Effect of molybdenum addition on aluminium grain refined by titanium on its metallurgical and mechanical characteristics in the as cast condition and after pressing by the equal angular channel process

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Abstract. Aluminium and its alloys are versatile materials which are widely used in industrial and engineering applications due to their attractive characteristics. However, they solidify in a columnar structure which tends to reduce their surface quality and mechanical strength. It is therefore, grain refined by grain refiners i.e. titanium or titanium+boron. The equal angular channel pressing, ECAP, process is a recent method for producing severe plastic deformation in materials. In this research work, the effect of addition of molybdenum either alone or in the presence of titanium to commercially pure aluminium on microstructure and mechanical behaviour is investigated in two conditions; first, in the as cast condition, and second after pressing by the ECAP process at room temperature. It was found that addition of Ti alone at a rate of 0.15% weight to commercially pure Al resulted in grain refining of microstructure and a grain size of 91µm was obtained. However, after pressing by the ECAP process further refinement was achieved and the grain size was reduced to 18µm. Addition of Mo alone to aluminium at a rate of 0.1% resulted in grain size of 76µm in the as cast condition and 32µm after pressing by the ECAP process. The combination of the two elements Ti and Mo together resulted in 48µm grain size in the as cast condition, compared to 40µm after pressing by the ECAP process. Furthermore, it was found that in the as cast condition: addition of Ti alone to Al resulted in enhancement of its mechanical behaviour by an increase of 5.2% in its flow stress at 20% true strain, whereas addition of Mo either alone or in the presence of Ti resulted in decrease of its flow stress at 20% by 9% and 5.6% respectively. However, after pressing by ECAP: it was found that addition of Ti or Mo either alone or together to Al resulted in increase of its flow stress at 20% strain by the following percentages 5.49, 4.74 and 10.3% respectively.

1. Introduction
Aluminium and its alloys are versatile metals. They widely used in industrial and engineering applications due to their attractive properties. These include: high strength-to-weight ratio, corrosion resistance and high electrical and thermal conductivities. Against these preferable characteristics, Al and its alloys solidify in a grain columnar structure which tends to affect their mechanical strength and surface quality. Therefore, it became customary in aluminium foundry to grain refine aluminium and its alloys by Ti or Ti+B, as well, different master alloys were developed, which are now commercially available. The grain refinement of aluminium and its alloys by the binary Al-Ti and ternary Al-5Ti-1B master alloys is well established and currently in use in the aluminium industry. However, the
mechanisms of grain refinement and the enhancement of grain refining efficiency by the presence of some elements and the deteriorating effect by the presence of others are still a controversial matter, although many attempts have been made and reported in the literature [1-4]. In earlier work [3] the effect of addition of Mo, up to 0.3% to commercially pure aluminum was investigated. In addition, the grain refined Al by 0.15% Ti was also investigated. The tests was carried on its hardness, mechanical strength and machinability and found that improvement up to 16% in hardness and more than 30% in flow stress at 20% strain were achieved by the addition of 0.3% Mo. Furthermore, the addition of Mo resulted in enhancement of the surface quality. Examination of the available literature review revealed that the effect of addition of grain refiner’s on the formability of aluminium and its alloys is very rare. The equal channel angular pressing which is referred to as ECAP is relatively recent processes for producing severe plastic deformation (SPD). This technique can effectively improve strength of various metallic alloys by producing ultrafine grain. ECAP is considered as a source of grain refinement mechanism, and it’s also used to produce ultra-fine grained materials. So far ECAP method was unsuccessful at attempts of obtaining nano-metric materials, i.e. materials with grain size under 0.1 µm [5-7]. Sivaramen and chhkingal have investigated the workability of commercial pure aluminium processed by ECAP and found an improvement in strength, grain refinement, and reduction in workability [5]. The effect of addition of grain refiners and ECAP on the formability of aluminium and its alloys has not previously reported except recently by the authors [8].

2. Materials and experimental work

2.1. Materials
Commercially pure aluminium wires supplied by the Jordanian electrical authority with the chemical composition shown in Table 1 were used in preparing the master and microalloys. Mo and Ti powders of 95.95% and 99.98% purity respectively were used as grain refiners.

Table 1. Chemical composition (wt %) of commercially pure aluminium.

| Element | Fe  | Si   | Cu   | Mg   | Ti   | V    | Zn   | Mn   | Na   | Al   |
|---------|-----|------|------|------|------|------|------|------|------|------|
| wt. %   | 0.09| 0.05 | 0.005| 0.004| 0.008| 0.005| 0.001| 0.005| 0.005| Bal. |

2.2. Equipment
The master and the microalloys were all prepared in graphite crucibles and stirring was carried out by graphite rods. The die which was designed and manufactured for carrying out ECAP tests consists of two parts which accommodate the punch and die in position is made of D2 steel. All tests were carried out on a universal testing machine at the maximum compressive load of 100 KN and cross head speed of 5 mm/min. All specimens and inner surface of the ECAP die were lubricated using a semi-solid lubricant, MoS2, to reduce friction. The autographic was obtained for each test after pressing. A schematic diagram and photograph of the ECAP die is shown in figure 1. The design which consists of two parts was introduced and manufactured by Electric discharge machining (EDM).

Figure 1. Isometric and photograph of the ECAP apparatus used.
2.3. Experimental procedures and Preparation of the different microalloys
The experimental procedures started with preparing the Al-Mo and Al-Ti master alloys followed by determining their chemical composition, then the microalloys were prepared. To prepare the Al-Mo master alloy; fifty grams of commercially pure aluminium were introduced into the graphite crucible under a layer of cryolite flux, charged into an electrical furnace at 1100°C for 15 min, after which 3 grams of pure molybdenum powder are added to the aluminium melt and stirred with graphite rod for one minute and brought back to the furnace for 30 min. finally the crucible is taken out of the furnace, stirred for one minute and left to solidify and cool down in air to room temperature. SEM was used to determine Mo weight % and found to be 6.01%. the same procedure was followed for preparing the Al-Ti master alloy using only 2 grams of pure Ti powder with 50 grams of commercially pure aluminium. The Ti weight% as determined by SEM was found to be 2.02%.

In addition to commercially pure aluminium four microalloys were prepared Al-0.1%M, Al-0.15%M, Al-0.15%Ti-0.1%M. The calculated amount of each master alloy was added to predetermined amount of aluminium at 1100°C in case of Al-Mo and at 800°C in case of Al-Ti master alloys. The mixture was agitated for two minutes in the graphite crucible using graphite rod and finally poured to solidify in hollow brass cylinders. The square cross section of brass die was 10 x50x100 mm. Mo was added to Al grain refined by Ti at a rate of 0.1% by weight, which corresponds to the peritectic limit on the Al-Mo phase diagram. The chemical analyses of different prepared microalloys are shown in Table 2.

| Alloy       | Mo wt.% | Ti wt.% | Al wt.% |
|-------------|---------|---------|---------|
| Al          | 0.00    | 0.00    | Rem.    |
| Al-Mo       | 0.05%   | 0.00    | Rem.    |
| Al-Mo       | 0.10%   | 0.00    | Rem.    |
| Al-Mo       | 0.15%   | 0.00    | Rem.    |
| Al-Ti       | 0.00    | 0.15%   | Rem.    |
| Al-Ti-Mo    | 0.1%    | 0.15%   | Rem.    |

Specimens from the casted microalloys were cut to the required dimensions using a CNC milling machine at 1000 rpm rotational speed (37.7 mm/min), 0.8 mm depth of cut and 600 mm/min using 12 mm diameter cutter with 4 cutting teeth to be pressed in the ECAP die set. Finally, two sets of each microalloy one in the as cast condition and another one after pressing were prepared for metallurgical examination by mounting in Bakelite, ground with different grades of silicon carbide abrasive paper and polished with 1 micron diamond paste and finally etched in a solution of 0.5 % HF acid + 2.5% HNO3+1.5%HCL+95.5% distilled water for a period ranging from 15 to 30 seconds for the metallurgical examination, which was carried out using Vickers optical microscope M17. The grain size was determined using the linear intercept method. The Vickers micro-hardness was determined using a load of 600 grf.

3. Results and discussion
3.1. Effect of Mo addition on the metallurgical aspects of Al grain refined by Ti
The effect of addition of Mo or Ti alone or both together on the grain size of Al is shown in the histogram of figure 2. It can be seen from this histogram that addition of 0.15% Ti to Al resulted in pronounced reduction in its grain size as 34.5% reduction was achieved in the as cast condition. However, after pressing by ECAP die, it produced better refinement as 87% reduction in grain size was achieved when compared to Al in the as cast condition and 43.8% when compared with Al after pressing in the ECAP die (see figure 2). This is also explicitly demonstrated by the photomicrographs of figure 3 (a), (b), (c), and (d) for Al and Al-Mo micro alloys as cast, and figure 3 (a’), (b’), (c’), and (d’) for Al and Al-Mo micro alloys after pressing, respectively. Addition of Mo at 0.1% weight to Al grain refined by Ti resulted in refinement of its structure in the as cast condition where 47.3% reduction was achieved in its grain size, but resulted in poisoning its grain size after pressing in the
ECAP die as 122.2% in grain size was obtained as indicated by figure 2. This means although their effect is positive when added together in the as cast condition, the effect is negative after pressing in the ECAP die. This may be explained due to the existence of the intermetallic phases of Al-Mo which do not respond to the refinement by pressing as the Al-Ti in the as cast condition. This however needs further verification by studying and analyzing these phases.

It is worth noting that although addition of Ti or Mo either alone or together to Al resulted in grain refinement of grain size in the as cast condition; however, addition of both Ti and Mo together (Ti+Mo in the Al-0.15%Ti-0.1%Mo) resulted in poisoning of the grain size after ECAP process. This means that the effect of addition of both of them together is not additive. This agrees with the previous findings for addition of other grain refiners to Al [8].

### 3.2. Effect of Mo addition on the mechanical characteristics and hardness of Al grain refined by Ti

The effect of addition of Ti or Mo either alone or both together to Al on its mechanical behaviour is presented by the true stress, $\sigma$, true strain, $\varepsilon$, in the as cast condition in figure 4. It can be seen from this figure that addition of Ti alone resulted in enhancement of Al mechanical behaviour whereas addition of Mo alone resulted in deterioration of its mechanical behaviour. Similarly the addition of both Ti and Mo together resulted in deterioration of its mechanical behaviour in the as cast condition as illustrated in table 3, but at less amount than when added alone. For example addition of Ti alone resulted by 5.2% enhancement in the flow stress at 20% strain and resulted in decrease of the flow stress at 20% strain by 9% and by 5.6% in case of Mo and Ti+Mo respectively. However, the work hardening index, n, was reduced by 3.2%, 11% and 6% in case of Mo, Ti and Mo+Ti respectively.
Figure 3. Photomicrographs of Al and Mo micro alloys in two conditions (a to d) in the cast condition and (a’ to d’) after pressing by ECAP process conditions, X250
**Table 3.** The mechanical characteristics of Mo addition to Al and Al grain refined by Ti in the cast condition.

| Micro Alloy                      | General equation representing the mechanical behaviour in the plastic region MPa | Flow stress (MPa) at strain=20% | Flow stress (MPa) at strain=50% |
|----------------------------------|---------------------------------------------------------------------------------|---------------------------------|---------------------------------|
| Pure Al before ECAP              | $\sigma = 143 \varepsilon^{0.3092}$                                           | 89.51                           | 115.59                          |
| Al- 0.1%Mo before ECAP           | $\sigma = 130 \varepsilon^{0.2994}$                                           | 81.45                           | 105.76                          |
| Al- 0.15%Ti before ECAP          | $\sigma = 143 \varepsilon^{0.2753}$                                           | 94.18                           | 118.51                          |
| Al- 0.15%Ti-0.1% Mo before ECAP  | $\sigma = 136 \varepsilon^{0.2908}$                                           | 84.50                           | 110.89                          |

After pressing by the ECAP process, the obtained results (see figure 4), shows that the behaviour is opposite to those obtained in the as cast condition. It can be seen from figure 4, that the mechanical behaviour is improved by the addition of Ti or Mo alone or both together to Al, being 5.5%, 4.8%, and 10.3%, respectively. The best improvement was achieved in the addition of both together followed by the addition of Ti alone and finally by addition of Mo alone. This improvement is explicitly demonstrated in table 4, which summarizes the mechanical characteristics of Al and its Mo and Ti addition to Al and Al grain refined by Ti in the cast condition.

![Figure 4](image_url)
microalloys and the Al-Ti-Mo ternary alloy. However, for 0.1% Mo alone, 0.15% Ti alone and in case of addition of both together respectively, the enhancement in flow stress at 20% strain was 4.75%, 5.5% and 10.3%. The enhancement in strength coefficient, K, was 4.25%, 7.8%, and 10.64% and an increase in the work hardening index by 12.55%, 10.2% and 9.4% as compared to Al after pressing by the ECAP process respectively.

**Table 4. Mechanical characteristics of Mo addition to Al and Al grain refined by Ti after pressing by the ECAP process**

| Micro Alloy                          | General equation representing the mechanical behaviour in the plastic region MPa | Flow stress (MPa) at strain=20% | Flow stress (MPa) at strain=50% |
|--------------------------------------|---------------------------------------------------------------------------------|---------------------------------|---------------------------------|
| Pure Al after ECAP                   | $\sigma = 141 \varepsilon^{0.1139}$                                        | 121.84                          | 130.95                          |
| Al- 0.1%Mo after ECAP                | $\sigma = 147 \varepsilon^{0.1282}$                                        | 127.61                          | 134.50                          |
| Al- 0.15%Ti after ECAP               | $\sigma = 152 \varepsilon^{0.1255}$                                        | 128.53                          | 139.80                          |
| Al- 0.15%Ti-0.1% Mo after ECAP       | $\sigma = 156 \varepsilon^{0.1246}$                                        | 134.38                          | 143.65                          |

**3.3. Effect of Mo addition on the hardness of Al grain refined by Ti**

The histogram of figure 5 shows that addition of Ti or Mo either alone or together to Al resulted in increase of its hardness in the as cast condition. The maximum increase is in the case of addition of Ti alone, being 22.2% followed by the addition of Ti and Mo together, 14.8% and only 3.7% in case of Mo addition. However after pressing in ECAP process, addition of Ti alone to Al resulted in very small increase in its hardness, only 2.27%, whereas resulted in decrease of its hardness in case of either addition of Mo alone or by the addition of Mo and Ti together being 9.1% and 13.6% respectively. This may be explained by the different response of the existing inter compounds of Ti and Mo in the Al matrix.
4. Conclusion

- Addition of Mo or Ti alone or together at any rate to Al within the experimental limitations, resulted in grain refinement. However, after ECAP it resulted in further refining in when Ti or Mo added alone, and poisoning effect, i.e. grain coarsening when added together.
- The addition of Mo to Al within the experimental limitations resulted in deterioration of its mechanical behaviour and reduction in its work hardening index, n, in the as cast condition. However Ti addition resulted in increase of the mechanical behaviour and also reduction in its work hardening index, n, in the as cast condition.
- Pressing Al and Al-Mo, Al-Ti, and Al-Mo-Ti micro alloys by the ECAP process resulted in enhancement of their mechanical behaviours.
- Addition of Ti or Mo either alone or together to Al resulted in increase of its hardness in the as cast condition, where after pressing in ECAP process, addition of Ti alone to Al resulted in very small increase in its hardness, whereas resulted in decrease of its hardness in case of either addition of Mo alone or by the addition of Mo and Ti together.

5. References

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**Figure 5.** Effect of addition of Ti and Mo to Al and Al grain refined by Ti on hardness.