Effect of hafnium addition on wear resistance of zinc-aluminum 5 alloy: A three-dimensional presentation

Adnan I. O. Zaid[1*], Ahmad O. Mostafa[2]

[1]Department of Industrial Engineering, University of Jordan, Amman, 11924, Jordan
[2]Department of Mechanical and Materials Engineering, Masdar Institute of Science and Technology, Masdar City, Abu Dhabi, P. O. Box 54224, United Arab Emirates

[*]Corresponding author: Tel: (+962)772481393; E-mail: adnan_kilani@yahoo.com

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Abstract

ZAMAK 5 alloy is known to solidify in a large grain dendritic structure, which negatively affects its mechanical properties and surface quality. It is therefore of prime importance to reduce its grain size in order to overcome these drawbacks. In this paper, the effect of addition of hafnium (Hf) on the microstructural and mechanical characteristics of ZAMAK 5 alloy has been investigated. An amount of 0.10 wt.% Hf was introduced to the starting alloy using the well-established microalloying technique. The microstructural examination revealed that addition of Hf transformed the large grained dendrites into fine grains, which turned to increase its hardness number by 2.5% and slightly enhance its both yield and fracture stresses. The wear resistance was determined using a pin-on-disc test at different loads, speeds and time periods and the mass loss results of both alloys, before and after Hf addition, were compared with each other. The results indicated that ZAMAK 5 possesses better performance against wear at minimum speed, load and time (23.4m/min., 5N and 15min). Whereas, the Hf-containing alloy showed 42% improved performance against wear at severe experimental conditions of 153.5 m/min., 20N and 60min. The cumulative mass loss results were presented by three dimensional graphs in terms of speed, time and load, which indicated that the mass loss is a function of the three parameters. However, the graphs did not specify the most influential factor on the wear behaviour of both alloys. Full factorial design of experiments was used to identify the effect of parametric interaction on the cumulative mass loss of tested specimens and accordingly the speed was considered to be the main factor. The grain refined alloy is recommended to work under reduced speed and load conditions for prolonged service life. Copyright © 2017 VBRI Press.

Keywords: Grain refinement, hafnium addition, zinc-aluminum alloy 5, wear resistance, three-dimensional wear.

Introduction

Zinc-aluminum alloys (ZA alloys) are used in many engineering and industrial applications due to their desired and attractive properties. They have the highest tensile strength as compared to the most widely used non-ferrous alloys [**1, 2**]. ZAMAK alloys [**3**], a family of ZA alloys, are mainly used in die casting due to their low melting points and clean cast-ability. They 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 [**4**]. Thus, they are normally used in die casting foundry for making a wide range of components for automotive, electronic devices, sports, toys and small engine parts [**5, 6**]. However, against these advantages the cast structure of die cast ZAMAK alloys is characterized by a large dendritic structure [**7, 8**], which tends to deteriorate their mechanical properties and surface quality. Therefore, it is of prime importance to avoid these drawbacks. One way to enhance the mechanical properties and metallurgical characteristics is by grain size reduction, which is very well established method, throughout introducing alloying elements, i.e. grain refining their microstructure [**9**]. 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 [**10**]. Fine structures have greater total grain boundary area that blocks the dislocation movement from one place to another more than coarse grained structures [**11**]. Thus, fine grained materials are having superior mechanical properties, such as strength, hardness and wear resistance, than the coarse grained materials. The relationship between yield stress and grain size can be described mathematically by the Hall-Petch equation [**12, 13**]:

$$\sigma_y = \sigma_o + (k_y \times d^{0.5})$$

where, σ_y is the yield stress, σ_o is a material constant, k_y is the strengthening coefficient for a specific material and d is the average grain diameter. Generally, ZAMAK alloys are grain refined by adding small amounts of rare earth elements, transition metals (Ti, Mo and V) and binary alloys (Ti+B) [**14**]. However, addition of Hf as a grain refiner to ZAMAK alloy was first introduced by previous work [**4**] of the same authors of the current study, where six microalloys were prepared with a range of Hf composition from 0.02 to 0.12 with a step of 0.02 wt.%. The microstructural examination revealed that the addition of Hf transformed the large dendritic structure into rosettes and/or equiaxed grains for all Hf additions. The wear resistance of the six prepared microalloys was determined according to ASTM G99 standard test [**15**] using a pin-on- rotating disc against a hard steel disc of 65 HRC. Schematic illustration of the pin-on-disc apparatus is shown in **Fig. 1**. The ZAMAK 5+0.01 wt.% Hf alloy showed the best wear resistance as compared with the original alloy and other Hf-containing alloys.

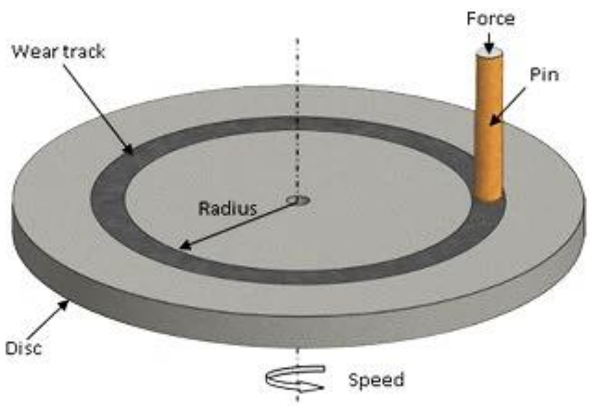

Fig. 1. Illustration of pin-on-disc wear test apparatus setup.

The main objective of this work is to investigate the wear behavior of ZAMAK 5 alloy grain refined by 0.10 wt.% Hf using a design of experiments approach and three-dimensional representation of the mass loss vs. speed, load and time. The wear behaviors of both ZAMAK 5 and ZAMAK 5+0.01 wt.% Hf alloys are compared with each other.

Experimental

Materials

The starting alloy used throughout this work was ZAMAK 5 that contains 4.3 Al, 1 Cu, 0.08 Mg, 0.1 Fe, 0.005 Pb, 0.004 Cd, 0.003 Sn and the balance is Zn in weight %. High purity hafnium powder (99.7%) was used as alloying element with a commercially pure aluminum wires (99+%) to prepare the Al-Hf master alloy.

Preparation of the master alloy

The pure aluminum wires were degreased, placed in a graphite crucible and charged into an electric furnace at 1100 °C. After 10 minutes, the crucible was taken out of the furnace to charge with Hf. The Hf powder was wrapped in aluminum foil in order to eliminate powder evaporation and to homogenize the melt composition. The Hf capsule was added to the melt under cryolite flux to avoid oxidation and stirred for one minute with a graphite rod. The crucible was then returned to the furnace at 1100°C for another 30 minutes. Finally, the crucible was taken out of the furnace with continuous melt stirring for one minute and casted over a thick cast iron mold to solidify in columnar pieces of less than 5 mm thickness. The weight percentage of Hf in the master alloy was determined using energy dispersive X-ray spectrometer (EDS), equipped on a Zeiss scanning electron microscope (SEM) type DSM950, and found to be 6.53 wt.%.

Preparation of ZAMAK 5+ 0.10 % Hf microalloy

The ZAMAK 5+0.10 wt.% Hf alloy was prepared as follows: a pre-calculated weight of ZAMAK 5 alloy was placed in a graphite crucible and heated up to 600°C in an electrical furnace. After 20 minutes, the crucible was taken out and a pre-calculated amount of the master alloy, wrapped in an aluminum foil, was added to the crucible and brought back to the furnace for another 10 minutes. Finally, the crucible was brought out and the melt was continuously stirred using a graphite rod for 1 minute before being casted in hollow thick brass cylinders.

Metallographic and mechanical examinations

Both alloys, before and after Hf addition, were cut and prepared for metallographic examination by mounting, grinding with different grades of SiC papers and polished using 1µm diamond paste. Polished samples were etched using 2%HNO_3+98% Ethanol for a period of 15 seconds. Metallurgical examination was carried out using an optical microscope equipped with a digital camera at 200X magnification which enabled to observe the microstructure of both alloys.

To investigate the effect of Hf on the mechanical behavior of ZAMAK 5 alloy, both starting alloy and microalloy were tested under compression using a universal testing machine (UTM). Specimens of 9mm diameter and 9 mm length were compressed at a cross head speed of 10 mm/min., up to 66% reduction in length. The load-deflection curves were acquired for each alloy, from which the engineering stress- engineering strain curves were obtained.

Microhardness tests were carried out using a Highwood HWDM-3 Vickers hardness tester with 100gm load. Six different values were taken at different locations on each specimen, from which the average HV number for each alloy was determined.

Wear test was carried out on a pin-on-rotating disc apparatus shown in **Fig. 1**. The disk was made of carbon steel, thermally sprayed with an abrasive material, having a hardness of 65 HRC. The wear test was performed using three different speeds (55, 125, and 287 rpm) at a track radius of 85 mm giving linear velocities of 29.359 m/min., 66.725 m/min. and 153.467 m/min., respectively, and three different loads of 5, 10, and 20 N. The total test period for each experiment was 60 minutes, where the pin was weighed after each 15 minutes interval to record the mass loss (gm). Accumulated mass loss was obtained after one hour from which wear rate was determined, using the following equation [**16**]:

$$K=V*3H/PD$$

where, K is the wear coefficient, V is volume of removed material, H is the hardness value, P is the applied load and D is the travelling distance. The experimental factors of wear test are listed in **Table 1**.

Table 1. Experimental factors and their values.

Factor	Values			
Speed (m/min.)	29.4	66.7	153.5	
Load (N)	5	10	20	
Time (Min)	15	30	45	60

Results and discussion

Optical micrographs of both ZAMAK 5 and ZAMAK 5+0.10 wt.% Hf alloys are shown in **Fig. 2 (a, b)**, respectively. The effect of 0.10 wt.% Hf addition to ZAMAK 5 alloy is clearly seen, where dendritic structure was demolished and new structure with finer equiaxed grains was produced.

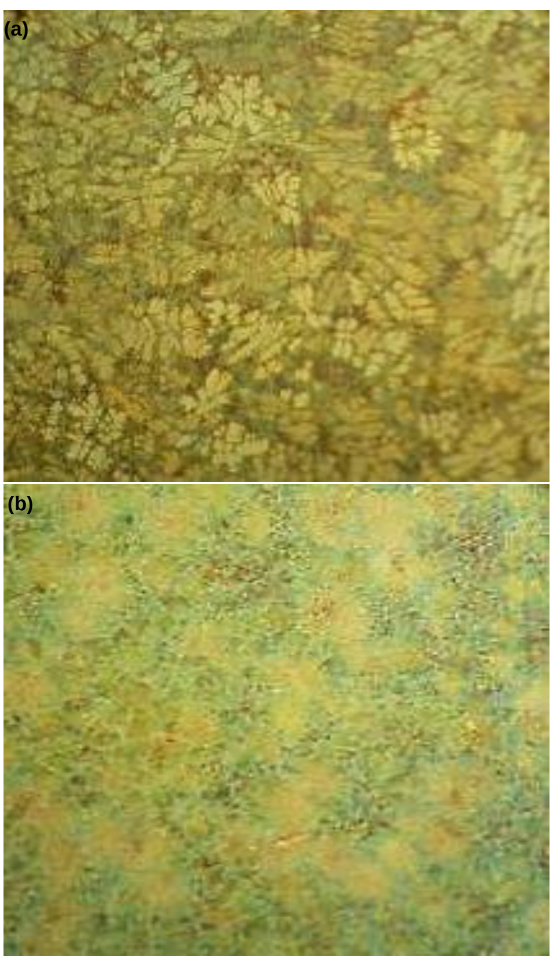

Fig. 2. Optical micrographs of (a) ZAMAK 5 and (b) ZAMAK 5+0.10 wt.% Hf alloys at 200X magnification.

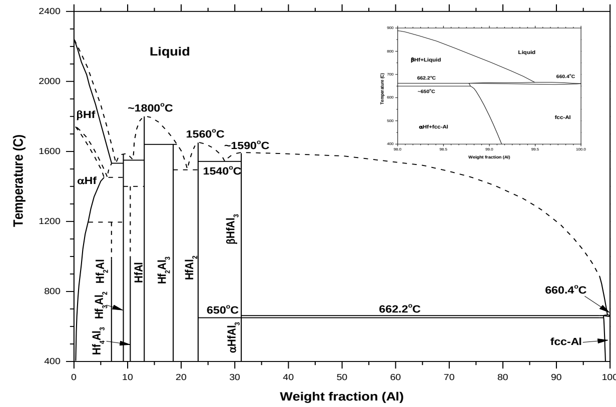

Fig. 3. The Al-Hf binary phase diagram redrawn after [**17**]. The inset shows enlarged Al-rich side.

The microstructural changes can be attributed to the formation of several nucleation cites, which were developed by Hf atoms. The Al-Hf binary masteralloy was prepared by heating the melt up to 1100°C and rapid cooled to room temperature. According to the Al-Hf binary phase diagram [**17**], shown in **Fig. 3**, the alloy containing 6.35 wt.% Hf falls within the liquid phase field at 1100°C. Upon cooling, the alloy enters the liquid+βAl_3Hf two-phase field leading to precipitate primary βAl_3Hf compound below 890°C. Al solid solution forms from the remaining liquid according to the peritectic reaction L+βAl_3Hf↔ fcc-Al at 662.2°C and 1.22 wt.% Hf. With further cooling, a peritectoid reaction takes place according to the following equation fcc-Al+βAl_3Hf↔αAl_3Hf at ~650°C. The above-mentioned phase relations were based on equilibrium phase diagram. However, the masteralloy solidified under non-equilibrium conditions. Thus, the phase diagram data are used as a roadmap only to predict the final microstructure at room temperature. The phase βAl_3Hf is known to melt congruently at around 1590°C and decomposes peritectically ~650°C [**17**]. The decomposition temperature is relatively low, comparing to the melting temperature, and thus the solid transformation is expected to be very slow [**18**], due to the low mobility of Hf atoms at 650°C, by which the diffusion process is restricted. Accordingly, the amount of transformed αAl_3Hf is expected to be very low. In conclusion, the final microstructure of the masteralloy may contain fine precipitates of peritectic βAl_3Hf, fcc-Al and αAl_3Hf. When the microalloy was prepared at 600°C, Hf-containing precipitates dispersed within the hosting alloy structure creating multiple nucleation cites (seeds). These seeds are favorable cites for nucleation, because they are the first solid to form during solidification.

The refined grained alloy is expected to have improved mechanical properties than the starting alloy. **Fig. 4(a)** and **(b)** shows the effect of 0.10 wt.% Hf addition on the microhardness and mechanical behavior of ZAMAK 5 alloy, respectively. It can be clearly seen from **Fig. 4(a)** that the microhardness number became 2.5% higher for the Hf-grain refined alloy with an average of 102HV as compared to 99.5HV for ZAMAK 5 alloy. Furthermore,

Fig. 4(b) shows a slight improvement in the yield and fracture stresses of the Hf-grain refined alloy. This improvement can be attributed to the large grain boundary area associated with the fine structure of the microalloy. The strengthening 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. The grain boundary areas are known to be much disordered than inside the grain. 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.

In order to investigate the influence of Hf addition on the wear behavior of modified alloy as compared to the behavior of original ZAMAK 5 alloy, dry sliding wear test was performed.

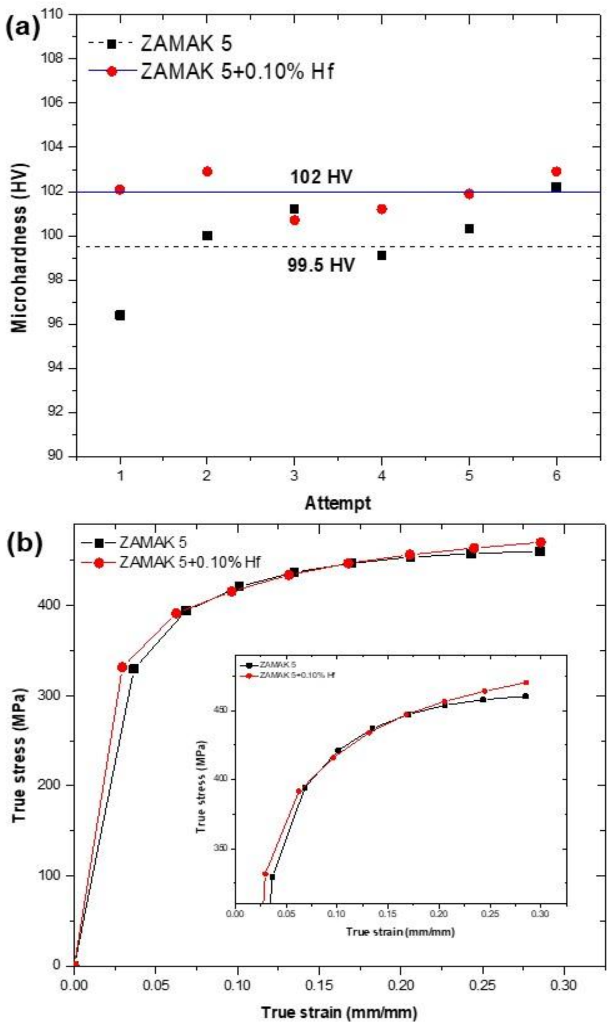

Fig. 4. Effect of 0.10 wt.% Hf on the (a) microhardness and (b) mechanical behavior of ZAMAK 5 alloy.

Fig. 5 is 3D presentation of accumulated mass loss vs. time and load for both ZAMAK 5 (left-hand-side column) and ZAMAK 5+0.10 wt.% Hf (right-hand-side column). The effect of speed on the wear behavior of both alloys are shown in **Fig. 5(a), (b)** and **(c)** at 29.4, 66.7 and 153.5 m/min., respectively. The color maps indicate the cumulative mass loss scale. **Table 2** summarizes the cumulative mass loss values obtained from each experiment at different load, speed and time parameters.

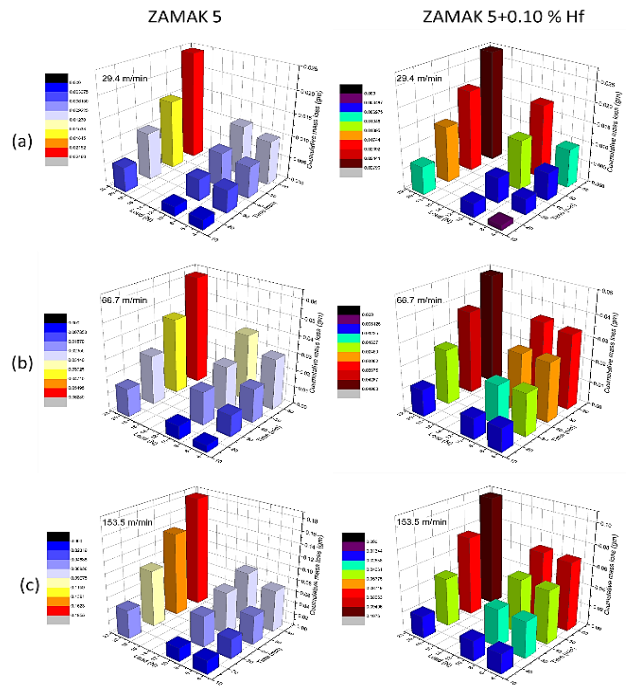

Fig. 5. 3D representation of cumulative mass loss for ZAMAK 5 and ZAMAK 5+0.10 wt.% alloys vs. load and time at (a) 29.4 m/min., (b) 66.7 m/min. and (c) 153.5 m/min.

Fig. 5 and **Table 2** showed that addition of Hf improved the wear behavior of ZAMAK 5 alloy at low speed of 29.4 m/min. and 5 N loading. When the loading increased to 10 and 20 N at the same speed, the Hf-grain refined alloy showed poorer wear resistance than that of ZAMAK 5 alloy as concluded from the mass loss values. The drop-in wear performance of the microalloy continued with further speed increase (66.7 m/min) and 5 N loading. The deteriorated wear behavior of the microalloy can be attributed to the particles detachment from the surface of tested specimens due to the small contact area between the neighboring grains in the refined structure. In contrast, the large grained structure of ZAMAK 5 alloy allowed the same applied load to distribute along large grain boundary areas; hence, the mass loss was minimum.

Table 2. Cumulative mass loss values per experimental parameters.

Load (N)	Time (min)	ZAMAK 5 (gm)	ZA5+0.2Hf (gm)
	Speed of 29.4 m/min.		
5	15	0.0022	0.0013
	30	0.0051	0.0039
	45	0.0071	0.0069
	60	0.0099	0.0096
10	15	0.0021	0.0035
	30	0.0049	0.0063
	45	0.0078	0.0124
	60	0.0113	0.0184
20	15	0.0056	0.007
	30	0.0106	0.014

	45	0.0155	0.0204
	60	0.0245	0.0279
Speed of 66.7 m/min.			
5	15	0.004	0.0104
	30	0.0123	0.0189
	45	0.0193	0.0264
	60	0.0295	0.0334
10	15	0.0078	0.0093
	30	0.019	0.0177
	45	0.0263	0.0261
	60	0.0382	0.035
20	15	0.0161	0.012
	30	0.0283	0.0245
	45	0.0436	0.0369
	60	0.0627	0.049
Speed of 153.5 m/min.			
5	15	0.0227	0.019
	30	0.0329	0.0354
	45	0.0484	0.0521
	60	0.0697	0.0674
10	15	0.0225	0.0195
	30	0.0519	0.0364
	45	0.0705	0.053
	60	0.0848	0.0688
20	15	0.0481	0.0215
	30	0.0951	0.047
	45	0.1401	0.0771
	60	0.1851	0.1071

The wear behavior of both alloys did not remain the same under all testing parameters during wear experiments. Instead, it has been changed dramatically after increasing the load to 10 N at 66.7 m/min., where the Hf-grain refined alloy showed superior improvement in the wear behavior as compared to ZAMAK 5 alloy. At this stage, the material removal mechanism cannot be the same as that occurred at low testing conditions of reduced speed and load.

Although Hf-containing alloy has relatively higher hardness than that of ZAMAK 5 alloy, it experienced severe mass loss under low speed and loading conditions. Under these conditions, no heat generation was expected. Thus, the material removal mechanism was explained based on the load distribution over large and/or small grain boundary areas. Whereas, the mechanism under high speed and loading conditions occurs in different scenario, because of frictional heat generation [**19**]. For instance, during the most severe testing conditions (153.5 m/min., 20 N and 60 min), the microalloy showed 42% improvement with a total mass loss of 0.1071 gm as compared to 0.1851 gm for ZAMAK5 alloy. The main reason for this improvement may be due to the reduction in the grain size, which provides an evidence of uniform distribution of fine and hard precipitates that improve the resistance to pulling-out forces. Furthermore, the formation of stable Hf-containing precipitates, which have high melting temperature, could improve the high temperature wear behavior. In fact, under severe loading and speed conditions, the material becomes soft as the frictional heat rises [**20**].

It is a clear evidence from **Fig. 5** that the mass loss of both alloys increases by increasing load, speed and testing time. However, it is still ambiguous to know which parameter or combination of parameters have the greatest influence on the wear behavior of tested alloys. The influence of one factor at a time might not be adequate to describe the wear behavior of tested alloys under several factors. To study the interactions between factors, full factorial design of experiments [**21**] was used taking the experimental factors and their values from **Table 1**. However, for each factor, $n=3$, two experimental levels ,$k=2$, were chosen (low and high) as follows: 29.4 and 153.5 m/min. for the speed, 5 and 10 N for load and 15 and 60 min for time. Accordingly, the number of parametric interactions $(n)^k$ were found to be eight.

Pareto charts, shown in **Fig. 6(a)** and **(b)**, indicate the major effect of interaction among different variables for ZAMAK 5 and Hf-grain refined alloys, respectively. **Fig. 6(a)** shows that wear behavior of ZAMAK 5 alloy is greatly influenced by the speed, at which maximum mass loss occur. On the other hand, the effect of combining speed with time is equal to the effect of load on the mass loss. In conclusion, the best wear performance for ZAMAK 5 alloy can be achieved by reducing the three factors (speed, time and load) all together.

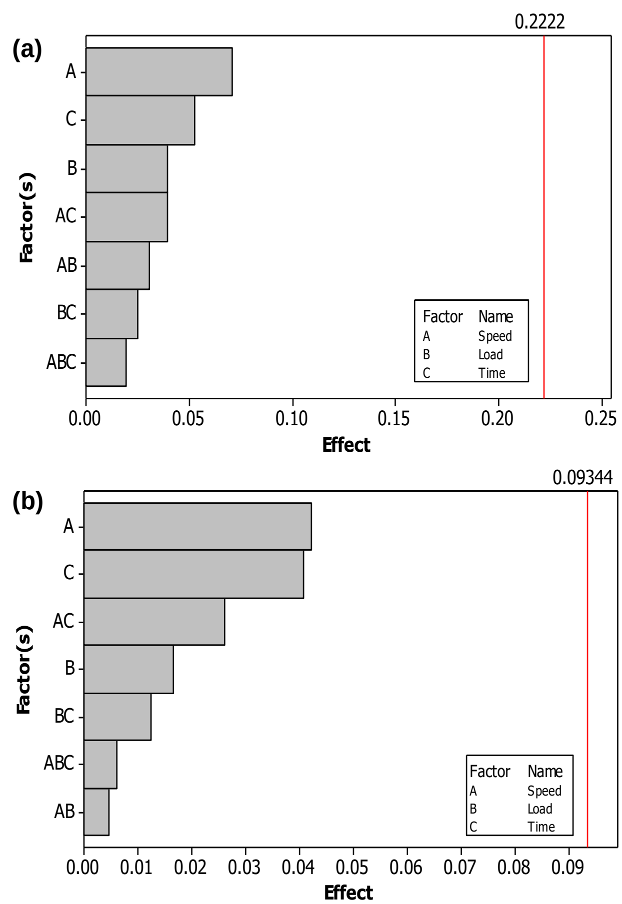

Fig. 6. Pareto charts of the main effect of parametric interaction for (a) ZAMAK 5 and (b) Hf-grain refined alloys.

There is no doubt that the speed is the most significant factor that decreases the wear performance of ZAMAK 5+0.1 wt.% Hf alloy, as could be concluded from **Fig. 6(b)**. However, the best wear performance for this alloy can be obtained by lowering both speed and load. This gives an indication that the Hf-grain refined alloy can be used under reduced speed and load service condition for prolonged periods of time. These conditions do not suit with ZAMAK 5 alloy, since it requires the service under shortest service time as possible.

Conclusion

In this work, Hf was added to ZAMAK 5 alloy as a grain refiner to modify its microstructure which in turn will enhance its mechanical properties and surface quality. The microstructural analysis have proven that addition of small wt.% of Hf (0.10%) to the starting alloy lead to transform the large dendrites into fine grained structure. It is expect that the grain refining effect of Hf was due to the formation of αAl_3Hf and βAl_3Hf precipitates under non-equilibrium cooling conditions, where the atomic diffusion was restricted.

The hafnium addition showed 2.5% increase in the microhardness number. Furthermore, it resulted in slight enhancement of its yield and fracture stresses. 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.

ZAMAK 5 alloy showed enhancement of its wear resistance under low speed and loading conditions. The material removal mechanism under these conditions was described based on the particle pull-out forces induced on the grains of the tested surface. The large grained structure of ZAMAK 5 alloy experienced minimum mass loss since the load was distributed over a large contacting area between the adjacent grains. However, the mass loss was greater in the grain refined alloy, because the induced load was acting over small contacting areas.

At severe wear test conditions, the grain refined alloy showed improvement in the wear resistance behavior 42% higher than that of ZAMAK 5 alloy. This improvement was attributed to the formation of high melting temperature Hf-containing compounds that resist the material softening due to the heat of friction.

The selection of a material for abrasive wear resistance is based on several factors as demonstrated by Phelps [**22**]. In this study, the design of experiments is proven to be a powerful tool for selecting the proper material and service conditions for dry pin-on-disc wear test. Accordingly, Hf-modified alloy is recommended to be used to serve under low speed and load conditions as it provides longer working life time.

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Author's contributions

Conceived the plan: AZ; Performed the expeirments: AM; Data analysis: AZ, AM; Wrote the paper: AM. Authors have no competing financial interests.

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