Different Methods for Grain Refinement of Materials

Safwan M. A. Al-Qawabah, Adnan I. O. Zaid

Abstract— Some metals and alloys solidify under normal casting conditions in columnar or dendritic structure with large grain size, unless the mode of solidification is carefully controlled, which tends to reduce their mechanical behavior, toughness and surface quality. Therefore, it is of vital importance to grain refine their structure to overcome these discrepancies. Different methods have been investigated by several authors and the results of their work are published in the open literature. It is therefore anticipated that reviewing of the different methods used for grain refinement is worthwhile doing. In this paper, critical review of these methods, (old and recent) including their advantages and limitations is carried out. Furthermore, a new method is described and the obtained results given and discussed.

Index Terms— Different methods, Grain refinement, Rare earth elements, Severe plastic deformation, Equal channel angular pressing

◆

1 INTRODUCTION

Researchers are always working for continued improvement of the strength, reduction in weight, i.e. high – strength-to weight ratio and surface quality of the manufactured products, as produced by the various forming and machining methods.

In this respect, three different methods which are used for the improvement of mechanical characteristics of materials in general and zinc aluminum alloys in particular by reducing the grain size will be reviewed and discussed namely:
(i). By addition of some rare earth elements e.g. Ti, Ti-B; (ii). By subjecting the material to severe plastic deformation, SPD, processes; and (iii). By combining both (i) and (ii) simultaneously.

1.1 Grain Refinement by Rare Earth Elements

Grain refinement of materials is the process of reducing the grain size several times resulting in very fine grain size which enhances the mechanical properties as it is well known that if a material is grain refined its mechanical behavior and its surface quality will be enhanced. The process dates back to1950 when Cibola reported that addition of Ti in small weight percentage to the Al melt prior to solidification will greatly reduce its grain size and change its microstructure from columnar structure with large grain size into equiaxed structure with fine grains, [1, 2]. Since then it became customary in aluminum foundry to grain refine Al and its alloys by either Ti or Ti-B and the binary Al-Ti and ternary Al-Ti-B alloys were manufactured and are now commercially available for this purpose.

Since then researchers started to investigate the addition of other rare earth elements, mainly, on aluminum and its alloys. It was found that if Ti is added to Al in the presence of boron it will improve the refinement efficiency although boron itself is not a refiner if added alone. Furthermore they found that some of them caused refinement e.g. titanium, vanadium, V, molybdenum, Mo, etc. Whereas others caused grain coarsening to the structure, referred to them as poisoners, e.g. zirconium, Zr, tantalum, Ta. Although these two elements are poisoners if each is added alone but they make a good refiner if they are added together. This means that the effect of grain refiners is not additive. The literature on Al and its alloys is voluminous and will not be dealt with because it is beyond the scope of this paper. A comprehensive review of the grain refinement of aluminum and its alloys is reported by the second author, [3]. Also it was found that addition of some rare earth elements to ZA alloys affects greatly the grain size of these alloys; this was investigated by various researchers. The effect of addition of Ti + B to ZA25 alloy on its microstructure was investigated in the range of 0.01 % Ti + 0.002 % B to 0.07 % Ti + 0.014 % B. The microstructure indicated fine petal-like grains of α instead of a coarse dendritic structure. Also he found that α refined grains increased with increasing the addition up to 0.03 % Ti + 0.006 % B, beyond which it did not produce any further increase in refinement. Increasing the addition beyond this level, however led to existence of massive TiAl3 crystals in the modified alloy, [4]. The effect of addition of 0.2 wt. % Al-5Ti-1B as grain refiner to ZA22 was investigated, [5]. Two alloys; the first one was Zn-22 wt. % Al with 1 wt. % Mn and 0.15 wt. % Mg while the second alloy had the same composition but with addition of the grain refiner. The specimens were prepared in form of 40 mm x 30 mm x 200 mm rectangular ingots. The ingots were melted to 50° C above its melting point before pouring into the mold to solidify. Tensile specimens were prepared from the solid solution heat-treated, annealed, and re-crystallized ingots with length of 6.2 mm. The specimens were tested on a universal testing machine, Instrun type, and these tests were conducted at 260° C and initial strain rate of 1.3 X 10-5 S-1, [6].

Addition of some alloying elements to ZA alloys affects greatly the grain size of these alloys; this was investigated by various researchers. Said et al (2003 studied the influence of silver addition on the mechanical properties of the Zn-Al eutectoid superplastic alloy in tension at a strain rate ranging

---

- *Safwan M. A. Al-Qawabah is currently an associate professor in 1Mechanical Engineering Department, Tafila Technical University, Jordan, Amman, E-mail: safwan1q@gmail.com*
- *Adnan I. O. Zaid is currently a professor in Mechanical and Industrial Engineering Department in Applied Science Private University, Amman 11931 Jordan, E-mail: adnan_kilani@yahoo.com*

from 2 ×10-4 to 9 ×10-1 s-1 at 230º C at a silver content of 1.0 and 6.15 wt. % Ag. In their study and after plotting the elongation to failure versus strain rate they found that these two alloys exhibit superplastic properties over a range of strain rates. Also the existence of silver raised the strain rate for the superplastic deformation from 5×10-3S-1 for the Zn-Al eutectoid alloy to 1×10-1 S-1 in the alloys of their study. Furthermore, the maximum deformation attained was about 1050 % at the temperature of deformation. Addition of some other alloying elements e.g. Zr to zinc aluminum alloys has adverse effect on grain refining efficiency resulting in coarsening the grain size, [7,8]. investigated the effect of addition of either Ti or Zr or both to zinc aluminum 5, ZAMAK5 alloy on its hardness. They found that addition of Ti or Zr alone to the alloy resulted in improvement of its Vicker's hardness. The enhancement was more pronounced in the case of Zr addition where an increase of 11 % was achieved which was attributed to the hard particles of the intermetallic compounds in case of Zr addition compared to the softer particles in case of titanium addition . Furthermore, they found that addition of both Ti and Zr together to the ZAMAK5 alloy resulted in decrease of its hardness which indicates the poisoning effect of Zr addition in existence of Ti which emphasizes that the effect of their existence together is not additive as mentioned before. ZA22, is one of the most common alloys in ZA series, where at this composition a eutectoid transformation occurs and it exhibits superplastic behavior at the eutectoid temperature of 275°C which makes it suitable to manufacture deep-drawn products. Review of grain refinement of ZA alloys is reported in [9]. Comprehensive review of the grain refinement of zinc aluminum alloys is given in [10].

Recently, in the last decade researchers got interested in the grain refinement, of titanium aluminum alloys, Ti-Al, due to their favorable advantages such as low density and high specific strength, make them the most attractive candidate materials for aircraft and aerospace applications, [11-13]. Furthermore, due to the high material cost and limited formability, Ti-Al based alloys tend to favor near-net-shape processes such as casting. Against their advantages they have the disadvantage of requiring high amount of boron in order to obtain a homogeneous and refined as-cast microstructure beside that the exact grain refinement mechanism is not clear due to the complex solidification sequence, [14]. Although several grain refinement mechanisms were proposed there is still a paradox about the mechanism of their grain refinement of aluminum and the refinement of zinc aluminum alloys as will be discussed later in the paper under the theoretical considerations section.

1.2 Grain Refinement by Severe Plastic Deformation, SPD

Researchers are always working for continued improvement in the strength- to- weight ratio and the surface quality in addition to reduction of the production cost of the manufactured parts produced by the various forming and machining methods. Severe Plastic Deformation (SPD) is a new discipline of metal forming technology used to produce an ultrafine grained (UFG) structure in metals from different coarse grained metals (e.g. aluminum, iron, copper, magnesium, etc.) in order to improve their mechanical and physical properties, [15]. Ultra-fine grained materials are currently of great scientific interest due to important mechanical and physical properties, increased fatigue life and high damage tolerances which can be obtained by these methods. The severe plastic deformation (SPD) methods such as rolling, extrusion, or forging, among others, allow obtaining very high strains in materials but this is usually associated with noticeable change in material dimensions. Investigations of the mechanics of severe plastic deformation help engineers to come up with better designs for processes as well as better prediction of the results of processes. Equal channel angular extrusion, ECCAE, is one of the SPD processes in which the billet is subjected to severe shear without change in its cross sectional area or its geometry; beside the advantage of repeating the process on the same billet many passes to obtain ultrafine structure in the billet material. In 2007, Tham et al, as cited in [16], procreated the relationship of grain refinement with extrusion pass, and the properties enhancements after ECAE processing including ultimate tensile strength and Vickers micro hardness were investigated to determine the effects of the number of ECAP passes on the mechanical properties of the extruded samples. ECAE processing of Al-6061 alloy for up to 16 passes has been successfully conducted and it was successful in reducing the grain size of the samples from 80 µm to 0.8 µm. and was no significant grain refinement after 8 ECAE passes. Uniaxial tensile testing reveals that the highest UTS of 340MPa was obtained after 8 ECAE passes. The highest hardness increase was also observed after 8 passes, from 40HV to 98 HV, about145% increase. A special SPD technique, termed equal channel angular pressing, referred to later as ECAP which was first developed by Segal et al. in 1972, cited in [17, 18], the former Soviet Union will only be dealt with in this section. It can be concluded that the equal-channel angular pressing (ECAP) is a useful tool for achieving an exceptional grain refinement in bulk metallic alloys, and the grain sizes produced through ECAP are in the sub micrometer range. As a consequence of these ultrafine grains, the as-pressed alloys may exhibit superplastic ductility at faster strain rates than in conventional superplastic alloys. Their results for a commercial Al-2024 alloy and Mg-0.6%Zr showed that superplastic ductility was achieved through the use of ECAP which was not attained in the cast alloy, [15]. The tensile strength, elongation, static toughness and fracture modes of casting Al–0.63 wt.% Cu and Al–3.9 wt.% Cu alloys subjected to equal channel angular pressing (ECAP) were investigated and the results are reported in Ref. [15]. It was found that the grains of the two alloys can be refined to submicron level after four passes of ECAP. The tensile fracture strength increased with increasing ECAP pass for both of the Al–Cu alloys. The static toughness of the Al–Cu alloys was enhanced at high ECAP pass. Furthermore, it was found that an ECAP process produced an ultrafine grain size in Zn-22% Al alloy. Tensile tests were carried on specimens from the produced alloy at a strain rate of 1.0 * 〖10〗 ^(-2) s^(-1)at 473 K and found that they yielded a very high elongation of 2,230% representing high strain rate super-plasticity. Furthermore tests were carted out to evaluate the role of internal cavitation and quantitative cavity measurements were also taken to investigate the significance of the internal cavities formed during super-plastic deformation. The results demonstrated that cavity nucleation occurred continuously throughout super-plastic flow, and there was a transition in the cavity growth mechanism from super-plastic diffusion growth at the smaller cavity sizes to plasticity-controlled growth at the larger sizes, [16]. The hardness and microstructure of the grain refinement of a copper alloy which has undergone ECAP process was investigated and the results showed that the grains became gradually more refined and the hardness increased as they underwent further processing. The super-elasticity of a Ti-35 wt% Nb alloy by fabricating an ultrafine-grain-structured specimen through equal channel angular extrusion, ECAE processing was explored and found that a complete super-elasticity of 3.5% was realized by refining the grain size down to about 0.25 mm and by inducing the precipitation of an ω-phase, [20]. The super-elasticity was possible because the β-phase was largely stabilized at room temperature as a result of the severe grain refinement and Nb enrichment in the matrix on account of the ω-precipitation.

It is now well established that the microstructure of a metal can be considerably changed by severe plastic deformation techniques such as high pressure torsion, extrusion and equal-channel angular pressing (ECAP) and exhibit super plastic behavior. However, it was reported that among these methods, ECAP is particularly attractive because it has a potential for introducing significant grain refinement and homogeneous microstructure into bulk materials. Typically, it reduces the grain size to the sub micrometer level or even nanometer range and thus produces materials that are capable of exhibiting unusual mechanical properties. The deformation intensity increased with increasing pass number. The grain size of the specimens effectively also decreased with increasing pass number. The grain size of a specimen was decreased from 10 μm to 300 nm after 14 passes; while at the beginning there was a banding tendency in the grains toward deformation direction, homogeneous and equiaxed grains were formed with increasing the pass number. This grain refinement was as a result of an interaction between shear strain and thermal recovery during ECAP processing. Hardness measurements showed that the hardness values increased up to 4 passes, decreased effectively at 6th pass, again increased at 8th pass and after this pass, the hardness again decreased due to dynamic recrystallization, [21]. Other tests were performed on annealed 1050 Al samples with coarse-grained microstructure of 600 mm by equal-channel angular pressing (ECAP) and the samples were processed up to four passes through a die with an internal angle of 〖90〗 ^o. The microstructure study was conducted on both the extrusion direction and the shear plane. The produced microstructure depends on the used route and number of passes. A study of mechanical behavior was conducted by using tensile and compression specimens from the specimens produced by ECAP in the extrusion direction. Enhanced strength was observed but with anisotropic behavior between tension and compression. The softening effect due to the recrystallization, which took place during the hot ECAE process, [22].

(iii). By Combing Both Methods; Addition of Rare Earth Element and SPD together

To the best of the author knowledge, the available literature reveals that work combining grain refinement method and the severe plastic deformation method, SPD, together is very rare and only very few papers have been published by the authors. Recently, the authors have investigated the effect of addition of Mo to zinc aluminum 22% alloy, ZA22 as a grain refiner and subjecting it to severe plastic deformation by the equal channel angular pressing, ECAP, is investigated and due to the large size of this paper, the obtained results will be published in a second paper.

2 THEORETICAL CONSIDERATIONS

In this section the theoretical aspects related to the grain refinement mechanism and the SPD, ECAE and ECAP processes will be dealt with

2.1 Grain Refinement of Materials

Grain refinement is a common industrial practice to develop fine equiaxed grains in the as cast structure either by increasing the number of nucleation sites or by grain multiplication, [23]. It is well recognized that grain refinement plays an important role in the determination of the properties of castings. This includes improvement of strength, finer and more homogeneous distribution of porosity and less probability of chemical segregation inside the casting. The pioneering work on grain refining started in the early 1950"s, when it was found that the presence of Ti in the Al melt prior to solidification resulted in grain refinement of its structure, [1]. Since then it became customary in the Al foundries to use Ti as grain refiner. Later, when addition of KBF4 and K2TiF6 salts to grain refine Al led to the first industrially used grain refiners based on the formation of TiB2 particles in situ in the melt by the addition of these salts, [24]. Unfortunately, this method suffered from rapid fade of the refining effect due to particle settling. The master alloy approach gave benefits in terms of providing (readymade) TiB2 particles of a more controlled and optimized size. A major breakthrough in the development of the use of refiners came with the availability of the alloy in rod form, first used in the mid 1960‟s. This allowed grain refiner additions to be made outside the furnaces, thus further reducing the fading effect of furnace additions and also the effects of (poisoning) in certain alloy systems; this allowed much lower addition levels to be made and a more consistent grain refining performance to be achieved. Adding rod outside the furnace put a greater emphasis on the need to develop refiners with clean microstructures; the major features to be addressed were to reduce boride agglomerations, oxide films and residual fluoride salts. Although the grain refinement of material alloys by binary and ternary master alloys is well established and currently in use in the many material foundry, the mechanisms for grain refinement and the enhancement of grain refining efficiency by these master alloys in the presence of some other 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. In this section, summary of these mechanisms is given and discussed.

2.1.1 The peritectic reaction theory

Researchers of this theory attribute the grain refinement to the nucleation of aluminum by the compound TiAl3 particles in the Al-Ti system, according to the following: peritectic temperature, [25]:

$$\textbf{Liquid + TiAl = TiAl3} \qquad \textbf{(1)}$$

The TiAl3 compound has a tetragonal structure. The liquidus curve falls steeply from the peritectic temperature almost to the pure aluminum where there is reputed to be peritectic.

$$\textbf{TiAl3 + liquid = Al at 650 °C} \qquad \textbf{(2)}$$

The limit of the peritectic horizontal is placed at 0.14 % wt Ti. The titanium aluminide TiAl3 crystals are presented in all commercial Al-Ti master alloys used to grain refine Al and it alloys. It was suggested by many authors that TiAl3 is an active substrate for the nucleation of α–Al. it was reported that the nucleation efficiency of these Al-Ti alloys is affected by the presence of other elements in the Al melt.

Jones and Pearson theory It is suggested that TiAl3 particles act as nuclei for the solidifying Al, and the role of the TiB2 particles is to stabilize a form of TiAl3 and extend the time it takes to dissolve. I is therefore expected that more than one mechanism is responsible for the grain refinement depending on the nucleant (master alloy) used, the chemical composition of the alloy cast and the processing conditions prevailing e.g. contact time, pouring temperature. They also suggested that grain refining is a result of two processes: firstly, the nucleation of the α-Al crystals and secondly, the subsequent growth of new crystals up to a limited size. Both of these processes need a driving force. Thus, other criteria than the presence of nucleants must also be fulfilled, and hence, the potency of a nucleus may be of secondary importance. A driving force of growth which may be a local under cooling in the surrounding of the particle is necessary to develop a fine grain microstructure. If this force is too small the nucleated crystal may remelt again. As mentioned before Zr, Ta and Cr have a poisoning effect, i.e. the grains become larger when the grain refiner is added or reducing the grain refining efficiency of Al-Ti and Al-Ti-B master alloys. This effect was attributed to the following chemical reaction: [26, 27].

$$\textbf{Zr (in the melt) + TiB2 = ZrB2 + Ti (in Al melt)} \qquad \textbf{(3)}$$

Based on chemical reaction the authors of reference [28] concluded that the above reaction is only possible when the mole fraction of Zr-content in the melt exceeds about four times that of excess Ti remaining in solution in the melt. Therefore, this condition does not apply except at a Zr-content of 0.2 wt. % or more. Experimental observation shows that the poisoning effect of Zr occurs at 0.05 wt. % and rises steeply with increasing Zr- content from 0.0 to 0.3 %. Detail discussion of these mechanisms is given in Ref. [28]. This mechanism was supported by the experimental results of Ref.[29].

2.2 The theoretical aspects of the grain refinement of titanium aluminum alloys

The theoretical aspects of the grain refinement of titanium aluminum alloys do not differ much from aluminum alloys and the zinc aluminum alloys because the proposed mechanisms of grain refinement of Ti-Al alloys with boron and boron borides were based on the mechanisms suggested for the grain refinement of Al alloys with boron addition. These are, as reported in Ref. [30].

(1) Un-dissolved boride particles acting as inoculants,[12, 31].

(2) Weakening effect of a boron solute on secondary dendrite arms roots resulting in breaking off of a solid into the liquid,[11, 32, 33].

(3) L → β + TiB2,

It was reported that homogeneous nucleation caused by boron enrichment induced compositional cooling [34]. A consensus has been reached that nucleation of the hexagonal close-packed, (hcp). α phase on borides appears to be the main mechanism of grain refinement in the case of low-boron content, [35, 38], borides are demonstrated to be mono-borides such as Ti-B with B27[35, 36], or B structure, [39, 40]. or (Ti-N),B, [41,42].

However, in conventional cast Ti-Al alloys undergoing peritectic reaction, borides tend to
form as diborides with a C32 structure,[43]. When the peritectic reaction interferes too much in the formation of α phase, the refinement becomes complex. It was indicated that with the influence of peritectic reaction, the refinement by low boron failed, [42]. Although the theories above seem to be reasonable for some refinement phenomena, little clear evidence is given to support the refinement mechanism especially in Ti-Al alloys with peritectic reaction, and there are still areas of uncertainty.

With the combinations of ductility, toughness and creep resistance, Ti–48Al–2Cr–2Nb emerged as the first to enter commercial jet engine service, [44]. However, the coarse cast microstructure resulting from the peritectic reaction (L + β → α) appears to be the obstacle for its further application. Grain refinement tends to be necessary for this alloy. On the other hand, grain refinement in cast Ti-Al alloys conducts mainly by adding boron, rather than borides. The compound of Ti and B, TiB2 contains an adequate boron element without any impurities, and is more economic than boron, [45]. Therefore, TiB2 has the potential to act as a participator of grain refinement. However, the grain refinement induced by TiB2 additives has never been studied systematically, [43, 46, 47], and the mechanism is unclear. The objective of their present work was to investigate the effect of trace TiB2 addition on the solidification micro-structure of cast Ti–48Al–2Cr–2Nb alloy was investigated in detail. The internal structure of borides and their refinement mechanism were discussed in detail. Furthermore, comparison between the effect of addition of boron and titanium boride was investigated, [30]. The results indicated that for equivalent B additions in both, the grain refinement effect was equal, except for the cavity defect.

2.3 Equal Channel Angular Pressing

Grain refinement can be achieved through ECAP for all metallic and intermetallic materials. The SPD on metals induces the refinement of grain size which affects the metal microstructures in a way that the material properties become more unique than those at the bulk scale, [19]. The final grain size of materials depends on the material and the processing parameters. It has been observed that ultra-fine grained materials produced by ECAP exhibit good hardness and high strength. It has also been observed that as grain size is reduced through the Nano scale regime, hardness typically increases.

2.4 The shearing characteristics associated with ECAP

There are several different processing routs for ECAP process. They differ in the way the sample is rotated between each press. The most common are route A, where there is no rotation; route BA, where the sample is rotated by 90° in alternate directions between passes; route BC, where the sample is rotated by 90° in the same sense between each pass; and route C, where the sample is rotated by 180° between passes, [48]. The analysis is conducted for standard conditions where Φ =90° and ψ=0°. It has been shown that in this condition a potential difficulty arises, as revealed by finite element modeling, in filling the outer corner at the intersection of the two channels when friction is present in, [49]. This analysis therefore, applies to an ideal frictionless condition, or more appropriate, to the central regions of the pressed sample where friction effects are small, [22]. The different slip systems associated with these various processing routes are depicted schematically in figure (2) where X, Y and Z planes correspond to the three orthogonal planes and slip is shown for different passes in each processing route – thus, the planes labeled 1 through 4 correspond to the first 4 passes of ECAP, [50]:

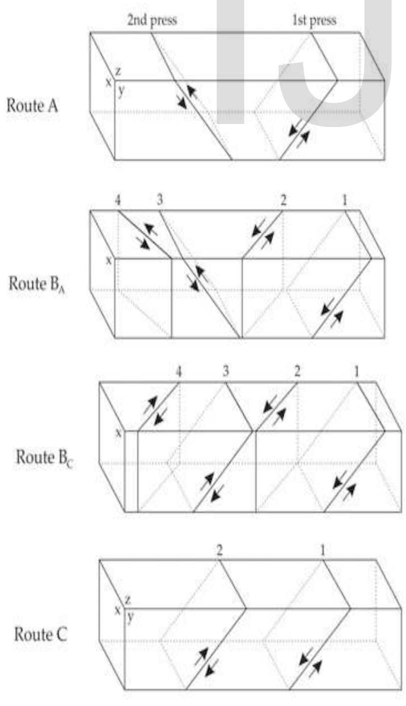

Fig. 1. The slip systems viewed on the X, Y and Z planes for consecutive passes using processing routes A, BA, BC and C

The theoretical analysis performed by V. M. Segal states that taking into consideration large enough billets and idealized frictionless conditions, materials experiment simple shear, producing a stationary plastic flow in the shear plane. The shear deformation is given by equation (4):

$$\gamma = \tan(\psi) = 2\cot(\Phi/2) \ldots\ldots\ldots\ldots\ldots (4)$$

Where ψ is the inclination angle of an element of distorted material in relation to the un deformed element and Φ is the angle between the extrusion channels, [51].

2.5 Estimation of the Strain and Required Pressure in ECAP Process

In ECAP pressing the cross-section of the intersecting channel does not change. Similarly, the cross sectional area of the billet does not change and remains constant during and after pressing. Plastic deformation occurs only at the channel bend, the mode of deformation is close to simple shear by a unit square changing its shape into a parallelepiped. In this way, the complete billet undergoes deformation of uniform strain, except the small end regions. The ECAP parameters, namely: amount of deformation shear strain (ε), number of passes (N), rotation angle between each repetitive pressing, the strain rate monitored by movement of punch, and the temperature in process greatly influence the final microstructure and thus the properties of the final product in ECAP, [52]. A schematic of the process is shown in figure (1), where Φ and ψ are the channel intersection angle and the curvature angle respectively. The magnitude of these angles along with the number of passes determines the shear strain induced into the sample. The strain increment (ε) that the material undergoes after each pass can be expressed in terms of punch pressure (P) and the flow stress of the material (σfs) and depends on the intersection angle (Φ) between two channels as shown in equation (5).

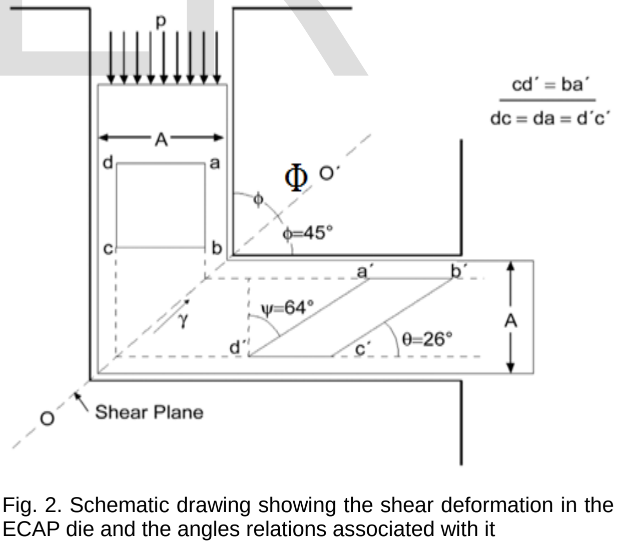

Fig. 2. Schematic drawing showing the shear deformation in the ECAP die and the angles relations associated with it

$$\varepsilon = P\,\sigma fs = 2\sqrt{3}\cot(\Phi/2) \ldots\ldots\ldots\ldots\ldots\ldots (5)$$

The process is to press a well-lubricated sample through two crossing channels and simple shear is applied to the sample at the intersection of the channels. Therefore, a very high shear strain can be accumulated in the material. Several analytical studies report the magnitude of shear strain imposing to the sample is determined by the channel angle (Φ) and the angle associated with the arc of curvature ψ. This relationship is presented in equation (6):[52].

$$\gamma = 2 \cot (\Phi+\psi 2) + \phi \operatorname{cosec} (\Phi+\psi 2) \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(6)}$$

The shear strain value greatly depends on the number of passes (N) and the curvature angle at the channel intersection and can be generalized as follows:

The equivalent strain (εeq) after number of passes (N) can be expressed in a general form by equation (7):

$$\varepsilon eq = N\sqrt{}3[2 \cot (\Phi+\psi 2)+ \phi \operatorname{cosec} (\Phi+\psi 2)] \ldots\ldots\ldots\ldots\ldots\ldots \text{(7)}$$

Equation (7) represents the average equivalent strain developed in the sample within frictionless condition but friction between the surface of the sample and the die wall is unavoidable in the practical ECAP process. These strains imposed to the sample with a hydraulic press. The pressing pressure requirement of sample (P) using upper-bound analysis is represented in equation (8):

$$P = \tau^{\circ} (1+m) [2 \cot (\Phi+\psi 2)+ \phi] + 4m \tau^{\circ} (li+l^{\circ}a) \ldots \quad \text{(8)}$$

where τ° , m, li, l° and a are the shear strength, the friction coefficient, instant length of the sample in the entry channel, instant length of the sample in the exit channel and the width of the extrusion channel, respectively. The strain rate in ECAP depends on the diameter (for round cross-section) or width (for square cross-section) of the billet and the plunger speed during the plastic deformation is a dynamic process governed by dislocation mobility, the strain rate in ECAP also affects the properties of final product and can be expressed by the following relationship of Strain rate, [53]:

$$\varepsilon. = N\sqrt{}3[2 \cot (\Phi+\psi 2)+\Phi \operatorname{cosec} (\Phi+\psi 2)]V\sqrt{}2\Phi L \ldots\ldots\ldots\ldots \text{(9)}$$

Where (V) is the ram speed and (L) is the width or diameter of the billet. The optimum property evolution by ECAP technique can be envisaged by minimum contact friction, sharp corner channels, and square long or flat billet. The degree of grain refinement in ECAP method depends on various factors like processing parameters, phase composition, and initial microstructure of a material, [52]

2.6 HIGH STRAIN RATE SUPER-PLASTICITY, HSRSP

Ultra-fine grained materials exhibit superplastic behavior. Super plasticity is the capability of some polycrystalline materials to exhibit very large tensile deformations without necking or fracture. As grain size decreases, the temperature at which super plasticity occurs decreases, and the strain rate for the occurrence of super plasticity increases. This superplastic behavior is often observed in ultra-fine grained and Nano crystalline metals and alloys when the temperatures are low and the strain rates are high. It is defined as the ability to achieve high superplastic tensile elongations at strain rates faster than a$10-2s-1$. It is now well established that the high tensile ductility associated with superplastic flow occur at intermediate strain rates of the order of ~$10-4$ – $10-3s-1$, in materials having small grain sizes lying typically in the range of ~2 – 10 µm. In practice the strain rate in superplastic forming is inversely proportional to the square of the grain size; a decrease in grain size displaces the superplastic regime to faster strain rates. It was reported that the strain rate in superplastic forming is inversely proportional to the square of the grain size, a decrease in grain size displaces the superplastic regime to faster strain rates, [49].

The microstructure of the material is refined by the action of simple shear imposed at the channels intersection. The strength of polycrystalline materials is related to the grain size d′, through the Hall-Petch equation which states that the yield stress, σy, is given by equation (10), [53].

$$\sigma y = \sigma^{\circ} + \mathrm{k}yd -½ \ldots\ldots\ldots\ldots \text{(10)}$$

Where, σ° is friction stress and ky is constant of yielding. It follows from this equation that the strength increases with a reduction in the grain size and this has led to an ever-increasing interest in fabricating materials with extremely small grain sizes. The strain hardening exponent n is also assumed to be determined by grain size d as,

$$\mathrm{n} = n^{\circ} + knd-12 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(11)}$$

Where n°, k, and n are constant values. The theoretical hardness value (HV) was calculated from Hall-Petch relationship using the equation following equation:

$$\mathrm{HV} = HV^{\circ} + 1.5(\mathrm{b}/\mathrm{d})\ 12 \ldots\ldots\ldots\ldots\ldots\ldots \text{(12)}$$

Where µ is the shear modulus, b is the Bergers vector and d the grain diameter, [54].

Ultra-fine grained materials normally exhibit super-plastic behavior which allows some polycrystalline materials to exhibit very large tensile strain without necking or fracture. As grain size decreases, the temperature at which super-plasticity occurs decreases, and the strain rate for the occurrence of super-plasticity increases, [16]. This superplastic behavior is often observed in ultra-fine grained and Nano crystalline metals and alloys when the temperatures are low and the strain rates are high. Also it should be possible to utilize the grain refinement introduced by ECAP to produce materials having excellent superplastic properties. Also because of the exceptionally small grain sizes produced by ECAP at very rapid strain rate will enlarge the number of materials having superplastic behavior.

3 CONCLUSIONS

In this paper, the available literature on the on the grain refinement and the different methods in obtaining it are reviewed and discussed. Although the grain refinement was discovered in the early fifties and despite the large amount of research work which has had been carried out and the voluminous research papers which has been published in the open literature; The subject is far from being complete from the theoretical and the experimental aspects as there is not a single suggested mechanism which explains the grain refining and the poisoning effects although several attempts were made but paradox exists among them. A single theoretical model is still required.

ACKNOWLEDGMENT

The second 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] Cibula. A, (1949-1950), Journal Institute of Metals, V.76, pp.321-360.

[2] Cibula. A, (1950-1951), Journal Institute of Metals, V.80, pp.1-15.

[3] Zaid, A.I.O., (2001), Grain refinement of Aluminum and its Alloys, . Proceedings of the 7*th* International Symposium on Advanced Materials, ISAM, 2001, Islamabad, Pakistan.

[4] Abdel Hamid, A.A. (1992), Structure Modification of the α-Phase in Zn-Al Cast Alloys by Microalloying. Metalkd, V.83, pp.314-318.

[5] Elbaradie, Z.M., (1998), Grain Refining of Zn22%wt Al Superplastic Alloy. Journal of Materials Processing Technology, V.84, pp. 73-78.

[6] Said R. Gasolco, J. Negrete-Sanchez, G. and Torres-Villosen-or, (2003),Influence of Silver on the Mechanical Properties of Zn-Al Eutectoid Super plastic alloy, Materials Characterization, V. 51, pp.63-67.

[7] Zaid, A. I. O. and Hussein, M.I.J., (2005), Effect of Zirconium Addition on the Mechanical Behavior and Wear Resistance of Zamak5 Alloy. Proceedings of the 9*th* International Symposium on Advanced Materials, ISAM, 2005, Islamabad, Pakistan.

[8] Zaid, A.I.O. and AL-Dous, Z. M.A., (2006), ―Effect of Zirconium Addition on the Ductility and Toughness by Titanium, Proceeding of the Second International Conference on the Frontiers of Advanced Engineering Materials, 2006, Lahore, Pakistan.

[9] Zaid, A. I. O. and Hussein, M.I.J., (2006), Effect of Zirconium Addition on the Mechanical Behavior and Wear Resistance of Zamak5 Alloy Grain Refined By Titanium. Proceedings of the 12*th* International Conference on Machine Design and Production, 2006, Kusadasi-Turkey.

[10] Zaid, A. I. O, (2006), Grain Refinement of Zn- Al Alloys", Proceedings of the Second International Conference on the Frontier of Advanced Engineering Materials, FAEM- 2006, Lahore, Pakistan.

[11] Kim, Y.W, (1992), Microstructural evolution and mechanical properties of a forged gamma titanium aluminide alloy, Acta Metall. Mater. V.40, PP.1121–1134.

[12] Clemens, H. Kestler, H, (2000), Processing and applications of intermetallic γ-TiAl-based alloys, Adv. Eng. Mater.,V.2 pp.551–570.

[13] Aguilar, J. Schievenbusch, A, Kattlitz, O, (2011), Investment casting technology for production of Ti-Al low pressure turbine blades process engineering and parameter analysis, Intermetallics V.19, PP.757–761.

[14] Christodoulou J.A. Flower H.M, (2000), The role of borides in near-γ titanium aluminides, Adv. Eng. Mater. V.2, PP.631–638.

[15] Fang, D.R. Zhang, Z.F. Wu, S.D. Huang, C.X. Zhang, H. Zhao, N.Q. and Li, J.J. (2006), Effect of equal channel angular pressing on tensile properties and fracture modes of casting Al–Cu alloys, Materials Science and Engineering, v. 426, pp305–313.

[16] Kawasaki, M. and Langdon, T. (2008), the development of internal cavitation in a superplastic zinc–aluminum alloy processed by ECAP, Journal Material of Science V.43, pp7360–7365.

[17] Molnár, P. Jäger, A. and Lejček, P. (2012), Effect of Temperature on Grain Refinement of Mg_3Al_1Zn Alloy Processed by Equal Channel Angular Pressing, Acta Physica Polonica, Vol. 122 Issue 3, pp461-464.

[18] Cheng, X. Zenji, H. Minoru, F. and Terence, G. L. (2004), Using Equal-Channel Angular Pressing for the Production of Superplastic Aluminum and Magnesium Alloys, Journal of Materials Engineering and Performance, Vol. 13, Issue 6, pp.683.

[19] Sanusi, K. O. Makinde, O. D. and Oliver, G. J. (2012), Equal channel angular pressing technique for the formation of ultra-fine grained structures. S Afr J Sci. Art, 7 pages.v108 (9/10).

[20] Arockiakumar, R. and Park, J. K. (2011), Superelastic behavior of ultrafine-grain-structured Ti-35 wt% Nb alloy fabricated by equal-channel angular extrusion, Philosophical Magazine Letters, v. 91, No. 9, pp591–598.

[21] Tekeli, S. and Gueral, A. (2011), Equal Channel Angular Pressing (ECAP) and Its Application to Grain Refinement of Al-Zn-Mg-Cu Alloy, the 4th AIP Conference Proceedings, Nanoscience and Nanotechnology Symposium (NNS2011). Journal Volume: 1415; Journal Issue: 1, Bali-Indonesia, 23-25 Sep 2011, pp214-217.

[22] Soliman, M.S. El-Danaf, E.A. and Almajid, A.A. (2012), Effect of Equal-Channel Angular Pressing Process on Properties of 1050 Al Alloy, Materials and Manufacturing Processes, 27: 746–75.

[23] 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.

[24] 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.

[25] 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.

[26] Jones, G.P. and Pearson, J. (1976), Factors Affecting Grain Refinement of Aluminum Using Titanium and Boron Additives Metallurgical Transactions, pp.223-234.

[27] 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.

[28] 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.

[29] 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.

[30] Jianchao Han, Shulong Xiao, Jing Tian, Yuyong Chen , Lijuan Xu, Xiaopeng Wang, Yi Jia, Zhaoxin Du, Shouzhen Cao, Grain refinement by trace TiB2 addition in conventional cast Ti-Al-based alloy, Materials Characterization, V.106, pp. 112–122.

[31] Larsen, D. E., Christodoulou L, Kampe S.L., Sadler R.,(1991), Investment-cast processing of XDTM near-γ titanium aluminides, Mat Sci Eng A. Vol. 144, PP. 45–49.

[32] Godfrey A.B., Ph.D. thesis, (1996) The University of Birmingham.

[33] Inkson B.J., Boothroyd C.B., Humphreys C.J.,(1993), Boron segregation in a (Fe, V, B) TiAl based alloy, Le Journal de Physique. Vol. 3, PP. 397–402.

[34] Cheng T.T., (2000), The mechanism of grain refinement in TiAl alloys by boron addition — an alternative hypothesis, Intermetallics. Vol.8, PP. 29–37.

[35] Hu D., Yang C., Huang A., Dixon M., Hecht U, (2012), Grain refinement in beta-solidifying Ti44Al8Nb1B, Intermetallics. Vol. 23, PP. 49–56.

[36] Hu D., Yang C., Huang A., Dixon M., Hecht U, (2012), Solidification and grain refinement in Ti45Al2Mn2Nb1B, Intermetallics. Vol. 22, PP. 68–76.

[37] Oehring M., Stark A., Paul J.D.H., Lippmann T., Pyczak F., (2013), Microstructural refinement of boron-containing beta-solidifying gamma-titanium aluminide alloys through heat treatments in the beta phase field, Intermetallics.Vol..32, PP.12–20.

[38] Kartavykh A.V., Gorshenkov M.V., Tcherdyntsev V.V., Podgorny D.A.,

(2014), On the state of boride precipitates in grain refined TiAl-based alloys with high Nb content, J Alloy Compd. Vol.586, PP. S153–S158.

[39] Yang C., Jiang H., Hu D., Huang A., Dixon M., (2012), Effect of boron concentration on phase transformation texture in as-solidified Ti44Al8NbxB, Scripta Mater. Vol. 67, PP. 85–88.

[40] Kitkamthorn U., Zhang L.C., Aindow M., (2006), The structure of ribbon borides in a Ti–44Al– 4Nb–4Zr–1B alloy, Intermetallic. Vol. 14, PP.759–769.

[41] Wang W. D., Ma Y.C., Chen B., Gao M., Liu K., Li Y.Y., (2010), Effects of boron addition on grain refinement in TiAl-based alloys, J. Mater. Sci. Technol. Vol. 26, PP. 639–647.

[42] Hecht U., Witusiewicz V., Drevermann A., Zollinger J.,(2008), Grain refinement by low boron additions in niobium-rich TiAl-based alloys, Intermetallics. Vol. 16, PP.969–978.

[43] Hyman M.E., McCullough c., Valencia J.J., Levi C.G., Mehrabian R., (1989), Microstructure evolution in TiAl alloys with B additions: conventional solidification, Metall Trans A. Vol. 20, PP. 1847–1859.

[44] Bartolotta P., Barrett J., Kelly T., Smashey R.,(1997), The use of cast Ti–48Al–2Cr–2Nb in jet engines, Jom-j Min Met Mat S. Vol.49, PP.48–50.

[45] http://www.sigmaaldrich.com/catalog/Compare.do?P_ID=200396|332445|ALDRICH+205183|336289|ALDRICH&returnURL=http%3A%2F%2Fwww.sigmaaldrich.com%2Fcatalog%2Fsearch%3Finterface%3DAll_ZH%26term%3D%25E7%25A1%25BC%26N%3D0%26mode%3Dmatch%2520partialmax%26focus%3Dproduct%26lang%3Dzh% 26region%3DCN.

[46] Godfrey A., Loretto M., (1996), The nature of complex precipitates associated with the addition of boron to a γ-based titanium aluminide, Intermetallic. Vol. 4, PP. 47–53.

[47] Wang W. D., Ma Y.C. , Chen B., Gao M., Liu K., Li Y.Y., (2009), Solidification features of Ti45Al alloys with different boron addition, J. Mater. Sci. Technol. Vol. 25, PP. 814–818.

[48] Cheng, X. Zenji, H. Minoru, F. and Terence, G. L. (2004), Using Equal-Channel Angular Pressing for the Production of Superplastic Aluminum and Magnesium Alloys, Journal of Materials Engineering and Performance, Vol. 13, Issue 6, pp.683 .

[49] Werenskiold, Jens C. (2004), Equal Channel Angular Pressing (ECAP) of AA6082: Mechanical Properties, Texture and Microstructural Development. Unpublished Doctoral Dissertation, the Norwegian University of Science and Technology (NTNU), Norwegian.

[50] Melicher, R. (2009), Numerical simulation of plastic deformation of aluminum workpiece induced by ECAP technology, Applied and Computational Mechanics, V.3, pp. 319–330.

[51] Luis, C. J. Garcés, Y. González, P. and Berlanga, C. (2002), FEM Analysis of Equal Channel Angular Processes, Materials & Manufacturing Processes, Vol. 17, Issue 2, pp. 223-250.

[52] Raj, K.H. Sharma, R.S. Sahai, A. and Sharma, S.S. (2008), Finite Element Simulation of Twist Extrusion ECAP on Al6061 Specimen, Institute of Materials Engineering Australasia, pp. 29-34.

[53] Hans Raj, K. Setia, R. Sharma, R.S. and Sahai, A, (2011). Artificial Neural Network Modeling of Equal Channel Angular Pressing for Reuse of Al6061, International Journal for Applied Engineering and Research in print ISSN No: 0973-4562 and Online ISSN No: 1087—1090, pp. 1024-1029.

[54] Umemoto, M. (2003), Nano crystallization of Steels by Severe Plastic Deformation, Materials Transactions, V-44, Issue 10, pp. 1900-1911.