The effect of melt shearing method on the micro-structure and corrosion resistance of 700-series cast aluminum alloys

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Abstract— In the present study, a vertical screw was used to apply shear stress on the melted 700-series cast aluminum alloy for various times; also the effect of Sn and melt shearing process was investigated simultaneously. In the following, the effect of this process on the microstructure and corrosion properties was investigated. Optical microscope and Scanning Electron Microscope (SEM) equipped with Energy Dispersive Spectroscopy (EDS) were used for analysis the microstructural changes. The experimental investigations showed that melt shearing with a vertical screw has a significant effect on the microstructure. When the shearing time increases, the dendritic grains change to equiaxed grains and also the large grains alter to fine grains. With increasing the shearing time, the coarse continuous intermetallic in the grain boundaries, change in to discontinuous fine intermetallic phases. In order to investigate the corrosion resistance of samples, the cyclic polarization tests were used. The results depicted that, when the shearing time increases, due to uniform distribution of cathodic and anodic intermetallic particles and reduction of their size, the corrosion resistance in artificial sea water increases considerably.

Index Terms— Aluminum alloy, Melt shearing, Intermetallic, corrosion resistance.

1 Introduction

It is well known that the electrochemical properties of aluminum alloys are strongly affected by the microstructure of the alloy during solidification [1-5]. For example, it is reported that three important parameters influence on corrosion resistance of Aluminum alloys: 1-cooling condition during casting which influence on dendrite microstructure. 2-Solute distribution 3-anodic or cathodic behavior of second phases [1].

The laser surface remelting process has provided a significant microstructural refinement in an Al–9 wt%Si alloy sample compared to that of an as-cast sample (the secondary dendrite arm spacing has been reduced in about five times) and has induced precipitation of silicon in the Al-rich matrix and/or the formation of a metastable phase due to the high cooling rates in refined microstructures, since such boundaries are more susceptible to the corrosion action [2].

Effect of grain size on the corrosion resistance of Aluminum and Zinc with commercial purity, showed that in both materials, coarser microstructures provides better corrosion resistance. These results for both coaxial and columnar microstructures established but generally coaxial microstructures have better corrosion resistance than columnar ones[3]. Coarser dendritic structures tends to improve the corrosion resistance of an Al–20wt% Zn alloy while finer dendritic structures provides lower corrosion rates than coarser structures for an Al–10 wt% Sn alloy[4].

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For a dilute Al–0.5 wt. % Fe alloy, it has been observed that coarse cells tend to improve the corrosion resistance mainly due to the reduction in cellular boundaries. Coarse cells trend has been detected, i.e., fine cells provide better corrosion resistance than coarse ones. A more extensive distribution of the intermetallic Al_6Fe particles, which is associated with smaller cellular spacing, provides a protective effect with the nobler Al_6Fe particles ‘‘enveloping” the Al-rich phase in the eutectic mixture, resulting in better general electrochemical behavior[5]. Melt shearing is a method to obtain fine and equiaxed microstructure [6-9].

Recently, the melt conditioning by advanced shear technology (MCAST) process has been developed for conditioning liquid metal under intensive forced convection before solidification and it has been demonstrated that naturally occurring oxides can enhance heterogeneous nucleation for microstructural refinement in commercial Mg–Al alloys. Oxide clusters and films are composites, whereas nano-scale oxide particles are embedded in a liquid metal matrix. Such oxide particles can be effectively dispersed by intensive forced convection and can be potent sites for heterogeneous nucleation since there is a good crystallographic match with the nucleated solid crystalline phases [6].

Both melt temperature and composition fields inside the MCAST machine are extremely uniform, owing to the strong dispersive mixing power of the twin screw mechanism. Heterogeneous nucleation occurs continuously throughout the entire volume of the melt conditioned liquid during solidification. All the nuclei can survive and contribute to the final microstructure [9-10].

As well known, the oxide films or other passive films are prone to nucleate at the crystalline defects, such as grain boundaries and dislocations. Melt shearing method process brings to the Al alloy not only significant grain refinement but also lots of crystalline defects with high internal energy, such as large fractions of grain boundaries and dislocations. Those energetic crystalline defects provide the Al alloy more nucleation sites for passive film forming. When the sample is soaked in the water solution, rapider and more drastic passive film forming reaction will happen, and more volume fractions of oxide film will be obtained on the sample surface [9-11].
The aim of this research is to study the microstructure and corrosion resistance of 700-series cast aluminum alloy. In fact it is tried to modify the microstructure of the alloy containing Al-Fe-Cu-Mg by a vertical screw; also the effect of this modification on electrochemical behavior of the alloy was studied. Furthermore, Tin element (Sn) was added in one of the samples to investigate the effect of melt shearing and this element simultaneously. Sn would transform the dendritic microstructure to coaxial one [12-13].

2- Experimental procedure

2.1 preparations of samples

For preparation of the alloy, some 700-series cast aluminum alloy ingot was used. Table.1 shows the weight percent of elements which used in this alloy concisely. The samples prepared by melt shearing method were studied for investigation of element distribution, microstructure morphology, size and distribution of intermetallic particles in interdendritic regions and primary grains. Corrosion resistance of the samples were analyzed and compared with each other.

Table. 1
Chemical composition of the alloy used in this research (Wt. %)

Al	Zn	Mg	Cu	Cr	Mn	Fe	Ni	Si
base	5.7	2.35	1.47	0.2	0.17	0.15	0.01	0.07

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The alloying procedure was done in an electrical resistance furnace inside a SiC crucible at 730°C. Then the homogeneous melt was poured in a copper mold. The produced alloy was remelted inside the resistance furnace. After removing the slag from aluminium alloy, the alloy melt was sheared about 4 minute at 700°C and 800 rpm. Finally the sheared melt was poured in a copper mold with thick section. In this research, 3 samples were prepared. The sample No.1 was poured in the mold without shearing. The melt of samples No.2 and No.3 were sheared for about 4 minutes; also 0.1% Sn was added in the melt of the third sample. In fact these three samples were studied to investigate the microstructure, distribution of alloying elements, phases and intermetallic particles. Fig.1 shows the screw which used in this study. Immediately after finishing the mentioned period of times, the samples of melt were poured in the mold copper with 12cm height and 2cm diameter and the samples were solidified. The casting conditions are summarized in the table. 2.

Fig.1 Steel screw used for melt shearing process.

Table. 2
Casting condition of melt shearing process.

Cast Temperature	Mold Material	Mold Temperature	Shearing Speed	Shearing Time	**weight percent of Tin added into the third sample**
700°C	Cu	30°C	800 RPM	0 , 4 min	**0.1% Sn**

2.2. Microstructure study

The samples were cut cross-sectional, smoothed down by sand papers and were polished in order to study of microstructure of the samples. Keller's reagent was used to etch the surface of the samples for 60 seconds. Optical microscope and scanning electronic microscope equipped with EDS analysis utilized to study the dendritic structure, dispersion of intermetallic particles in microstructure and grain size.

2.3 corrosion resistance

Potentiodynamic polarization tests of the samples were done using a three electrode EG&G machine in 3.5%NaCl solution. These samples were immersed for one hour in the solution before test. Saturated calomel and platinum electrodes were used as reference and counter electrodes respectively. The potentiodynamic polarization tests were carried out at potential scan rate of 10mV/s and the results were analyzed by NOVA software.

3. Results and discussion

3.1 microstructure and morphology results

The effect of melt shearing time on morphology of dendritic array and morphology of intermetallic particles is shown in Fig.2. As seen in this figure, melt shearing process has strong influence on the microstructure of the dendrite array and intermetallic particles. According to Fig (2.a), the sample without shearing process is containing of coarse (Al-α) dendrites with continuous and coarse precipitations of intermetallic compounds. Fig. (2.b) shows the sample with 4 minutes shearing process, as shown in this figure; dendritic array and intermetallic particles are fine and continuous form. Fig. (2.c) shows the sample with 4 minutes shearing process, also 0.1% Wt Sn element was added in this sample. As seen in this Figure, dendritic array and intermetallic particles are fine but discontinuous form.

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By applying the melt shearing process, liquid metal is subjected to intensive shearing under high shear rate and high intensity turbulence. It appears that shearing enhances the homogeneity in the alloy melt with respect to temperature and composition and uniformly distributes the nucleating agents throughout the melt. This, in effect perhaps produces uniform nucleation throughout the melt and a higher survival rate of the nuclei (increased effective nucleation rate) compared to conventional liquids casting. These will promote the nucleation of primary α-Al phase, offering fine and uniform microstructure. Formation of aluminides (Al_3Fe and Al_6Fe) which have a good wettability with aluminum is another potential possibility for formation of fine grain size in the liquid state. It is also believed that the liquid metal has a high potential to be oxidised at elevated temperatures and usually consists of oxide particle clusters and oxide films. These insoluble particles have low wettability in liquid metal clearly demonstrated that shearing offers the potential to overcome this wetting problem and these particles were observed to have a fine size, narrow and uniform distribution throughout the liquid melt. Therefore, it is believed that with present understanding the insoluble particles may contribute to nucleation during solidification [14-15].

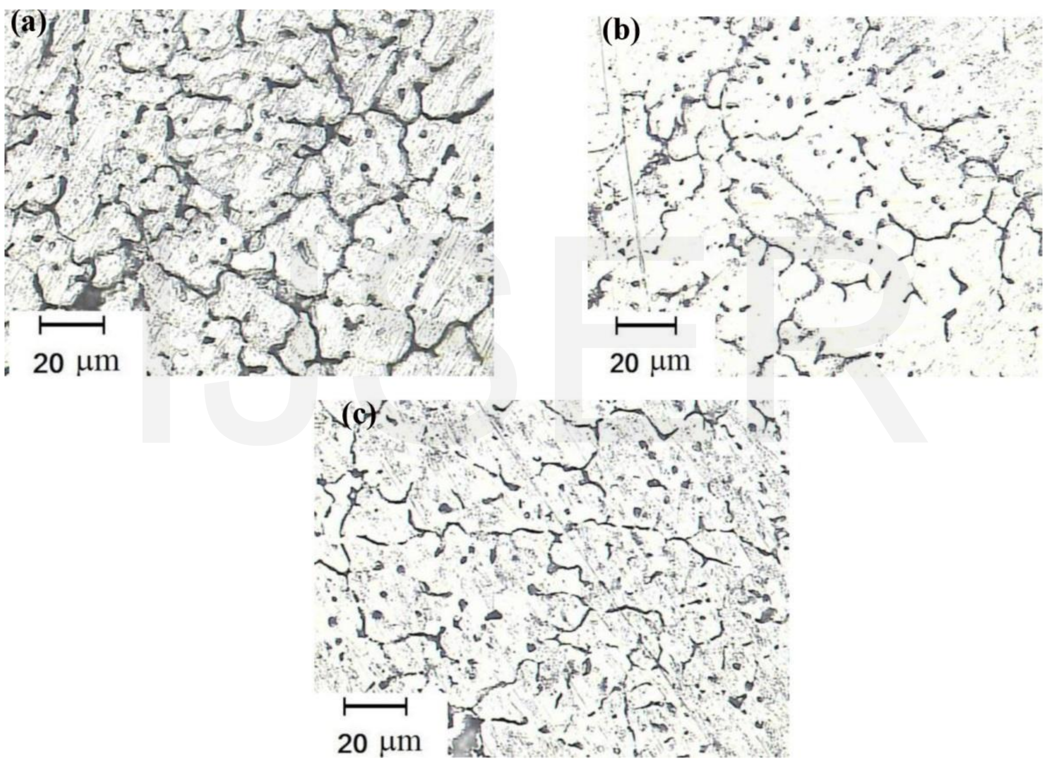

Fig.2 Optical microstructure of samples (a) without shearing process (b) 4minutes shearing (c) 4 minutes shearing with adding 0.1%Wt Sn.

Fig.3 shows the results of hardness tests. It can be seen that the initial hardness of the non-Sheared sample was 137.7 VHN that decreased to 108.8 VHN after four minutes of melt shearing. The hardness changes must be explained by means of the effects of melt shearing on the volume fraction of the hard intermetallic particles such as Al_6Fe phase. As shown in Fig.2 (b), intermetallic particles dispersed more uniform than Fig.2 (a). In fact coarse and continuous phases change to fine and discontinuous ones. This may be a reason for decreasing of hardness of the second sample with respect to the first one. By adding Sn element in to the third sample, the hardness increased to 126.4 VHN. The existence of Sn element in the melt may cause hardness improvements. Standard deviation of measured harnesses is depicted in the top of each bar graph by a scale. As shown in Fig.3, standard deviation of the first sample (without

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shearing process) is greater than the other ones. It means that melt shearing process is effective on the quality distribution of hard intermetallic particles in the samples.

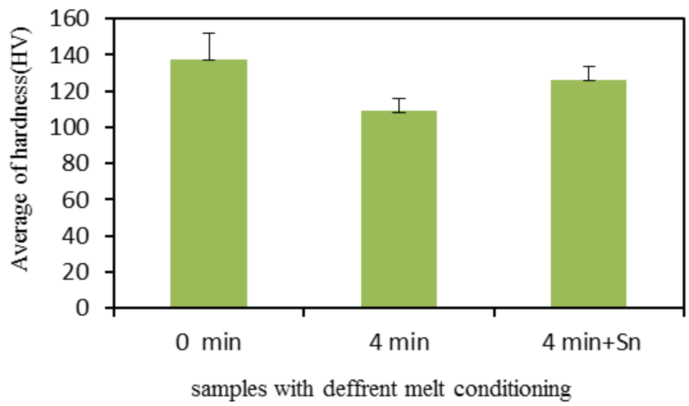

Fig.3 Changes of hardness of the samples in different melt conditions.

3.2 Corrosion result

Polarization cyclic tests were used for investigation of corrosion rate of the samples (fig.6). As depicted in this figure, with increasing of melt shearing time, the cyclic graphs shift to the left side. It means that the corrosion rates should significantly decline as a consequence of melt shearing process. In fact, cathodic and anodic curves intersect at less current density which leads to corrosion resistance improvement. This event can be related to increasing of process time. Table.3 shows the parameters of polarization test in different conditions of melt shearing process. In addition, the samples used in this study have been numbered in the table. It is observed that current density of sample No.1 is $10^{-5/34}$A/cm^2 which is about ten times bigger than the current density of the sample No.3 ($10^{-6/40}$A/cm^2). It is concluded that applying of melt shearing process to the alloy melt, causes improvement of corrosion resistance of this alloy in artificial sea water solution. It can be concluded that melt shearing process can improve corrosion resistance of structures made of 700-series cast aluminum alloys in marine corrosive media.

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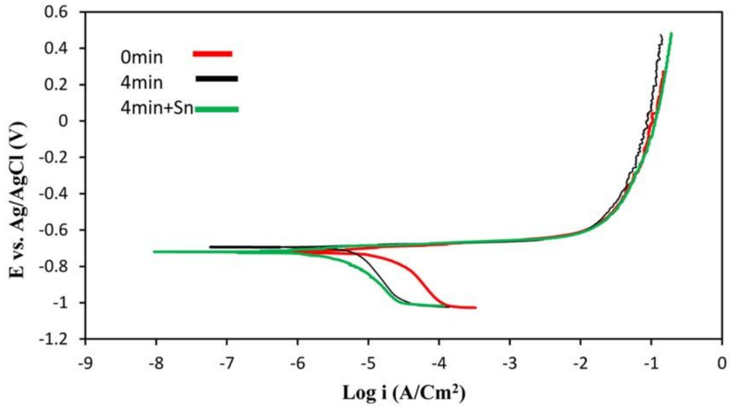

Fig.4 polarization tests of the samples made in different condition of melt shearing process.

Table.3
Polarization test parameters for three different samples.

Sample Number	**1**	**2**	**3**
Melt shearing time	0min	4min	4min
Added element	_	_	0.1% Sn
Log i (A/Cm^2)	-5.3432	-5.5968	-6.4075
E (Volt)	-0.7294	-0.7018	-0.7261

3. SEM Results

The microstructures were investigated by SEM equipped with EDS analyzer to study the morphology and types of phases exist in the samples. Fig.5 shows microstructure of three samples which were studied in this research. The shape and distribution of intermetallic particles in matrix was analyzed. As depicted in this figure, the phases which formed in the sample No.1 (Fig.5.a), are very coarse and heterogeneous while these particles in the sample No.2 (Fig.5.b) seem finer and more homogeneous and in the sample No.3 (Fig.c.5), intermetallic particles were dispersed almost fine and uniform and morphology of the phases change from coarse and fiber shape to fine and Spherical one.

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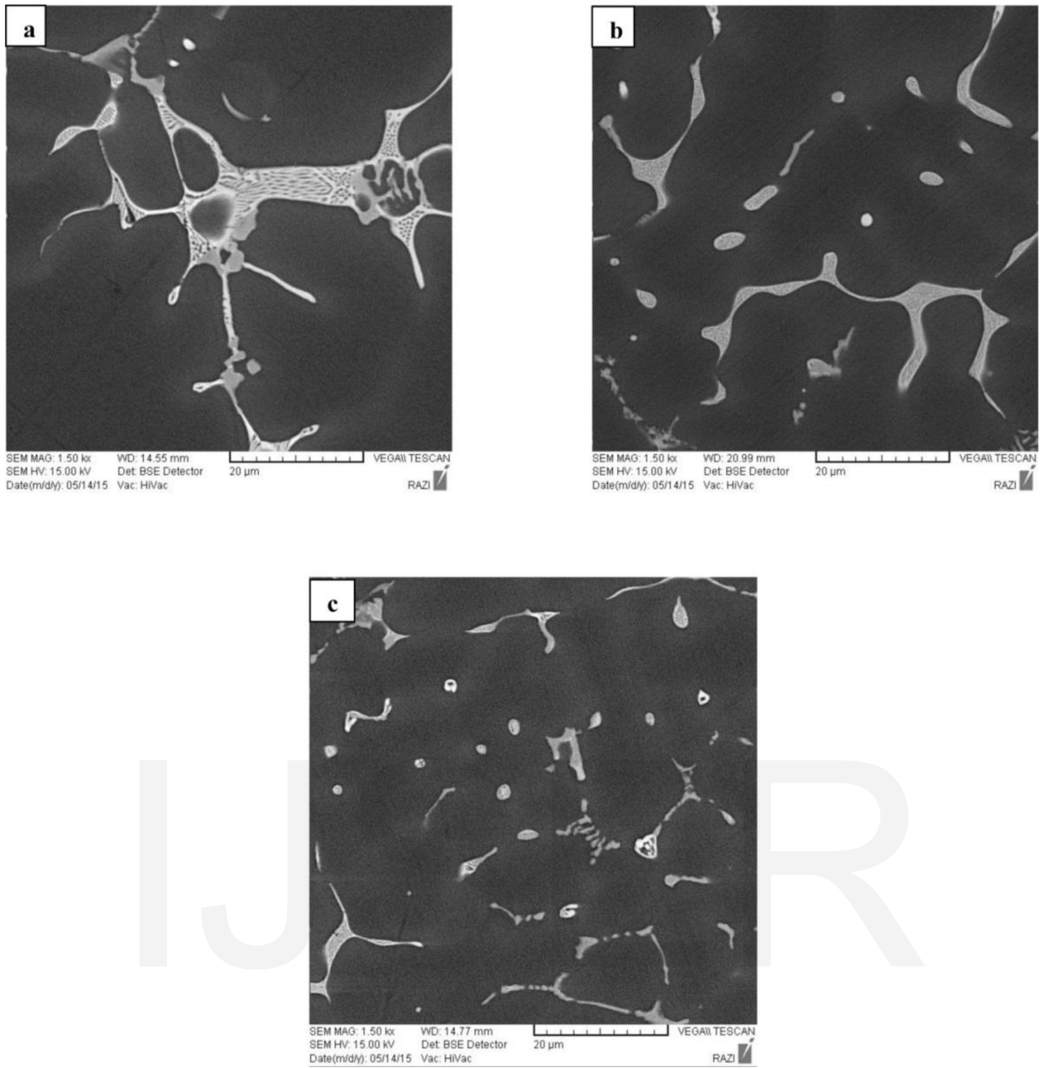

Fig.5 microstructure of the sample (a) without shearing process (b) 4minutes shearing and (c) 4 minutes shearing with adding 0.1%Sn.

EDS point analysis was used to distinguish types of intermetallic compound formed in the samples. Analysis of points shown in Fig.6 proved that these particles are rich in copper and iron elements. Iron and copper elements are electrochemically nobler than aluminum base alloy. In fact when this alloy is placed in the corrosive media, an electrochemical galvanic cell is formed. Iron or copper intermetallic compounds play the role of cathode while, aluminum alloy plays the role of anode. Zinc and Magnesium elements which are more active than aluminum would dissolve in aluminum and form solid solution. It is obvious that in a galvanic cell, the active element should be corroded faster than the nobler one. Usually in alloys with noble intermetallic compounds, uniform distribution of fine size intermetallic particles improves the corrosion resistance of the alloy [16].

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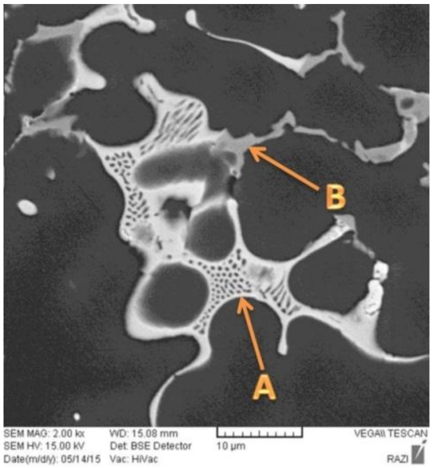

Fig.6. EDS analysis for detection of phases in the sample without shearing process.

Fig.6 is related to the sample without shearing process. In this Figure, points A and B show two types of phases. As seen, point A and B are white and gray respectively. Table.4 depicts analysis of these points is effective for detection the chemical composition of points A and B. point A shows eutectic phase formed at interdendritic regions. This phase can be consisted of Al-α and $MgZn_2$. The result of EDS represents that some copper element exist in this phase. It is concluded that copper atoms penetrate into the Zinc lattice (Zinc element exists in $MgZn_2$ compound) and replace the Zinc element which lead to formation of $Mg(Al,Cu,Zn)_2$ compound. This phase is a type of solid solution which consists of four elements; Also analysis of atomic percentage of point B shows that the amount of aluminum is almost 6 times bigger than the amount of iron element. It can be concluded that the intermetallic compounds which formed in this region, is Al_6Fe.

Table.4
Analysis of atomic percentage by EDS at points A and B.

Element	Mg	Al	Fe	Cu	Zn
Point A	23.26	48.12	-	11.53	17.10
point B	0.93	81.86	13.98	3.23	-

Conclusion

1-Applying of melt shearing process to the melt for 4 minutes by a vertical screw, caused refining of microstructure; also adding of Tin element to the melt, intensified refinement of copper-rich and iron-rich intermetallic particles and dispersion of these particles would be uniformed.

2-Copper-rich and iron-rich intermetallic particles with minor size and uniform dispersion have healing properties. It means that the existence of fine and uniform distribution of intermetallic particles is desirable because a maximum ratio of anode to cathode is established and local corrosion is minimum.

3-The oxide films or other passive films are prone to nucleate at the crystalline defects, such as grain boundaries and dislocations. Melt shearing method process brings to the Al alloy not only significant grain refinement but also lots of crystalline defects with high internal energy. Those energetic crystalline defects provide the Al alloy more nucleation sites for passive film forming. When the sample is soaked in the water solution, rapider and more drastic passive film forming reaction will happen, and more volume fractions of oxide film will be obtained on the surface which leads to corrosion resistance improvement.

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