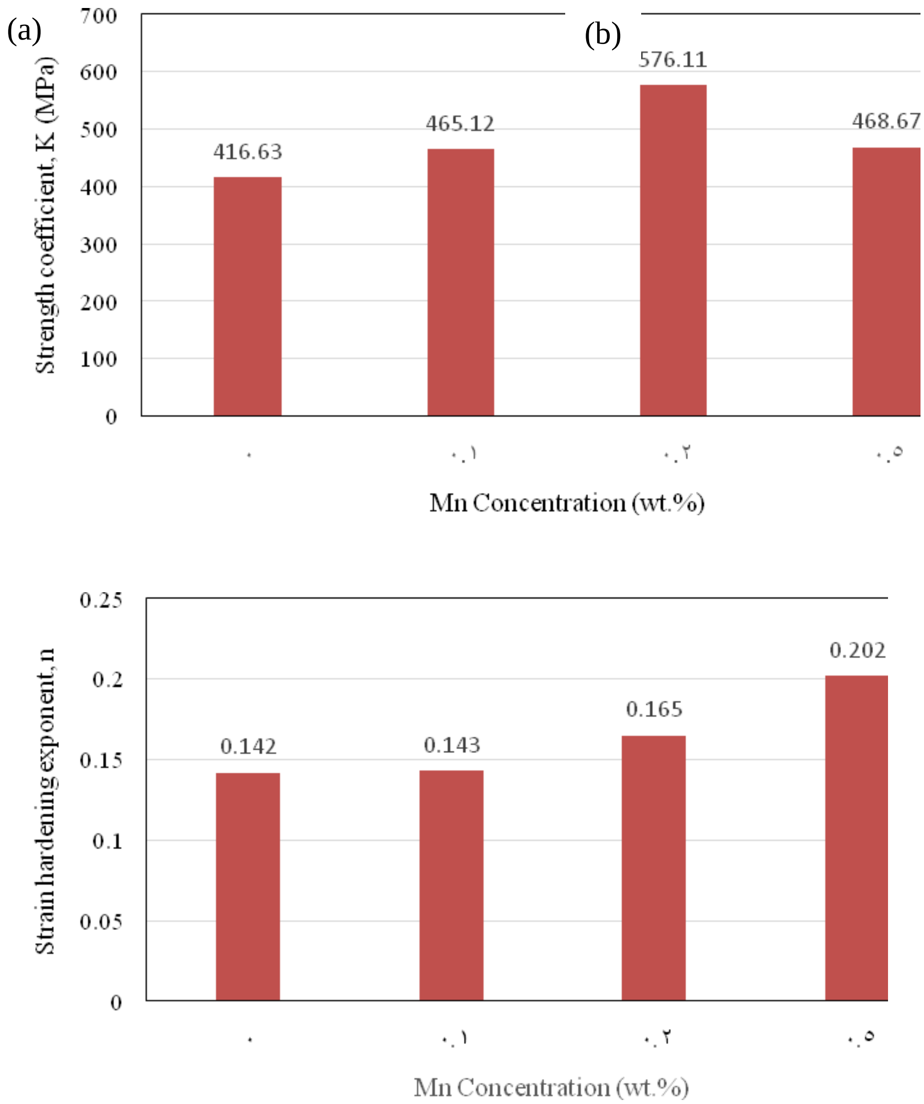


Figure 7: (a) Strength coefficient, K, and (b) strain hardening exponent as functions of Mn wt.% in Zamak 5 alloy

4. Conclusions

In this work, 0.1, 0.2 and 0.5wt.% Mn was added to Zamak 5 alloy as a grain refiner to modify its microstructure. Microalloying process was adopted to control the Mn concentrations in Zamak 5. The microstructural analyses have proven that addition of 0.1 and 0.2 wt.% Mn to the starting alloy transformed the large dendrites into fine equiaxed grains. When 0.5 wt.% Mn was added, coarse equiaxed grains originated from the lamellar $\alpha+\eta$ large eutectic were formed. It is expected that the grain refining effect of Hf was due to the formation of $Al_{12}Mn$ precipitates in the Zamak 5 matrix as proved by thermodynamic calculations and phase assemblage diagrams. The addition of 0.1, 0.2 and 0.5 wt.% Mn showed 16.6%, 44.4% and 33.3% increase in the microhardness number, respectively. This improvement was correlated to the large grain boundary area possessed by the fine-grained structure, which blocks the dislocation movement from one place to another. Because of the same reason, both yield strength and strength coefficient have improved for Zamak 5+Mn microalloys. From the results obtained from all examined specimens, addition of 0.2 wt.% Mn produce optimum mechanical properties at ambient temperature.

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