68th WFC - World Foundry Congress
7th - 10th February, 2008, pp. 189-193

OP-35

Grain Refinement of Light Alloys

T.R. Ramachandran, P.K. Sharma and K. Balasubramanian
Nonferrous Materials Technology Development Centre
Kanchanbagh Hyderabad 500 058
India

ABSTRACT

Grain refinement studies on aluminium and magnesium alloys have attracted considerable attention in the last five decades. Inoculation of the melt with intermetallic compounds (Al_3Sc, Al_3Zr etc.), and borides and carbides of Al and Ti leads to heterogeneous nucleation of aluminium grains. This results in several advantages in the casting stage, and subsequent thermal, mechanical and surface treatment steps. A review of grain refinement in aluminium and magnesium alloys is presented in this paper with emphasis on production, commercially important grain refiners and their performance and theories proposed to understand the formation of fine grains. Trials in progress, for minimizing fluoride emissions associated with the production of the Al-Ti-B grain refiners, are summarized. Some of the methods proposed offer the advantages of achieving grain refinement along with melt treatment for minimization of hydrogen, inclusions and dissolved elements such as Na and Ca.

Keywords: grain refinement, light alloys, inoculants, mechanisms, pollution control

INTRODUCTION

The use of aluminium and magnesium alloys in the automobile industry is continuously increasing. The driving force is reduced green house gas emissions resulting from light weighting of the vehicles and efficient scrap recycling. The present consumption of aluminium and magnesium in passenger cars is 120-140 kg and ~ 5 kg per vehicle respectively; these figures are expected to rise further in the next decade. In order to maintain this momentum it is necessary to pay attention to all processing (solidification, mechanical and thermal) aspects of the alloys and optimize the properties. Grain refining plays an important role in this context. Reduction in grain size can be achieved in three different stages – during solidification of the molten metal, thermomechanical treatments involving recovery and recrystallization of the deformed material and severe plastic deformation using processes such as equichannel angular processing (ECAP), hydrostatic extrusion and roll bonding. The resulting grain size varies from a few hundred µm (molten metal solidification) to a fraction (severe plastic deformation) of µm. Grain refinement resulting from solidification is the mother of all these treatments and is applicable to both cast and wrought alloys. In view of the increasing applications of the light alloys in the automobile sector many of these studies are revisited in the recent years and fine tuning done to ensure that the process is efficient and environmentally friendly.

Grain refinement offers a number of advantages in foundry operations and in subsequent mechanical and thermal processing and surface finishing stages. Benefits in the foundry operation include improved feeding, reduced chemical segregation, porosity and hot tearing and increased pressure tightness; the advantages during the subsequent processing stages are improved mechanical properties in heavier sections, consistent properties after heat treatment, improved machinability and better appearance in anodized coatings.

Grain refinement during solidification involves the formation of fine equiaxed grains at the expense of dendrites. The methods favoring the formation of fine grains include addition of trace elements in the form of master alloys, inoculation of borides and carbides, use of ultrasonic treatment or electromagnetic field, introduction of fine gas bubbles and applying coatings to the mold surface. Inoculation is the most commonly employed method and is carried out using grain refiners such as Al-Ti, Al-Ti-B, Al-Ti-C, Al-B and Al-Sr-B alloys. Studies on the performance of grain refiners indicate that the grain size attains a minimum value after a certain length of time, followed by an increase (fade). Alloying elements like Si, Zr and V are found to poison the grain refiners, thereby reducing the efficiency of grain refinement. Al-Ti-C alloys are more effective and are not poisoned by Zr or V, but suffer from disadvantages of easy fade and inferiority to Al-Ti-B in the treatment of recycled material. Aluminium-free magnesium alloys are commonly grain refined by the addition of Zr in the form of Mg-Zr master alloy. Introduction of carbon in the aluminium-containing alloys leads to grain refinement but there is ample scope for improving the process. The standard method for the manufacture of Al-Ti-B involving the use of K_2TiF_6 and KBF_4 results in considerable fluoride emissions and formation of fluoride salts as slag. Trials are currently in progress to minimize these effects and control pollution. These aspects are briefly dealt with in this presentation. The mechanisms proposed for grain refinement are based on heterogeneous nucleation of the aluminium grains on the inoculants, solute retardation of grain growth and edge-to-edge matching of planes in the substrate and the solidifying grain. The ultimate aim of understanding the mechanism is to predict the grain refiners that would be suitable for a given alloy.

GRAIN REFINEMENT METHODS

Aluminium Alloys

Trace additions of Mn, Cr and Zr (in the form of master alloys) to aluminium refine the grain size, the effect being prominent after thermomechanical treatments. Fine (a few tens to hundred nm size) dispersoids of Al_3Zr, Al_6Mn and Al_7Cr are effective in pinning grain boundaries, thereby restricting their movement. Scandium is an efficient addition to aluminium to achieve grain refinement during solidification of the molten metal and also during subsequent mechanical and thermal processing stages. The extent of addition for efficient grain refinement depends on the nature of the alloy. For example ~0.6-0.7% Sc is necessary for refining pure aluminium while for an Al-Zn-Mg-Zr alloy ~0.2%Sc is sufficient [1]. The lower amount of Sc in the presence of Zr is attributed to the formation of composite Al_3Sc-Al_3Zr particles as well as to the possible lowering of eutectic composition in the ternary system [1]. Similar results are also obtained with AA356.0 alloy. In view of the prohibitively high cost of Al-Sc master alloys, use of reduced amounts is desirable. The addition of carbon and iron also contribute to grain refining although the effect is not prominent. Also iron forms insolubles of the Al_3Fe, AlFeSi type which are detrimental to the mechanical properties.

Salt flux treatment for grain refining and production of Al-Ti and Al-Ti-B master alloys are both based on the interaction between double fluoride salts and aluminium melt in accordance with the following equations:

$$3K_2TiF_6 + 4Al \rightarrow 3Ti + 4\,AlF_3 + 6KF \qquad (1)$$

$$2KBF_4 + 3Al \rightarrow AlB_2 + 2AlF_3 + 2KF \qquad (2)$$

$$3K_2TiF_6 + 6KBF_4 + 10Al \rightarrow 3TiB_2 + 10AlF_3 + 12KF \qquad (3)$$

Flux treatment leads to *in-situ* generation of the nucleants such as AlB_2 and TiB_2; the production of master alloys based on the above chemical equations results in a fine dispersion of the borides in aluminium which can be subsequently added to aluminium alloys. Process control is somewhat difficult in flux treatment as the borides may get entrapped with the slag particles leading to less efficient grain refinement and the introduction of slag inclusions in the solidified aluminium alloy. Other disadvantages of using fluxes include their hygroscopic nature, release of corrosive fumes during melting, possibility of reaction with modifying agents such as Na and Sr (in Al-Si Alloys) and the unpredictable recovery behaviour of Ti and B. Master alloys are usually produced in induction furnaces and are cast as in-got, waffle, sheared rod or shotted product. The main problem encountered in making the alloys is the pronounced tendency for the particles to segregate arising from differences in melting points of the elements and the density of the phases (molten Al, Al_3Ti and borides).

Different practice for salt addition introduce marked changes in microstructure and hence the grain refining efficiency of the Al–5Ti–1B master alloys. Mixing the halide salts before addition and a high rate of addition both lead to improved grain refining efficiency. Stirring during addition and reaction temperatures exceeding 850 °C are undesirable. The morphology of Al_3Ti particles in the master alloy depends on the temperature of pouring and has considerable influence on grain refining ability. Consequently an optimum procedure for production of efficient grain refiners consists of melting commercial purity aluminium, rapid addition of pre-mixed salts at 800°C, to facilitate spontaneous reaction and gently mixing the salts with the aluminium melt without introducing any stirring [2].

Al-Ti-C master alloys are produced through several routes - adding C, TiC, C_2Cl_6 Al_4C_3 or a mixture of K_2TiF_6 and carbon to the melt, feeding C rod, CCl_4 or TiC through a flux.

Information on commercially available grain refiners is summarized in Table 1. The most commonly used alloy is Al-5Ti-1B but recent studies show that some of the dilute alloys can be equally effective. The ratio of Ti to B for the formation of TiB_2 in Al-Ti-B alloys is 2.21:1. The Al-3Ti-1B alloy would, therefore, contain most of the Ti and B in combined form. Since the other compositions have excess Ti, a certain amount of Al_3Ti would co-exist with the boride phase. Also in alloys with low B (such as Al-5Ti-0.2B and Al-10Ti-0.4B), the concentration of borides is low; these alloys are preferred for grain refinement operations where the ingot is to be rolled into thin foils. The low carbon concentration of the Al-Ti-C alloys implies small amounts of TiC; the excess Ti would be present as Al_3Ti. The Al-B alloys would contain AlB_2 particles dispersed in aluminium matrix. The Sr-B alloy fulfils the twin objectives of grain refinement (by AlB_2) and modification (by Sr) of the eutectic structure in Al-Si alloys. Typical size of the boride particles is ~ 1μm in the Al-5Ti-1B alloy, 2-3 μm in Hydloy and 0.05 μm–1 μm in TiBloy [3].

Table 1

Commercially Available Grain Refining Alloys

Alloy type	Composition
Al-Ti	Al-10Ti, Al-6Ti
Al-Ti-B	Al-3Ti-1B, Al-5Ti-1B, Al-5Ti-0.6B, Al-3Ti-0.2B, Al-5Ti-1B, Al-5Ti-0.2B, Al-10Ti-0.4B, Al-1.6Ti-1.4B (TiBloy for hypoeutectic Al-Si alloys), Al-1.2Ti-0.5B (Hydloy), Al-3Ti-3B, Al-1Ti-3B
Al-B	Al-10B, Al-5B, Al-3B, Al-10Sr-2B, Strobloyä, (Al-10Sr-1.6Ti-1.4B)
Al-Ti-C	Al-6Ti-0.02C, Al-3Ti-0.15C
Al-Sc	Al-1Sc, Al-2Sc
Mg-Zr	AM cast (Mg-25Zr), Zirmax (Mg-33.3Zr)

The performance of a grain refiner can be evaluated by withdrawing samples at different times following its addition and determining the grain size of the solidified alloy. A number of standard tests are available for this purpose but the more commonly employed one is the AA TP1 test [4]. This uses a tapering steel (or copper) mold immersed in water up to a certain height, thereby introducing different rates of cooling simulating various cooling conditions encountered in casting processes. The performance characteristics of a set of grain refining additions (flux, Al-Ti and Al-Ti-B) are schematically illustrated in Fig. 1(a). The important points to note are the finite time taken by each type of refiner to produce the minimum grain size, the phenomenon of fade where the grain size starts increasing after a certain length of time and the distinct advantage of Al-Ti-B over Al-Ti and flux additions. Macrostructures of aluminium samples grain refined with Al-1.2Ti-0.5B alloy using the AA TP 1 test and withdrawn after various time intervals are shown in Fig. 1(b). The fading effect is clearly brought out in the macrographs corresponding to long time interval after addition. The phenomenon of fade is associated with agglomeration of the boride particles; large agglomerates present in the grain refiner and their growth by absorption of smaller (and therefore slower settling particles) are responsible for loss of grain refining [3]. These agglomerates lead to a number of quality problems - streaking and porosity in thin foils, scratch-like liner surface defects in litho and bright anodized sheet, internal cracking in extrusion billets, crack initiation in high strength aluminium alloy plate and forgings. A good grain refiner needs to have a short incubation period for reaching the minimum grain size and a sustained time interval before the onset of fade.

The grain refining behaviour of the Al-Ti-B alloys (particularly the 5Ti-1B alloy) can be adversely affected by solutes such as Si, V and Zr. This poisoning phenomenon is observed in Al-Si alloys when the Si content exceeds ~2% and in the high strength wrought alloys such as those in the 2xxx and 7xxx series. It can be counteracted by excess additions of the grain refiner which adds to the cost of grain refinement. Another possibility is to reduce the Ti content in the master alloys e.g Al-3Ti-3B in Table 1. The poisoning phenomenon in Al-Si alloys is attributed to the formation of Ti_5Si_3 [5].

Studies on grain refinement of various aluminium alloys by the Al-TI-B master alloys indicate that the Hydloy (1.2Ti-0.5B) is consistent in producing the lowest grain size at about the same addition level (typically 1.5-2.0 kg/t) [6]. The lower titanium content of this alloy implies lower cost and lower concentration of the boride particles and hence less carry over of the inactive nucleants into the solidified product.

Al-Ti-C alloys offer the advantages of higher casting speed, higher yield due to fewer oxide particles, less cracking and agglomeration. However, they are sensitive to casting temperatures and have high fading potential; higher temperatures of pouring reduce grain refining efficiency. The TiC particles are softer than those of TiB_2 and hence there is less die wear during drawing and extrusion operations [7]

MAGNESIUM ALLOYS

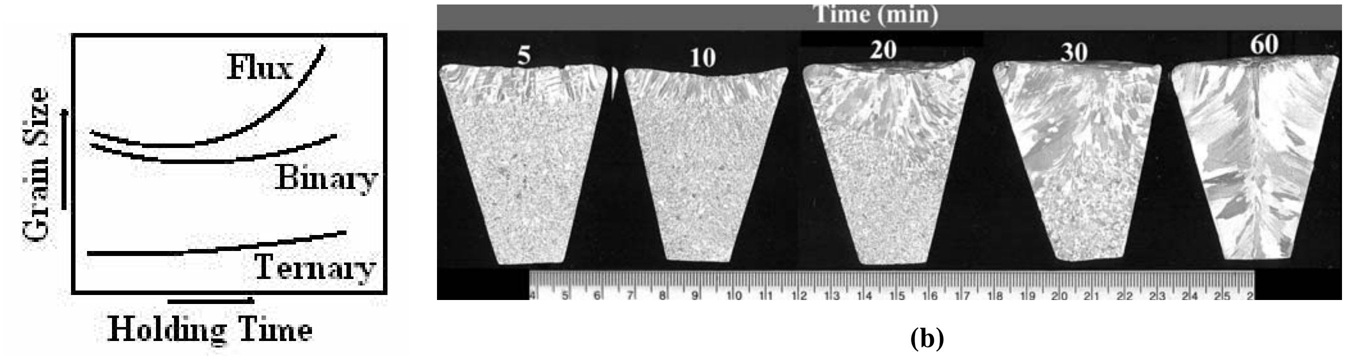
Magnesium alloys can be generally classified into two broad groups; those containing aluminium and the ones free from aluminium. The aluminium-containing alloys are more difficult to refine than those free from aluminium; Zr is effective in the treatment of the latter group of alloys. The subject of grain refinement of magnesium alloys has recently been reviewed by St.John et al. [8]. The methods available include superheating, carbon addition, the Elfinal process, agitation and treatment with Mg-Zr master alloys.

Super heating method of grain refinement involves heating to about 180°-300°C above the liquidus for a short time followed by rapid cooling to the pouring temperature. Presence of at least 1% Al, and smaller amounts of Mn and Fe, adhering to the superheating temperature range strictly and minimum holding time at the pouring temperature, are essential to successful grain refining.

Efficient grain refinement of Mg-Al alloys with more than 2%Al is achieved by the addition of graphite, paraffin wax, lamp black, C_2Cl_6 and carbides such as Al_4C_3, SiC and CaC_2 or bubbling the melt with carbonaceous gases such as CO_2, C_2H_2 and C_2Cl_6. CaC_2 and C_2Cl_6 appear to be more effective; elements such as Be, Ti, Zr and rare earths interfere with the process. The formation of fine grains is encouraged by aluminium carbide particles.

The Elfinal process involves the addition of 0.4% to 1.0% anhydrous ferric chloride at temperatures between 740°C to 780°C. The refining effect is attributed to intermetallic compounds of Fe and Al acting as heterogeneous nucleation sites. Zr and Be inhibit the refining process.

Increasing the aluminium content of hypoeutectic Mg-Al alloys leads to a continuous reduction in grain size up to 5% Al, no further refinement is observed when the Al content is



(a)

(b)

Fig. 1 : (a) Schematic of grain size variation with holding time for aluminium using flux, binary Al-Ti and ternary Al-Ti-B alloys (b) Macrographs of commercial aluminium grain refined by Al-1.2Ti-0.5B, 50 ppm Ti addition

increased. Sr is good for grain refinement of low Al-containing alloys; however no refinement is observed when the Al content is 9%. Additions of Zr, Si and Ca to pure Mg result in efficient grain refinement, due, mainly to retardation of grain growth [9].

The commercial practice of grain refinement of magnesium alloys with Zr is based on the peritectic mechanism proposed by Emley [10]. This requires an addition of 0.6% Zr, normally introduced through a master alloy (e.g. Zirmax); the low recovery of Zr and the high cost of the master alloy make the grain refining process expensive. Reassessment of the phase compositions in recent years indicate that the peritectic composition is substantially lower, ~ 0.4%. It should, therefore, be possible to add lower amount of Zr for grain refinement which would reduce the cost of the operation. Recent studies on Mg-3.8%Zn-2.2%Ca alloy indicate that the Zr content in the equiaxed grains ahead of the columnar front is between 0.2%-0.3%; this is an encouraging result as grain refinement can be obtained with Zr content of < 0.3% [11]. There is some evidence that simultaneous addition of Zr and Sc is useful in grain refining the aluminium-containing AZ31 alloy; the effect, brought about by the pinning of the grain boundaries by precipitating phases containing Zr and Sc, is particularly noticeable when the alloy is subjected to severe plastic deformation through ECAP [12].

Native grain refinement, associated with the purity of magnesium used in alloy making, is reported in Mg-Al alloys; Mg-Al alloys made from high purity magnesium have a finer grain size compared with those made from less pure metal. In contrast Mg-Zn and Mg-Ca alloys exhibit native grain coarsening. Al_4C_3 particles present in the alloys are reported to be responsible for native grain refinement; impurities such as Fe and Mn present in the less pure metal counteract the effect of the carbide nucleants [13]. However, this hypothesis is in conflict with the benefits of Fe introduced by the Elfinal process.

The use of Al-Ti-B type grain refiners in magnesium alloys has not attracted much attention. A recent study indicates that AZ31 and ZA84 alloys can be grain refined by the use of an Al-4Ti-5B master alloy (14); TiB_2 particles are reported to be the heterogeneous nucleation sites. The use of the standard composition master alloys (Table 1) needs a careful study.

While several methods are available for grain refining magnesium alloys, the mechanisms involved are not clear; consequently empirical approaches are often employed and this leads to unsatisfactory results. Attention is now paid to understanding the mechanisms better with a view to developing grain refiners based on theoretical considerations.

ENVIRONMENTAL CONSIDERATIONS

As pointed out earlier, the production of Al-Ti-B grain refiners involves reaction of molten aluminium with KBF_4 and K_2TiF_6. The process is associated with considerable fluoride emissions due to vaporization of the salts and their reaction with moisture leading to the formation of hydrogen fluoride. Besides the slag formed contains potassium and aluminium fluoride; this presents disposal problems. Consequently several trials have been / are in progress to minimize these effects. The development of the low Ti and B (1.2Ti-0.5B) alloy is a step in this regard. A second approach is to replace KBF_4 by other boron-containing compounds such as borax and boron trioxide and replacing K_2TiF_6 by titanium sponge. Changes in the nature, size and distribution of the boride particles introduced by these processes and the consequent effect on grain refining efficiency and reduced recovery of Ti are problems to be sorted out [15].

It is recently reported [16] that grain refinement in aluminium can be achieved by using fine argon gas bubbles (introduced through a graphite diffuser) to agitate the melt. This method has great potential for combining grain refinement with melt treatment (an essential prerequisite for producing good quality castings and dealing with minimization of dissolved hydrogen, Na and Ca and inclusions). The process avoids introduction of borides and their aggregates in the metal and therefore offers longer metal filter life and better mechanical properties.

A recently developed method for grain refinement involves the in-situ formation of boride nuclei in molten aluminium immediately preceding the casting stage. The process (fy-Gem process) developed under a Department of Energy of the US Government project is carried out by introducing argon - typically 1% BF_3 or BCl_3 mixture into the molten metal in the form of fine bubbles [17]; the trihalide is introduced during the in-line melt treatment stage. Boron dissolving in aluminium combines with Ti, V, Fe, Mn in the metal to form a fine dispersion of borides. BCl_3 can be produced by chlorination of boron carbide at 1000°C. An important step in the process is the design of the rotor head for the introduction of the gas in the form of fine bubbles. The manufacture of the trihalide is considerably simpler than preparing the conventional Al-Ti-B or Al-B grain refiners and has the advantages of environmental, capital and energy savings. Also the process avoids clusters of borides, salt and oxide inclusions that affect adversely the properties of the cast metal. Prolonged experimental trials on the foundry aluminium alloys show that the fy-gem process is as efficient as the best grain refiners currently available; the performance is slightly inferior with the wrought alloys and the Zr-containing alloys pose problems.

THEORIES OF GRAIN REFINEMENT

The mechanisms proposed for grain refinement are based on (i) heterogeneous nucleation of aluminium grains on inoculant particles (borides and titanium aluminide), (ii) grain growth retardation by solute additions and (iii) edge-to-edge matching of the planes in the inoculant particle and nucleating aluminium grain [18,19,20]. Heterogeneous nucleation on the substrate would depend on compatibility between the crystal structures and lattice parameters of the phases involved. A consideration of these factors indicates that Al_3Ti can be an efficient nucleant. However at the typical levels of addition (a few hundred ppm Ti) for grain refinement, particles of this phase are unstable. Careful high resolution electron optical observations indicate that a thin layer of Al_3Ti formed on TiB_2 facilitates heterogeneous nucleation. Retardation of grain growth is based on the mechanism of constitutional supercooling; the nucleating substrates are mainly the borides with the solute atoms affecting the dendritic growth and building up a constitutionally supercooled zone in front of the solidifying interface which facilitates the nucleation process. The efficiency of the solute atoms in promoting grain refinement is related to the growth restriction factor, $m(k-1)C_0$ where C_0 is the solute concentration, m is the slope of the liquidus line at C_0 and k is the equilibrium partition coefficient between the melt and the primary aluminium grains. The higher the value of the growth restriction factor, the smaller will be the grain size. The value of m(k-1) is the highest for Ti in Al and Zr in Mg [19,21]. B and Sc, elements of interest in grain refinement of aluminium, have relatively low values of m(k-1). Ta has a high value for m(k-1) in aluminium and is, therefore, of interest; there are very few references in the literature about the use of Ta for grain refinement. The edge-to-edge model is capable of predicting the orientation relationships between the parent and product phases and corresponding habit planes from first principles; it is based on the minimization of strain energy of the interface. It has been applied to both aluminium and magnesium alloys; studies in aluminium alloys indicate that although TiC, Al_3Ti, TiB_2 and AlB_2 are all effective heterogeneous nucleants, the predicted efficacy of the substrates varies. Al_3Ti is the best grain refiner for Al alloys. The other three are less efficient. Also orientation relationships predicted by the model are in agreement with those from previous observations [18]. It is possible to use the edge-to-edge matching model as a theoretical guide to the discovery of new and more effective grain refiners; this may be of particular relevance to systems that are traditionally difficult to grain refine, such as the Al–Li and Al–Si alloys. This model has been used to identify a new grain refiner, ZnO, for the Mg-Al alloys [22].

SUMMARY

Al-Ti-B alloys are efficient grain refiners for aluminium alloys but the workhorse Al-5Ti-1B alloy is slowly giving way to the more dilute alloys such as Al-1.2Ti-0.5B. In-situ formation of the boride nuclei by injection of BCl_3 or BF_3 offers significant advantages in terms of lower amount of nucleants and improved environment. Injection of fine gas bubbles into the melt satisfies the requirements of both grain refinement and melt treatment; the method requires more elaborate study. Al-free magnesium alloys can be efficiently refined by Zr; the emerging trend is to use lower amount of Zr (typically 0.3%), thereby contributing to economy of the operation. The aluminium-containing alloys are grain refined by the introduction of the carbide nucleants through addition of carbonaceous material. Rapid strides are made in understanding the mechanisms of grain refinement with the ultimate objective of predicting a suitable refiner for a given alloy but more information needs to be collected in this regard.

REFERENCES

1. Royset J, and Ryum N, International Materials Reviews, 50(1), 2005, pp.19- 44
2. Birol Yücel, J. Alloys and Compounds, 420, 2006, pp. 207-212.
3. Schaffer P L, and Dahle A K, International Conference on Advances in Solidification Processes, Materials Science and Engineering, A 413-14, 2005, pp. 373-378.
4. Monograph on Standard Test Procedure for Aluminum Alloy Grain Refiners, Aluminum Association,1990
5. Qiu D, Taylor J A, Zhang M-X, and Kelly P M, Acta Materialia, 55(2007), pp.1447-1456.
6. Schneider W E, Quested T E, Greer A L, and Cooper PS, Light Metals TMS 2003, pp. 953-959
7. www.kballoys.com
8. StJohn D H, Qian Ma, Easton M A, Cao Peng, and Hildebrand Z, Metall Mater. Trans. 36A, 2005, pp.1669-1679.
9. Lee Y C, Dahle A K, and St. John D H, Metall Mater. Trans. A31 (2000) pp. 2895-2906.
10. Emley E F, Principles of magnesium technology, Pergamon Press, Oxford (1966) p. 126.
11. Qian Ma, and Das A, Scripta Materilia, 54, 2006, pp. 881-886
12. Wang S C, and Chou C P, J. Materials Processing Technology (to be published).
13. Cao Peng, Qian Ma, and StJohn D H, Scripta Materialia, 53(2005), pp. 841-844.
14. Wang Yingxin, Zeng Xiaoqin, and Ding Wenjiang, Scripta Materialia, 54(2), 2006, pp. 269-273.
15. Birol Yücel, J. Alloys and Compounds, 440 (1-2), 16th August 2007, pp. 108-112; 443(1-2), 27thSeptember 2007, pp. 94-98.
16. Wannasin J, Martinez R A, and Flemings M C, Scripta Materialia, 55(2), July 2006, pp.115-118.
17. New Process for Grain Refinement of Aluminum, Contract No. DE-FC07-98ID13665, September 22, 2000.
18. Maxwell I, Hellawell A, Acta Metall., 23, 229(1975)
19. Easton M and StJohn D, Metall Mater. Trans. A30 (1999) pp. 1613-33.
20. Zhang M-X, Kelly P M, Easton M A, and Taylor J A, Acta Materialia, 53 (2005), 1427-1438.
21. Zhang M-X, Kelly P M, Qian Ma, and Taylor J A, Acta Materialia, 53, 2005, 3261-3270.
22. Fu H M, Qiu D, Zhang M-X, Wang H, Kelly P M, and Taylor J A, J. Alloys and Compounds (to be published).