(54) Title: APPARATUS AND METHOD OF PRODUCING A FINE GRAINED METAL SHEET FOR FORMING NET-SHAPE COMPONENTS

(57) Abstract: A method and apparatus for producing ultra-fine grained metal alloy preferably magnesium material sheets. The apparatus molds and rapidly solidifies a metal alloy material to form a fine grain precursor. The precursor is then subjected to deformation strains that alter the grain structure of the precursor so as to form a ultra fine grained structure in sheet form. The sheet form may then be subjected to superplastic forming to form a net shaped article.
APPARATUS AND METHOD OF PRODUCING A FINE GRAINED METAL SHEET FOR FORMING NET-SHAPE COMPONENTS

BACKGROUND

1. Field of the Invention
[0001] The present invention relates to producing net shaped components of increased strength. More particularly, the invention relates to producing magnesium alloy sheet components, having micrometer sized grain structures, that can be subsequently used in the production of net shaped sheet components of increased strength.

2. Related Technology
[0002] Over the last several decades, magnesium (Mg) alloy development has been inhibited by certain barriers. While wrought magnesium has the potential for making thinner structures, anisotropy in mechanical properties limits the applications of Mg alloys and their wrought products. The strength of Mg alloys is rather low in certain directions in comparison to most widely used structural materials, such as steels and precipitation-hardened aluminum (Al) alloys. For example, in-plane compression, yield strength can be only 85MPa in basal textured Mg alloy; AZ31B Mg alloy sheet in the H24 temper could have a high-value normal anisotropy parameter (R) of 3.2 in the transverse direction. A high value of normal anisotropy in sheet is helpful for deep drawing, but may not be suitable for other applications, particularly if in-plane strength is also anisotropic. In fact, this base element has not been a friendly host for extensive alloy strengthening.

[0003] The alloying elements that improve corrosion resistance and castability, such as Al, unfortunately introduce eutectic intermetallic phases. These envelope the primary grains in a coarse and brittle morphology. Furthermore, it is difficult to attain efficient age hardening by fine precipitates within the grains, as exemplified by the case of inefficient Al additions. Elements that promote age hardening, such as rare earth metals, are costly, detrimental to castability and ineffective in resisting corrosion. As a consequence of these barriers, increases in strength have been marginal, at best, and decade-old Mg alloys, such as AZ31 and AZ91D, still dominate the tonnage of commercial sheet and casting markets.

[0004] Hexagonal close packed (HCP) structured Mg alloys have low symmetry of slip systems that contributes to high anisotropy of mechanical properties. Slip is a crystallographic shear process associated with dislocation glide that underlies the large plastic deformation of crystalline metals. At room temperature, "basal a" slip (0001)<1120> is predominant, while "prism a" and <c+a> slip are difficult because of their significantly high critical resolved shear stresses (CRSS), which are reported in regions of high stress
concentration such as grain boundaries and twin interfaces. Twinning is a deformation mechanism in which small, often plate or lens shaped, regions of a crystal or grain reorient crystallographically to adopt a twin relationship to the parent crystal. Deformation twinning is often observed in polycrystalline Mg to compensate for the insufficiency of independent slip systems. The most common twinning modes are (1012) and (1011) twinning, which accommodate the c-axis extension and contraction, respectively.

[0005] If profusion of "tension" and "compression" twinning occur homogeneously, good strain hardening and large ductility could result in titanium (Ti) and zirconium (Zr). However, in Mg, twinning is inhomogeneous, and different modes of twinning are not initiated simultaneously. A single twinning mode cannot fully accommodate plastic deformation. When basal slip is inhibited at ambient temperatures, twinning deformation can be localized, which leads to low ductility in Mg.

[0006] Two major drawbacks restrict the application of wrought Mg alloys. First the symmetry of hexagonal close packed crystal structures has the effect of limiting the number of independent slip systems, thus providing alloys with poor formability and ductility near room temperature. Second, forming Mg alloys at elevated temperatures (>300°C), although helpful to overcome the restriction of slip, makes oxidation problems more severe.

[0007] Another means to strengthen Mg alloy, relative to Al and steel, is by grain refinement. By the well-established Hall-Petch relation, strength is proportional to \(d^{-1/2}\), where \(d\) ~ grain size. Whereas conventional Mg alloy sheets and extrusions have a grain size in the range of 10 to 90 \(\mu m\), reducing the grain size to about 1 \(\mu m\) or less (thus nanostructured and herein referred to as an "ultrafine grain size") offers a striking opportunity to escalate the strength/density of Mg to levels above Al and steel. An ultrafine grain size could enable superplastic deformation to be carried out at lower temperatures and higher strain rates. At room temperature, grain refinement strengthens many polycrystalline metals. This is true for cubic structured metals such as Al, copper (Cu) and iron (Fe). However, for HCP metals, such as Mg alloys, grain refinement may also cause texture variation, and inadequate strengthening in certain directions.

[0008] Expensive and elaborate schemes to reach an ultrafine grain size in Mg have been developed in various research and development efforts. A number of known methods of grain refinement, such as rapid solidification, vapor deposition, and powder processing are practiced in the lab. These processes are costly, time consuming and have not enjoyed commercial success. Several other schemes for severe plastic deformation (SPD) have proven to be unpractical for manufacturing larger quantities of ultra-fine grain metals. Techniques now available for performing severe deformation of bulk material include reciprocating extrusion, three-axis plane-strain forging, torsion under hydrostatic pressure,
and equal angular channel extrusion or pressing (ECAP). When these processes are used in a repeated manner, the overlap of shear zones within the bulk material from individual steps causes extensive grain subdivision and formation of fine grain structure. Concurrent recovery and recrystallization processes transform subgrains with low-angle boundaries into high-angle boundary grains. It is generally accepted that grain refinement leads to a decrease in strain hardening as yield strength is increased, but the variation of strain rate sensitivity with grain refinement in Mg alloys is not clearly documented. This may offset any loss in ductility due to reduced strain hardening. The combination of strain hardening and strain rate sensitivity provides a synergistic effect of a higher tensile elongation, even when strain hardening exponent \( n = c/(\log\sigma/c/(\log\varepsilon)) \) may be lower. Deformation by several deformation passes through equal channels (so called ECAP) has been practiced in the lab on Mg bars, but is not practical for Mg sheets.

[0009] Since 1999, the University of Michigan conducted research aimed at producing sheets or billets of ultra-fine grain size, without using a closed shearing die as used in ECAP, but by using a multiple corrugation and flattening (MCF) process or a sine wave deformation process (SWP) that might be more suitable for a sheet product. The potential of the process was demonstrated with various aluminum alloys containing dispersoid particles. This repeated reversed plastic deformation approach was shown to achieve very fine grain size on the surface of the sheet, which progressively reaches the core regions of the sheet after several repeated passes. That research showed that changes in alloy chemistry, and use of dispersoid particles in the alloy, can take advantage of this simpler process to produce ultra-fine grain alloys. Application of this and other approaches to magnesium alloys was a subject of significant interest since these alloys possess inherently low ductility.

[0010] Under basic research funding from the National Science Foundation, it was previously demonstrated by the University of Michigan that, although hexagonal close packed metals, like Mg, have inherent problems with the breakdown of coarse grains due to textural and twinning-related issues, it is believed that either a deformation strain, such as for example, tension-compression or pure compression, or a constrained SWP has the capacity to overcome these problems under suitable temperatures and process conditions.

[0011] Superplasticity is an attribute associated with fine-grained alloys. This plastic-type property is utilized commercially in automobiles and aircrafts to form complex net shapes in titanium (Ti) and Al. To date, Mg alloys have not enjoyed this advantageous processing in commerce. First, Mg alloy castings do not have the prerequisite grain boundary crystal structure and, secondly, wrought Mg sheets have been too coarse grained and/or too textured for superplastic forming.
Turning to more definitive discussion of nanotechnology, nano-size strengthening phases of about 100 nanometers are desirable within the grains. This is another strengthening mechanism, heretofore not available in weakly alloyed AZ31 sheets. However, construction and assembly of such a microstructure for bulk structural parts, ab-initio from nano-powders, is a very costly and laborious. Also, there are safety and health concerns for handling such fine particles in the workplace. It seems to be safer and more practical to generate such nano-strengthening particles in-situ during processing of the already assembled bulk component.

Grain size has a major effect on the formability of Mg alloy sheets. Currently, commercial wrought Mg alloy sheet is available only in low strength AZ31 alloy. It is fabricated from direct cast (DC) slabs (0.3m thick) having a grain size of 200-1000 μm. Twin roll casting (TRC), a prototype process, is offered at 2 to 5 mm thicknesses with 60 to 2000 μm grain sizes and is currently only capable of 432 mm wide sheets. Fabrication from DC or TRC promotes strong texture because of the limited slip systems and twinning occurring in Mg alloys with such large grain sizes. Extrusions formed from such a base source are also textured to the extent that strength is 50% and toughness is 72% in one direction as compared to the cross direction. The grain boundary structure in conventionally prepared Mg alloy is not favorable to complex deformation without premature fracture, unless an elevated forming temperature is used. The pressing and deep drawing of 3-D shapes is limited by the texture and the inherent non-uniform deformation that results from twinning, such as for example, "earring", where shapes resembling ears are formed in portions of the grain microstructure. Although twinning in some directions of the sheet causes increased elongation during tensile testing, twinning is an impediment to the formation of complex parts due to the anisotropy it produces in coarse grain Mg alloy, resulting in anomalies in work hardening and non-uniform deformation. Further, the modeling of forming processes and performance in the dies is not reliable with such non-uniformity in structure. Also, the coarse surface finish of present coarse grain Mg alloys poses a challenge to their acceptance as automotive sheet parts.

To minimize the adverse effects of coarse grains and twinning, conventional wrought alloy processes use multiple rolling and annealing operations until the grain size becomes finer. The TRC product is typically too thin to refine the grain size below 7 μm by such hot processing. The TRC structure also suffers from centerline porosity. Continuous cast Mg alloy may have promise, but currently this technology is not fully developed and many individual pieces of technologies are required for its full implementation, the scope of which is incompatible with small business operations and may not have the flexibility offered by the process of the present invention. Further, the slag and dross of known processes
would be conducive to the attacking of the refractories by the processed material; SF₆ gas (a global warming gas) may be a manufacturing by-product; and trapped inclusions may result from any necessary flux. The many stages involved in breaking down large-grained conventional sheet precursors to produce the sheet form cause current wrought Mg alloys to be expensive, on the order of $5.00 to $10.00/lb.

[0015] As seen from the above, there exists a need for an apparatus and process that can be carried out in a rapid and automated manner so as to change alloy composition and grain structure, thereby allowing such processed alloys to be subsequently worked into net-shaped sheet products.

SUMMARY OF THE INVENTION

[0016] In achieving the above object, the inventors have discovered a practical new process and apparatus to generate inexpensive ultra fine grain structured sheet comprising a magnesium metal alloy, where grain sizes of less than or equal to about 2µm are achieved, which can be subsequently deformed via superplastic forming processes, or any other suitable forming process, to form net shaped, sheet formed articles.

[0017] The present process involves the deformation strain processing of fine grain structured sheets initially formed from various rapid solidification molding methods that can produce an ultra fine grain precursor, including injection molding and variations on injection molding and extrusion molding. Thereafter, the final net shaping of parts can be accomplished by superplastic forming, drawing or stamping, etc. Thus, the present invention provides for the initial formation of a fine grain precursor having a grain size of less than about 10 µm. Thereafter, the fine grain precursor is subjected to deformation straining, which may include for example, tension-compression, compression and/or sine-wave deformation (SWP), which breaks down the microstructure of the precursor and produces new grain boundaries. The resulting sheet has an ultra fine grain structure lending itself to final net shaping by superplastic forming processes. Accordingly, in one aspect the present invention is a method of forming a sheet material having a refined grain structure, the method comprising the steps of: providing a magnesium metal alloy material; molding and rapidly solidifying the metal alloy to form a fine grain precursor, therein molding includes substantially melting the metal alloy material; and imparting plastic deformation to the fine grain precursor by a deformation strain to form an ultra fine grain structured sheet form.

[0018] In another aspect, the fine grain precursor has an isotropic grain structure.

[0019] In another aspect, the step of providing the magnesium metal alloy material and the step of molding and rapidly solidifying are repeated to form a plurality of fine grain precursors and the method further comprises stacking the plurality of fine grain precursors to
form a stack and the step of imparting plastic deformation includes plastically deforming the 
stack by the deformation strain.

[0020] In another aspect, a ratio of a thickness of the stack to a thickness of the ultra 
fine grain structured sheet form is in the range of approximately 3:1 to 30:1. In yet another 
aspect, a ratio of a plan view area of the ultra fine grain structured sheet form to a plan view 
area of the stack is in the range of approximately 3:1 to 30:1.

[0021] It is of further aspect, the step of imparting plastic deformation bonds the fine 
grain precursors together to form the ultra fine grain structured sheet form. Still another 
aspect is that at least two of the fine grain precursors are molded from respectively different 
metal alloys having correspondingly different properties. A further aspect is that at least one 
of the fine grain precursors has comparatively more corrosion resistant than another fine 
grain precursor. In another aspect, at least one of the fine grain precursors has 
comparatively higher elongation than another fine grain precursor. In a further aspect, at 
least one of the fine grain precursors has comparatively higher strength than another fine 
grain precursor. In yet another aspect, reinforcing elements are disposed between the fine 
grain precursors to form a composite ultra fine grain structured sheet form. It is also 
another aspect that the reinforcing elements are selected from the group consisting of 
whiskers, graphite fibers, ceramic fibers, wires, wire mesh and metal fibers.

[0022] In yet another aspect, rapidly solidifying the metal alloy material is at a cooling 
rate of at least 80°C/sec to form the fine grain precursor.

[0023] It is also another aspect the fine grain precursor has a thickness not 
exceeding about 4 mm. Still another aspect is that the fine grain precursor has a total 
porosity not exceeding about 2 percent. A further aspect is that the fine grain precursor has 
a gas porosity not exceeding about 1 percent.

[0024] In another aspect the deformation strain is at a strain rate and the step of 
impacting plastic deformation is performed while the fine grain precursor is heated to a 
temperature, wherein the strain rate, the temperature and the deformation strain cooperate 
to recrystallize the fine grain precursor to the ultra fine grain structured sheet form.

[0025] In a further aspect, the grain structure is recrystallized by a mechanism 
including continuous dynamic recrystallization producing the ultra fine grain structure with at 
least 50 percent high angle boundaries.

[0026] In yet another aspect, the ultra fine grain structured sheet form has an 
intensity of basal (0002) texture not exceeding about 5. In another additional aspect, the 
ultra fine grain structured sheet form has a yield strength anisotropy not exceeding about 10 
percent. In another aspect, the deformation strain rate is in the range of approximately 0.1
to 50s⁻¹. In still another aspect, the temperature is in the range of approximately 150°C to 450°C.

[0027] In another aspect, the strain rate (ε) and the temperature (T) produce a Zener factor (Z) of greater than about 10⁹ s⁻¹ as determined by the formula \( Z = \frac{\epsilon}{\exp(Q/RT)} \), where Q is the activation energy (135kJ mol⁻¹), and R is the gas constant.

[0028] In another aspect, the deformation strain is at least 0.5.

[0029] In yet another aspect, imparting plastic deformation occurs substantially by slip between grain boundaries of the fine grain precursor with less than about 10 percent twinning of the grain structure. In another aspect, imparting plastic deformation occurs without substantial shear banding of the grain structure. In another aspect, the step of molding and solidifying develops a multiphased microstructure in the fine grain precursor. In an additional aspect, the multiphased microstructure includes pinning particles that minimize grain growth.

[0030] In another aspect, the step of imparting plastic deformation includes the step of causing the formation of new grain boundaries having high misorientation suitable for warm forming or superplastic forming.

[0031] In another aspect, the molding step and the imparting plastic deformation step are performed in an integrated apparatus. In still another aspect, the molding step and the imparting plastic deformation step are performed by separate machines. In an additional aspect, the molding step includes semisolid metal injection molding of the metal material. In one aspect, a solids content of the semisolid metal material does not exceed about 30 percent. In another aspect, a solids content of the semisolid metal material does not exceed about 10 percent. In yet another aspect, the semisolid metal injection molding includes delivering the semisolid metal material to a mold via a hot runner system. In still another aspect, a plurality of the fine grain precursors are formed with at least 80 percent production yield. In another aspect, the semisolid metal material is injected with a screw shot velocity of at least 1.5 m/sec. In another aspect, the molding step further includes providing argon gas to the metal alloy material. In a further aspect, the molding step further includes extruding of the metal alloy material. In yet another aspect, the molding step further includes vacuum molding of the metal alloy material.

[0032] It is also an aspect the method further comprises, after the step of imparting plastic deformation, the step of net shaping the nano-sized grain structure sheet. Still another aspect the method further comprises the step of heat treating the net shaped part to impart creep resistance to the net shaped part. A further aspect the step of net shaping includes one of stamping, drawing, deep drawing and superplastic forming. In another aspect, the step of net shaping forms an automotive component.
In a further aspect, an apparatus for performing the method is provided. In yet another aspect, an article formed by the method is provided.

It is also an aspect that the step of imparting plastic deformation includes die pressing of the fine grain precursor. Still another aspect that the step of imparting plastic deformation includes rolling the fine grain precursor. Still another aspect that the step of imparting plastic deformation further includes constraining edges of the fine grain precursor. Still another aspect that the edges of the fine grain precursor are constrained by a Turks Head arrangement.

A further aspect the step of imparting plastic deformation includes rolling the fine grain precursor in a plurality of rolling passes with a plurality of respective deformation strains. In another aspect, the corresponding deformation strain of each rolling pass is at least 50 percent. In a further aspect, the step of rolling includes a first rolling pass at a temperature above ambient, wherein each successive pass is at a lower temperature. In yet another aspect, the plurality of rolling passes are cross rolled.

In an additional aspect, the step of imparting plastic deformation includes extrusion of the fine grain precursor. In another aspect, the step of imparting plastic deformation includes forging of the fine grain precursor. In still another aspect, the step of imparting plastic deformation includes flow forming of the fine grain precursor.

In another aspect, the sheet form is provided having a grain structure of less than about 5 micrometers. In another aspect, the sheet form is provided having a grain structure of less than about 2 micrometers. In yet another aspect, the sheet form is provided having a grain structure of less than about 1 micrometer.

In another aspect, the precursor is provided having a grain structure of less than about 10 micrometer. In another aspect, the precursor is provided having a grain structure of less than about 5 micrometer.

In an additional aspect, the step of imparting plastic deformation is performed while the precursor is heated above ambient.

In still another aspect, the magnesium metal alloy is provided with a moisture content less than about 0.1 percent.

In another aspect, the step of imparting plastic deformation includes plastically deforming the fine grain precursor by a combination of alternating tensile strain and compressive strain to form an SWP sheet, wherein the steps of providing a metal material, molding and rapidly solidifying and plastically deforming are repeated to form a plurality of SWP sheets; stacking the plurality of SWP sheets to form a SWP stack; and plastically compressing the SWP stack to form the ultra fine grain structured sheet form.
In a further aspect, the step of plastically deforming includes corrugating the fine grain precursor in a first direction and subsequently corrugating the fine grain precursor in a second direction. In another aspect, the step of plastically deforming the fine grain precursor further includes flattening the corrugated fine grain precursor. In still another aspect, the compressive strain is imparted at least in part by flattening the work piece while constraining lengthening of the work piece in at least one direction.

In another aspect, an apparatus for refining grain structure and producing ultra-fine grained metal material sheets, wherein the apparatus comprises a receptacle having an inlet, a discharge outlet remote from the inlet, and a chamber defined between the inlet and the discharge outlet; a feeder coupled with the inlet, the feeder configured to introduce a metal material into the chamber via the inlet; a heating device for transferring heat to the metal material located within the chamber such that the metal material is at a temperature above its solidus temperature; discharge means for discharging the metal material from the receptacle through the discharge outlet; forming means for forming and rapidly solidifying the discharged metal material into a fine grained precursor; and plastic deformation means including a pair of opposing forming members for imparting deformation strain into the precursor article forming a sheet of the metal material having an ultra-fine grain size.

In another aspect, the opposed forming members are dies. In further another aspect, the opposed forming members are rolls.

In another aspect, the apparatus further includes means for stacking a plurality of the precursor articles into a stack, and wherein the pair of opposing forming members are configured for imparting deformation strain into the stack to form the sheet of the metal material having the ultra fine grain size.

In another aspect, the plastic deformation means further including means for imparting tensile and compressive strain into the precursor article, the plastic deformation means deforming the precursor article into a corrugated work piece and including a second pair of opposing forming members having protrusions formed on a surface thereof, the protrusions of one second forming member being offset from the protrusions of the opposing second forming member; the plastic deformation means further including flattening means for flattening the corrugated work piece, wherein the stacking means stacks a plurality of the flattened work pieces to form the stack.

In still another aspect, the second opposed forming members are dies. In another aspect, the second opposed forming members are rolls. In an additional aspect, the stacking means further including means for disposing reinforcing elements between the precursor articles. In yet another aspect, the stacking means further includes means for
arranging the precursor articles in a pre-determined position. In another aspect, the apparatus further comprises net shaping means for shaping the sheet form of the metal material into a net-shaped article. In another aspect, the shaping means is one of a drawing press and a superplastic forming machine. In a further aspect, the receptacle, feeder, heating means, discharge means and forming means are part of an injection molding machine. In another aspect, the receptacle, feeder, heating means, discharge means and forming means are part of a semi-solid metal injection molding machine.

BRIEF DESCRIPTION OF THE DRAWINGS

[0048] Figure 1 is a schematic illustration of a manufacturing cell and method embodying the principles of the present invention;

[0049] Figure 2 is a side view of roll dies in accordance with an embodiment of the present invention;

[0050] Figure 3 is a schematic illustration of a manufacturing cell and method embodying the principles of the present invention;

[0051] Figure 4 is a schematic illustration of a manufacturing cell and method embodying the principles of the present invention;

[0052] Figure 5A is a perspective view of the longitudinal roll dies as seen in Figure 4 and used in connection with the present invention;

[0053] Figure 5B is perspective view of transverse roll dies as seen in Figure 4 and used in connection with the present invention;

[0054] Figure 6 is a flowchart of one possible process in accordance with the present invention;

[0055] Figure 7 is a diagrammatic illustration of the present invention incorporating an extrusion device;

[0056] Figure 8 is a graphical comparison of the effect of grain size (d) on hardness (Hr) for SWP AZ91 D and AZ31 B; and

[0057] Figure 9 is a representation of the results of a superplastic bulge test (processed at 280°C and 200 psi) as a function of initial grain.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0058] According to one aspect and embodiment of the present invention, a fine grain precursor is formed by the injection molding (IM) of metal, such as by the Thixomolding™ process of Thixomat, Inc., Ann Arbor, Michigan. With use of this process, melt temperatures can be lowered to near liquidus, some 80 to 100°C lower than in DC or
TRC. These lower temperatures assist in faster cooling to nucleate finer grains upon solidification. As injection molded, Thixomolded™ Mg alloys are isotropic, that is they have a homogeneous microstructure, with 4 to 5 μm grain size α phase. Moreover, these injection molded Mg alloys have non-columnar grains with less gas and shrink porosity. Through the use of multiple feeding ports, the rapid injection molding of large sheet bars is possible. Moreover, a hot runner system may be employed for delivery of the liquid metal to a mold for solidification, which may improve production yields of the large sheet bars. Suitable sheet bar would be readily molded in existing commercial Thixomolding machines, of sizes up to 1000 tons, with sheet dimensions up to about 5 x 400 x 400mm.

[0059] Table 1 compares current production methods to the present invention (IM + SWP and IM + Deformation Straining) for a precursor work piece, such as sheet bar, as well as for a range of resulting grain sizes.

<table>
<thead>
<tr>
<th>Process</th>
<th>Condition</th>
<th>Grain Size (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Direct Cast</td>
<td>As Cast Billet (300 mm)</td>
<td>200</td>
</tr>
<tr>
<td>Direct Cast</td>
<td>Extruded</td>
<td>8-90</td>
</tr>
<tr>
<td>Twin-roll Cast</td>
<td>As Cast (2-5 mm)</td>
<td>60-2000</td>
</tr>
<tr>
<td>Twin-roll Cast</td>
<td>Hot Rolled</td>
<td>7-10</td>
</tr>
<tr>
<td>Injection Molded</td>
<td>As Molded</td>
<td>4-5</td>
</tr>
<tr>
<td>Injection Molded + SWP</td>
<td>As SWP</td>
<td>≤1</td>
</tr>
<tr>
<td>Injection Molded + Deformation Strain</td>
<td>As Deformation Strained</td>
<td>≤1-2</td>
</tr>
</tbody>
</table>

[0060] Referring to Figure 1, this figure schematically illustrates an apparatus, generally designated at 8, embodying the principles of the present invention. The apparatus 8 includes a molding machine 10 for the metal injection molding of sheet bar. As seen in Figure 1, the construction of the molding machine 10 is, in some respects, similar to that of a plastic injection molding machine. The machine 10 is fed with feedstock 11 via a hopper 12 into a heated, reciprocating screw injection system 14, which maintains the feedstock under a protective atmosphere, such as argon. More particularly, the feedstock is received into a barrel 15 via an inlet 16 located at one end of the barrel 15. Within the barrel 15, the feedstock is moved forward by the rotating motion of a screw 18 or other means. As the feedstock is moved forward by the screw 18, it is also heated by heaters 20 (which may be a resistance, induction or other type of heater) while being stirred and sheared by the action of
the screw 18. This heating and shearing is done to bring the feedstock material into a substantially melted state such that the feedstock material is injectable. This injectable material passes through a non-return valve 22 and into an accumulation zone 24, located within the barrel 15 beyond the forward end of the screw 18. Upon accumulation of the needed amount of injectable material in the accumulation zone 24, the injection portion of the cycle is initiated by advancing the screw 18 with a hydraulic or other actuator 25. Advancement of the screw 18 causes the material in the accumulation chamber 24 to be ejected through a nozzle 26 into a mold 28 filling, the mold cavity defined thereby and forming a precursor work piece such as sheet bar 30. In at least one embodiment, the screw 18 shot velocity is at least 1.5 meters/second. A hot runner system (not shown) may optionally be used to assist delivery of the material to the mold cavity thereby minimizing any heat loss. Moreover, because this process may result in a "frozen plug", that is the metal solidifies where the mold receives the injectable material, pulling a vacuum on the mold during molding is feasible and may further be used to decrease resulting porosity of the sheet bar 30. This initial formation of the precursor allows developing of a multiphase microstructure with pinning particles or phases to pin grain boundaries to minimize grain growth.

[0061] In one preferred embodiment, the metallurgical process of the machine 10 results in the processing of the particulate feedstock into a solid plus liquid phase prior to its injection into the mold 28. Various versions of this basic process are known and two such versions are disclosed in U.S. Patent Nos. 4,694,881 and 4,694,882, which are herein incorporated by reference. The process generally involves the shearing of the semisolid metal so as to inhibit the growth of dendritic solids and to produce non-dendritic solids within a slurry having improved molding characteristics which result, in part, from its thixotropic properties. (A semisolid non-dendritic material exhibits a viscosity that is proportional to the applied shear rate and which is lower than that of the same alloy when in a dendritic state). Variations on this process of forming the sheet bar 30 may include providing the alloy material initially in a form other than a particulate; heating the alloy material to an all liquid phase and subsequently cooling into the solid plus liquid phase; employing separate vessels for processing of the alloy and injecting of the alloy; utilizing gravity or other mechanisms to advance the alloy through the barrel to the accumulation zone; alternate feeding mechanism, including electromagnetic; and other variations on the process.

[0062] In another preferred embodiment, metallurgical process of the machine 10 results in the processing of the particulate feedstock into an all liquid phase that is injected into the mold 28 and rapidly solidified.
[0063] In another preferred embodiment, the liquid phase material in the mold is rapidly solidified at a cooling rate of at least 80°C/second.

[0064] In another preferred embodiment, the sheet bar 30 has a thickness not exceeding about 4 mm.

[0065] In another preferred embodiment, metallurgical process of the machine 10 results in the sheet bar 30 having a total porosity not exceeding about 2 percent. The total porosity comprises both a shrinkage porosity, which is derived from shrinkage of the metal, and a gas porosity. Shrinkage porosity comprises voids which are more linear or flattened shaped and formed in the eutectic regions around the grain boundaries, whereas gas porosity comprises voids which are more spherically shaped and formed between the grain boundaries.

[0066] In another preferred embodiment, the protective argon atmosphere with a feedstock moisture content of less than about 0.1 percent, minimize gas porosity to not exceed 1 percent with minimal formation of oxides.

[0067] Once the fine grained sheet bar 30 is formed, it is subjected to a deformation strain. The deformation strain may be, for example, a tensile-compressive strain, a compressive strain or a strain or combination of strains otherwise defined by a strain tensor or tensors. In at least one other embodiment, the deformation strain involves imparting plastic deformation by at least compressively straining the sheet bar 30. This second step of deformation straining permits storage of dislocations within the microstructure, which leads to the formation of new grain boundaries with high misorientation suitable for subsequent warm forming or superplastic forming.

[0068] In one implementation of this deformation process, the sheet bar 30 is heated to a temperature during deformation straining at a strain rate. The temperature in combination with the deformation strain and the strain rate cooperate to recrystallize the grain structure to an ultra fine grain structure. This recrystallization may include a continuous dynamic recrystallization mechanism producing at least 50 percent high angle grain boundaries and an intensity of basal (0002) texture not exceeding about 5. Moreover, the strain rate ($\dot{\varepsilon}$) and the temperature (T) preferably produce a Zener factor (Z) of greater than about $10^9$ s$^{-1}$ as determined by the formula $Z = \{\dot{\varepsilon} \exp(Q/RT)\}^{1/2}$, where Q is the activation energy (135kJ mol$^{-1}$), and R is the gas constant.

[0069] In at least one embodiment, the deformation strain rate is in the range of approximately 0.1 to 50s$^{-1}$. The temperature of the sheet bar 30 during deformation straining may be in the range of approximately 150C to 450C and further, the deformation strain may be at least 0.5. The deformation strain may further plastically deform the sheet bar by predominately a slip mechanism of the grain microstructure with less than 10% twinning and substantially no shear banding.
In one further implementation of this deformation process, the precursor is subjected to shaping of the material between a pair of corresponding members having forming surfaces. The shape of the forming surfaces imparts a large strain or strains, breaking down the cast microstructure and producing new grain boundaries in the precursor. Beginning with the sheet bar, initially formed so as to have a fine grain structure of 10 µm or less, this precursor work piece is then shaped, for example, compressively into a thinner flattened piece, between two forming members having corresponding smooth forming surfaces. Preferably, the deformation process is conducted at a warm temperature and the temperature of the material is progressively lowered if any additionally passes between the forming surfaces occurs.

Various schemes can be envisioned for deforming the sheet bar 30. The sheet bar 30 may be passed through a rolling mill 200 having at least a first set of matching rolls 202 or a series of matching rolls (not shown) or opposing pressing dies (not shown), any of which may be heated. Also, the deformation process may be performed separately from the formation of the sheet bar 30 or may be integrated directly into the processing cell whereby the apparatus 8 is provided with a transfer mechanism (which may be any known variety and which is represented by line 204) to transfer the sheet bar 30 from the mold 28 to a rolling or pressing mill 200.

In the illustrated rolling mill 200, the sheet bar 30 is passed through at least one set 202 of opposed rollers 206. The surfaces 208 of the rollers 206 are each designed to compressively flatten the sheet bar 30. To achieve this, the rolls 206 may be provided with smooth surfaces 208 that engage and compress the sheet bar 30 as it passes between the rollers 206. The rolls 202 or roll sets may be impressed towards each other by backup rolls 33 (shown in phantom) as is commonly known.

Referring to Figure 2, alternatively, the opposed rollers may be part of a flow forming arrangement 230. The flow forming arrangement 230 may comprise of a first roll 232 having a first shape 234 and/or a second shape 236. The work piece 30 may be plastically deformed against the first roll 232 to form an ultra fine grained shaped piece 238 by being spin formed and impressed thereon by a second roll 240, which travels from a first end 242 to a second end 244 of the first roll 232. Such a technique, generally referred to as flow forming, may be used to produce, for example, cylindrical shapes.

In at least one embodiment, lateral expansion of the sheet bar is constrained. This may be achieved, referring back to Figure 1, by one of the rolls, for example, the lower roll 206, providing raised lands 210 on the opposing ends of the roll 206. The raised lands 210 are matched with the ends of the upper roll 206 in such a way to constraint the sheet bar 30 from expanding laterally beyond the lands 210 of the rolls 206. Moreover, by adjusting the
lateral position and constrain provided by the lands 210 of the rolls 206, the thickness of the resulting sheetstock material 212 can be controlled in relation to the original thickness of the sheet bar 30.

[0075] Alternatively, a Turks Head arrangement (not shown) may be used to constrain edges of the sheet bar 30. A Turks Head arrangement utilizes two or more pairs of rolls, one pair is arranged vertically and the other pair horizontally. The vertical rolls are spaced apart with the sheet bar 30 disposed between them such that the edges of the sheet bar 30 contact the vertical rolls, which limit the expansion, while the horizontal rolls compress and flatten the sheet bar 30.

[0076] In at least one other embodiment, the work piece 30 passes through the first set of rolls 202 and is received by a second set of rolls (not shown), which may have a substantially smooth surface similar to the surfaces 208 of the first set of rolls 202. The second set of rolls further flattens the work piece 30 by imparting a deformation strain. Additional set of rolls (not shown), subsequent to the second set of rolls, may be used to further flatten the work piece by imparting additional deformation strains. In at least another embodiment, the work piece 30 is rotated between progressive rolls sets, such as for example, rotating the work piece 30 ninety degrees subsequent to passing the first set of rolls 202, but prior to being received by the second set of rolls.

[0077] Referring to Figure 3., at least one other embodiment is provided. In this embodiment a set of the sheet bars 30 are stacked 250, wherein the stack 250 is subjected to a deformation strain. The stack 250 of sheet bars 30, which now form layers, may be passed through the rolling mill 200. Again, the deformation process may be performed separately from the formation of the sheet bar 30 or may be integrated directly into the processing cell whereby the apparatus 8 is provided with a transfer mechanism 252, which may be any known variety, such as for example, a robotic or rail-gantry arrangement, to transfer the sheet bars 30 from the mold 28 to the stack 250 and thereto the rolling or pressing mill 200.

[0078] In at least another embodiment, the stack 250 is plastically deformed by the rolling or pressing mill 200, which bonds the sheet bar layers 30 together. In one embodiment, the bonding process occurs from friction strain welding of the sheet bar layers 30.

[0079] Moreover, reinforcing elements may be disposed between any of the sheet bar layers 30 to provide a composite structure. For example, reinforcing elements selected from the group consisting of whiskers, graphite fibers, ceramic fibers, wires, wire mesh and metal fibers may be disposed between two of more sheets bar layers 30 by any suitable automated process, such as by a robotic or rail-gantry arrangement, or a manual process during stacking of the layers 30. Then when the stack 250 is plastically deformed by the rolling or pressing mill 200, the sheet bar layers 30 bond together including the reinforcing
elements, wherein the reinforcing elements provide an enhanced load bearing function to the composite sheet 212.

Alternatively, properties of the sheet 212 may be enhanced by using selectively placed sheet bar layers 30 within the stack 250, wherein the sheet bar layers 30 are molded from respectively different metal alloys having correspondingly different properties. For example, the stack 250 may comprise a top and/or bottom sheet bar layer 30 which is molded from a metal alloy material having high corrosion resistance, such as for example, to a salt spray. Moreover, the stack 250 may comprise other sheet bar layers 30 which are molded from metal alloy materials having higher yield and/or ultimate strength and/or higher elongation. The stacking of these layers 30 may be in a predetermined manner so as to adjust the properties of the finished sheet 212 to a desired performance. For example, a controller, or other device capable of performing logical sequences, may be programmed accordingly and interface with a robotic or rail-gantry arrangement which performs automated stacking of these layers 30 in a specific order.

As an alternative scheme for deforming the sheet bar 30 or the stack 250, at least one set of pressing plates (not shown) may be used in place of the rolling mill 200. The plates may also be provided with smooth, substantially flat surfaces or any other suitable contour, which compressively deforms the sheet bar 30 or stack 250.

Referring to Figure 4, at least one other embodiment is provided. The finished sheet may include layers formed from an SWP process, which were stacked and subjected to deformation straining. The SWP process involves the imparting of plastic deformation by a combination of alternating tensile and compressive strains or deformations. This step of deformation straining also permits storage of dislocations within the microstructure, which leads to the formation of new grain boundaries with high misorientation.

In one implementation of the SWP process, the precursor is subjected to repeated shaping of the material between a pair of corresponding members having corrugated or sine-wave shaped forming surfaces. The shape of the forming surfaces imparts large strain, breakdown the cast microstructure and producing new grain boundaries in the precursor. Beginning with sheet bar 30, initially formed so as to have a fine grain structure of 10 μm or less, this precursor work piece is then shaped, with or without lateral constraint, between two members having corresponding corrugated forming surfaces, in what is essentially a plane-strain stretch-bend operation. After the first shaping, the work piece is again shaped. During this second shaping, however, the corrugations are preferably, but not necessarily, oriented in a direction different from the corrugations of the first shaping. An orthogonal orientation for the second shaping is believed to produce the best end results. Preferably, the two shaping steps are then repeated with the corrugations
in these third and fourth steps being the inverse of those seen in the first two shaping steps. By the term inverse, what is meant is that the ridges and valleys of the third corrugation are reversed or out of phase from the ridges and grooves of the first corrugations. Thus, these subsequent shaping cause a reverse deformation (pushing in the opposite direction) of ridges resulting after the first two shapings. After all four shaping steps, and additional shaping steps if desired, the work piece is preferably flattened to remove any waviness to the shape.

Preferably, SWP is conducted at a warm temperature and the deformation temperature of the material is progressively lowered after each pass, for example, starting at 350°C and decreasing to 170°C for the final flattening step. This can be achieved in several ways, including providing heated shaping members or rolls, as described below.

As seen in Figure 4, the sheet bar 30 is passed through a first set 332 of opposed corrugated rolls 334. The surfaces of the rolls 334 are each provided with corrugations 336 extending circumferentially about the rolls 334. The corrugations 336 of each roll 334 generally correspond with respect to one another such that a ridge on one of the rolls 334 is received in a valley of the opposing rolls 334. As the sheet bar 30 passes through the first set 332 of rolls 334 a lengthwise corrugation, parallel to the direction of travel of the sheet bar 30, is imparted into the sheet bar 30. This results in a sine wave shape being imparted to the work piece that is oriented in a direction orthogonal to the direction in which the work piece is passed through the rolling mill 331. Accordingly, the induced strains, tensile and thereafter compressive, will be generally in the direction of the sine wave shape itself.

Having been corrugated or worked by the first set 332 of rolls 334, the worked sheet bar or work piece is passed to a second set 340 of rolls 342. Upon encountering this second set 340 of rolls 342, the work piece encounters corrugations 344 that are oriented orthogonally, 90 degrees from the corrugations 336 of the first set 332 of rolls 334. As such, the corrugations 344 are oriented axially with respect to the rolls 342 and transverse with regard to the direction of travel of the sheet bar 30. As with the prior set 332 of rolls 334, the corrugations 344 of the second set 340 of rolls 342 are provided such that the ridge of a corrugation on the upper roll 342 is received within the valley of a corrugation 344 of the lower roll 342.

From the second set 340 of rollers 342, the worked sheet bar is passed in the illustrated rolling mill 331 between a third set 348 of rolls 350 designed to flatten the worked sheet bar. The rolls 350 may be provided with smooth surfaces 352 that engage and compress the worked sheet bar as it passes between the rolls 350. As the work piece is flattened, compressive strain is imparted to the work piece to form an SWP sheet stock material 378. The rolls 340 and 350 are shown in more detail in Figures 5A and 5B.
As thus far described, SWP occurs generally according to the process illustrated by the flowchart of Figure 6. As shown therein, SWP starts at box 366 wherein a sheet bar 30 is received and subjected to corrugating in a lengthwise or parallel direction in box 368. After lengthwise corrugating of the sheet bar 30, the work piece undergoes transverse corrugation in box 370 and subsequently is flattened as indicated in box 372. After being flattened in box 372, the lengthwise and transverse corrugating of the work piece may be repeated as indicated by line 374. Optionally, as indicated by phantom line 376, the work piece can undergo subsequent lengthwise and transverse corrugation prior to being flattened in box 372. However, it is believed to be preferable that flattening according to box 372 occurs prior to subsequent corrugation of the work piece. After proceeding through the corrugation process wherein both lengthwise and transverse corrugation occurs twice (thus corrugating of the work piece four times) the work piece is finally flattened in box 372 and flat sheetstock material 378 is outputted and the process ends in box 380.

As illustrated in Figure 4, a stack 380 of SWP sheet stock material 378 may be passed through the rolling mill 200 to form the ultra-fine grain finished sheet 212. Again, the deformation straining process may be performed separately from the formation of the sheet bar 30 or may be integrated directly into the processing cell whereby the apparatus 8 is provided with a transfer mechanisms 329, 382, which may be any known variety, such as for example, a robotic or rail-gantry arrangement, to transfer the sheet bars 30 from the mold 28 to the SWP rolling process 331 to the stack 380 and thereto the rolling or pressing mill 200.

As previously mentioned, various schemes for the manufacturing of the initial precursor, the sheet bar 30 discussed above, are believed possible if proper and precise control of the manufacturing process and rapid solidification thereof is done. Figures 7 schematically illustrates an additional manufacturing scheme wherein the injection molding machine 10 of the first embodiment is alternately replaced with an extrusion machine 400.

The extrusion machine 400 includes a barrel 402 within which is located a screw 404. In that the other components of an extrusion machine are well known to those skilled in the art, additional discussion of the extrusion machine 400 is not provided herein. Material is extruded from the extrusion machine 400 and rapidly solidified between a pair of molds 406 such that a continuous sheet of solid material is transferred from the extrusion machine to the rolling mill 408. By precisely controlling the process of the extrusion machine, it is believed that the required fine grained microstructure can be achieved in a continuous sheet, which operates as the precursor material into the rolling mill 408 in accordance with the present invention. The rolling mill 408 illustrated in Figure 7 is similar to
either the rolling mill 200 or 331 discussed in connection with the prior embodiments. Accordingly, reference is hereby made thereto and further discussion is not required.

[0092] With a 5 x 400 x 400 mm sheet bar 30 as the precursor, the foregoing described processes can reduce the thickness of the sheet to about 1 to 2 mm, wherein the final sheet dimensions could be 1250 x 1250 mm. In at least one embodiment, the stack of precursors is reduced in thickness, such that, the ratio of the thickness of the stack to the thickness of the final sheet is in the range of approximately 3:1 to 30:1. Additionally, a ratio of a plan view (top view) area of the final sheet to a plan view area of the stack is in the range of approximately 3:1 to 30:1.

[0093] When an integrated automated manufacturing cell, such as one of those previously described, combines the rapid solidification of metal injection molding with the deformation straining process as part of the same manufacturing cycle, the rate of production in one machine is anticipated to be about 1 sheet bar per 20 seconds. Moreover, because of the fine grain microstructure of the sheet bar, production yields of at least 80 percent are also anticipated.

[0094] As would be surmised from the preceding discussion of the invention, the as-molded grain size and α content of an injection molded metal sheet bar is a favorable starting point to attaining sub-micron grain size and low-anisotropy, typically not exceeding 10 percent in yield strength, in the subsequently plastically deformed sheet. It appears that the deformation straining process, with its vigorous thermomechanical working, subdivides intermetallic particles into nano-sizes, and, probably, encourages partial solution and more homogeneous reprecipitation of fine arrays within the grains. Some sub-divided residual β phase could serve to pin grain boundaries during dynamic recrystallization and heat treatment. The subdividing of this inherently coarse β phase is beneficial to the ductility of Mg alloys. More specifically, by minimizing twinning to less than about 10 percent, deformation occurs substantially by slip in the grain and grain boundaries without substantial shear banding, resulting in a more ductile alloy.

[0095] The aforementioned β phase effect is but one aspect of the new opportunities to redesign Mg for this new process. The literature is replete with new Mg alloying discoveries that have yet to be applied to a low cost sheet form. These alloying additions are easily reduced to sheet form by the present invention, especially utilizing "blending" techniques. Such alloying additions as Ca, Sr, Y, Zr and Zn-Y can boost the modest strength of the commercial sheet alloy AZ31. Additionally, the large melts and alloy cross contamination, which are inherent in DC and TRC, can be avoided by using the above mentioned injection molding deformation straining process. Purging of the previous alloy and addition of granules of new blends can be accomplished in minutes in an injection
molding machine, without the wasted crucible charges, slag and dross typically associated with DC or TRC operations.

[0096] Ductility during warm temperature stamping (and superplastic forming) of metals is enhanced by the presence of many grain boundaries, but grain boundaries developed from current casting processes are unsuitable for forming applications because they do not permit rolling or sliding between grains. Grain boundary character has a major effect on the phenomena of sliding and shearing properties of grain boundaries during deformation. Even at modestly elevated temperatures (150-200°C), Mg alloys can be formed easily by warm forming processes, provided they have a fine grain structure (about 1-3 µm) and favorable grain boundaries produced by deformation processing. While forming of an alloy at room temperature is preferred, 150-200°C temperatures are not unusual for inexpensive forming applications (plastics are often formed at such temperatures). Unlike plastics however, Mg parts can be heat treated to grow larger grain size and become creep resistant, or can be alloyed appropriately to make them creep resistant. Low temperature forming can however keep energy usage low during forming and avoid undesirable oxidation encountered during the superplastic forming process.

[0097] The rapid solidification during the injection molding process provides a fine grain structure that does not exhibit twinning during subsequent deformation. However, grain boundaries created from the liquid state are crystallographically related, and may possess "special" boundaries that do not permit grain boundary sliding. Special boundaries may have high misorientation angles, but they could have a significant fraction of coincident lattice sites (CSL) and low grain boundary energies to make sliding difficult. While the strain contributed by grain boundary sliding is not large during warm forming, if it is capable of providing accommodation locally, it prevents fracture of the material along grain boundaries. Thus, the boundaries required for enhanced formability must not be those produced by the casting process, but those generated by the plastic working process. The plastic working generates additional dislocations near the grain boundaries and renders then into configurations of higher disorder or higher energy, suitable for enhanced formability.

[0098] Extensive deformation of injection molded material and the like, to change grain boundary character, requires the extensive deformation process that is accomplished in the present approach. The other approaches available for such extensive deformation (e.g. ECAP, high pressure torsion), do not appear suitable for commercial scale-up, nor can they be easily automated for producing thin, wide sheets.

[0099] Accordingly, via the present invention, an end resultant can be produced, by initially providing a net-shape sheet bar alloy with a uniform microstructure and an original fine grain size of less than 10 µm through rapid cooling during forming, with minimum
segregation through the thickness of the material. This can be achieved by various forming methods including injection molding and other variations on injection molding, including semi-solid metal injection molding, and extrusion molding. Afterward, the microstructure is refined to a nano-structure by processing the sheet into an untextured sheet that exhibits superior formability. This can be achieved by hot-pressing, rolling or other processes utilizing appropriately shaped surfaces in the dies as previously discussed. The final net-shaped part is thereby after formed by either superplastic forming (SPF), warm drawing, warm stamping or other methods. (Initial grain size may be reduced to lower the SPF working stress, to lower the SPF temperature for better surface finishes, and to raise the SPF rate.) Once the net-shaped part is formed, optional heat treating (annealing, etc.) may be done to the final part to grow the grains so as to stop SPF and to impart creep resistance to the final article. As a result, what is attained is an inexpensive, light-weight part with very high strength to weight ratio, along with enhanced toughness.

[00100] As seen above, the process starts with un-textured sheet alloy having a fine grain size of less than 10 µm. However, the sheet alloy may be two phase and/or include high-angle grain boundaries; the former to control grain growth, promote grain boundary shear during SPF and strengthen the final part, and the latter to promote final net shaping and decrease texture. In refining the microstructure to obtain a grain size of about 1 micron, severe slip deformation is imparted to generate simultaneous recrystallization to micron-sized grains faced with high-angle grain boundaries. Thereafter, the coarse second phases are further sub-divided and/or reprecipitated into nano-sized arrays. In the above, twinning and the generation of textures are both minimized.

[00101] As an example, a commercial AZ31B Mg alloy, notably not semi-solid injection molded, in the form of hot-rolled plate, with thickness of 6.35 mm, was used as a precursor material work piece. The chemical composition of this alloy is 3.0 wt% Al, 1.0 wt% Zn, 0.45 wt% Mn and the balance Mg. An 89 x 89 mm square work piece was cut from the as-received plate, and then processed by SWP as described above. The initial bimodal structure of the as-received alloy was refined into a nearly uniform ultrafine grain structure. The bimodality of the initial structure and its change toward a more uniform structure were characterized by a detailed grain size distribution analysis using known computer image analysis software. Based on image analysis, the initial bimodal microstructure of the as-received alloy contains 31% area fraction of coarse grains of size 22.1 µm, but has an average grain size of 9.8 µm. The final microstructure after SWP had an average grain size of 1.4 µm, which contained less than 3% area fraction of coarse grains.
[00102] Mechanical properties of AZ31B Mg alloy for different alloy processing conditions at room temperature are presented in Table 2 in terms of strength, elongations (including uniform and post-uniform elongations), and normal anisotropy ratio (R).

<table>
<thead>
<tr>
<th>AZ31B Mg Alloy (room temperature)</th>
<th>Tensile yield strength, MPa</th>
<th>Ultimate tensile strength, MPa</th>
<th>Elongation* %</th>
<th>ε_u** %</th>
<th>ε_p** %</th>
<th>Normal Anisotropy Ratio (R)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-Received #</td>
<td>160</td>
<td>274</td>
<td>13.0 (13.5)</td>
<td>11.9</td>
<td>1.1</td>
<td>3.8</td>
</tr>
<tr>
<td>As-Processed</td>
<td>280</td>
<td>308</td>
<td>22.6 (29.0)</td>
<td>8.4</td>
<td>14.2</td>
<td>6.0</td>
</tr>
<tr>
<td>As-Processed + Annealed at 250°C</td>
<td>218</td>
<td>271</td>
<td>24.4 (32.3)</td>
<td>13.4</td>
<td>11.1</td>
<td>5.0</td>
</tr>
</tbody>
</table>

* Reported elongation is over 12.7 mm gauge length. A shorter gauge length of 5.0mm gives a higher value of elongation shown in the parenthesis.

** ε_u and ε_p refer to uniform strain and post-uniform strain, respectively.

# For the as-received material, mechanical test data are from interior region of plate (fine grain region)

[00103] Table 2 shows that the fine grain as-processed alloy has improved mechanical properties such as higher tensile yield strength and higher post-uniform elongation, and higher (R) value. Annealing increases tensile elongation values further. When examined for microstructural changes, no twinning was observed in the processed material. Further, the as-received alloy displayed a rough surface similar to "orange peel" white effect, the fine grain processed alloy exhibited a smooth surface after the test. In addition, the degree of necking is found more gradual in the as-processed alloy.

[00104] For comparison, an Mg-9Al alloy (AZ91D) sheet bar measuring 100 x 150 x 3 mm was semi-solid metal injection molded in a commercial 280 ton Thixomolding® machine at Thixomat, Inc. (Ann Arbor, Michigan). This sheet bar was pressed at 190°C between opposing sine-wave dies having a corrugated surface pattern through 4 cycles, turning the sheet 90° between cycles. The sheet was press flattened after the 4th pressing cycle. The
total reduction of thickness was from 3 mm to 0.8 mm, i.e. 73%. The resultant tensile strengths are compared to commercial AZ31 (Mg-3Al) sheet in Table 3.

Table 3

<table>
<thead>
<tr>
<th>Material</th>
<th>0.2% YS, MPa</th>
<th>UTS, MPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>AZ91D, as injection molded sheet bar</td>
<td>150</td>
<td>220</td>
</tr>
<tr>
<td>AZ91D, SWP 4 Cycles</td>
<td>260</td>
<td>300</td>
</tr>
<tr>
<td>AZ31, commercial sheet*</td>
<td>150</td>
<td>255</td>
</tr>
</tbody>
</table>

*ASM Handbook

As seen from Table 3, yield strength was increased by 73% compared to the original sheet bar and the commercial AZ31. Ultimate tensile strength was respectively increased 36% and 18%.

This resultant SWP sheet was then annealed at 150 or 250°C. Hardness of the fine grained material derived from the original liquid phase in the as-semi-solid metal injection molded, SWP, SWP + rolled/annealed state were measured and the results are presented in Table 4.

Table 4

<table>
<thead>
<tr>
<th>Material</th>
<th>Microhardness, MPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>AZ91D, as SS MI molded, 5 μm grain size</td>
<td>772</td>
</tr>
<tr>
<td>AZ91D, SWP</td>
<td>932</td>
</tr>
<tr>
<td>AZ91D, SWP + Annealed @ 150°C</td>
<td>958</td>
</tr>
<tr>
<td>AZ91D, SWP + Annealed @ 250°C</td>
<td>858</td>
</tr>
<tr>
<td>AZ31, commercial sheet, 10 μm grain size</td>
<td>600</td>
</tr>
<tr>
<td>AZ31, commercial sheet, 1 μm grain size</td>
<td>720</td>
</tr>
</tbody>
</table>

The fine grained original liquid region of the as semi-solid metal injection molded sheet bar had a 772 MPa hardness, which was increased to 932 MPa by SWP. Annealing at 150°C increased the hardness further to 958 MPa. Compared to previous data from AZ31, as presented in the graph of Figure 8, the SWP material from AZ91D was harder than equivalent grain size AZ31. Part of this hardness increment over AZ31 is believed attributable to nano-size β phase in the Al rich AZ91D alloy. Microstructures confirmed that
the coarse β phase of the starting material had been sub-divided and reprecipitated as nanoparticles, some at grain boundaries.

[00108] The feasibility of SPF of the SWP sheet has also been demonstrated by the inventors. As Figure 9 demonstrates, the depth of cup produced via a bulge test of the SWP AZ91D is deeper than that of a sheet (of corresponding thickness) of the starting material formed by Thixomolding (semi-solid metal injection molding process of Thixomat, Inc., Ann Arbor, Michigan) only. In fact, the depth is much greater than that formed in commercial 10-20 μm AZ31 sheet.

[00109] In another example, AM60 magnesium alloy was semi-solid injection molded in the commercial Thixomolding ® machine to produce 3X50X1 50mm sheet bars. The bars were heated to 375°C and rolled in a mill in both stacked and un-stacked arrangements. Table 5 provides the results of these tests.

<table>
<thead>
<tr>
<th>Number of Bars in the Stack</th>
<th>Percentage Reduction</th>
<th>Separation Force (PSI)</th>
<th>Number of Passes</th>
<th>RPM of Rollers</th>
<th>Bonding</th>
<th>Grain Size (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>58</td>
<td>81,000</td>
<td>1</td>
<td>45</td>
<td>--</td>
<td>2-3</td>
</tr>
<tr>
<td>2</td>
<td>76</td>
<td>98,000</td>
<td>1</td>
<td>45</td>
<td>Excellent</td>
<td>1-2</td>
</tr>
<tr>
<td>5</td>
<td>85</td>
<td>140,000</td>
<td>1</td>
<td>Slow</td>
<td>Excellent</td>
<td>1-2</td>
</tr>
<tr>
<td>1</td>
<td>42</td>
<td>64,000</td>
<td>1</td>
<td>45</td>
<td>--</td>
<td>2-3</td>
</tr>
<tr>
<td>3</td>
<td>81</td>
<td>114,000</td>
<td>1</td>
<td>45</td>
<td>Excellent</td>
<td>1-2</td>
</tr>
</tbody>
</table>

[00110] As illustrated in Table 5, in cases with 76 percent reduction or greater, an ultra-fine grain microstructure was achieved as well as excellent bonding between the sheet bar layers of the stacked samples.

[00111] Potential markets for products manufactured by the present invention are envisioned in the automotive and aerospace fields, among others, where weight savings can be gained by replacing steel and aluminum with magnesium. Complex 3-D net-shapes can be SPF to greatly reduce the number of sub-assemblies and the costs of multiple fabrication and assembly. High tensile strength and high toughness will be attained by sub-micron grain sizes, second phase nanocrystals and by the selection of ductile alloys. The unique microstructure so attained will greatly reduce texture and its usual barrier to formability.

[00112] Automobile companies are predicting very significant increases in Mg tonnage for automotive vehicles, as much growth as from 5 Kg/car up to 200 Kg/car. There
is a need to enable the United States automotive industry to lead this sea change in light-weighting. Additional markets should further open in the aerospace, defense and other industries.

[0013] Deformation strain processing of suitable alloys should reduce the cost of making thin sheet material by eliminating multiple stages of rolling and annealing. This process changes the grain boundary character and increases the ability to be formed by warm forming or superplastic deformation. If deformation strain processing is carried out immediately following injection molding, the sensible heat in the molded blank can be utilized. Following immediate rolling or pressing of the sheet bar, it can be formed by SPF into complex part shapes. Such forming can be accomplished at 200°C. Thus, the entire component fabrication technology can be set into a continuous operation without storage of coils of sheets, considerable coil annealing, coiling and uncoiling operations. The removal of all of the steps involved with coiling and cranes handling transport of coils would minimize investment in plants. A leaner manufacturing process for parts would emerge.

[0014] It is envisioned that the deformation strain processing can be accomplished by integrating injection molding machines for metal with conventional pressing and rolling equipment and should be feasible on process equipment already used in the aerospace and automotive industries. Deep drawing also can be practiced on conventional presses.

[0015] As a person skilled in the art will readily appreciate, the above description is meant as an illustration of implementations of the principles of this invention. This description is not intended to limit the scope or application of this invention in that the invention is susceptible to modification, variation and change, without departing from spirit of this invention, as defined in the following claims.
CLAIMS

1. A method of forming a sheet material having a refined grain structure, the method comprising:
   providing a magnesium metal alloy material;
   molding and rapidly solidifying the metal alloy material to form a fine grain precursor having a grain structure of less than 10 micrometers, wherein molding includes substantially melting the metal alloy material; and
   imparting plastic deformation to the fine grain precursor by a deformation strain to form an ultra fine grain structured sheet form having a grain structure of less than 5 micrometers.

2. The method of claim 1 wherein the fine grain precursor has an isotropic grain structure.

3. The method of claim 1 wherein the step of providing the magnesium metal alloy material and the step of molding and rapidly solidifying are repeated to form a plurality of fine grain precursors and the method further comprises stacking the plurality of fine grain precursors to form a stack and the step of imparting plastic deformation includes plastically deforming the stack by the deformation strain.

4. The method of claim 3 wherein a ratio of a thickness of the stack to a thickness of the ultra fine grain structured sheet form is in the range of 3:1 to 30:1.

5. The method of claim 3 wherein a ratio of a plan view area of the ultra fine grain structured sheet form to a plan view area of the stack is in the range of 3:1 to 30:1.

6. The method of claim 3 wherein the step of imparting plastic deformation bonds the fine grain precursors together to form the ultra fine grain structured sheet form.

7. The method of claim 3 wherein at least two of the fine grain precursors are molded from respectively different metal alloys having correspondingly different properties.

8. The method of claim 7 wherein at least one of the fine grain precursors has comparatively more corrosion resistant than another fine grain precursor.
9. The method of claim 7 wherein at least one of the fine grain precursors has comparatively higher elongation than another fine grain precursor.

10. The method of claim 7 wherein at least one of the fine grain precursors has comparatively higher strength than another fine grain precursor.

11. The method of claim 6 wherein reinforcing elements are disposed between the fine grain precursors to form a composite ultra fine grain structured sheet form.

12. The method of claim 11 wherein the reinforcing elements are selected from the group consisting of whiskers, graphite fibers, ceramic fibers, wires, wire mesh and metal fibers.

13. The method of claim 1 wherein rapidly solidifying the metal alloy material is at a cooling rate of at least 80C/sec to form the fine grain precursor.

14. The method of claim 1 wherein the fine grain precursor has a thickness not exceeding 4 mm.

15. The method of claim 1 wherein the fine grain precursor has a total porosity not exceeding 2 percent.

16. The method of claim 1 wherein the fine grain precursor has a gas porosity not exceeding 1 percent.

17. The method of claim 1 wherein the deformation strain is at a strain rate and the step of imparting plastic deformation is performed while the fine grain precursor is heated to a temperature, wherein the strain rate, the temperature and the deformation strain cooperate to recrystallize the fine grain precursor to the ultra fine grain structured sheet form.

18. The method of claim 17 wherein the fine grain precursor is recrystallized by a mechanism including continuous dynamic recrystallization producing the ultra fine grain structured sheet form with at least 50 percent high angle boundaries.

19. The method of claim 17 wherein the ultra fine grain structured sheet form has an intensity of basal [0002] texture not exceeding about 5.
20. The method of claim 17 wherein the ultra fine grain structured sheet form has a yield strength anisotropy not exceeding about 10 percent.

21. The method of claim 17 wherein the strain rate is in the range of approximately 0.1 to 50s⁻¹.

22. The method of claim 17 wherein the temperature is in the range of approximately 150°C to 450°C.

23. The method of claim 17 wherein the strain rate (ε) and the temperature (T) produce a Zener factor (Z) of greater than about 10⁹ s⁻¹ as determined by the formula

$$Z = \left( \frac{\varepsilon}{\exp(Q/RT)} \right)^{-2},$$

where Q is the activation energy (135kJ mol⁻¹), and R is the gas constant.

24. The method of claim 17 wherein the deformation strain is at least 0.5.

25. The method of claim 17 wherein imparting plastic deformation occurs substantially by slip between grain boundaries of the fine grain precursor with less than about 10 percent twinning of the grain structure.

26. The method of claim 17 wherein imparting plastic deformation occurs without substantial shear banding of the grain structure.

27. The method of claim 1 wherein the step of molding and solidifying develops a multiphased microstructure in the fine grain precursor.

28. The method of claim 27 wherein the multiphased microstructure includes pinning particles that minimize grain growth.

29. The method of claim 1 wherein the step of imparting plastic deformation includes the step of causing the formation of new grain boundaries having high misorientation suitable for warm forming or superplastic forming.

30. The method of claim 1 wherein the molding step and the imparting plastic deformation step are performed in an integrated apparatus.
31. The method of claim 1 wherein the molding step and the imparting plastic
deformation step are performed by separate machines.

32. The method of claim 1 wherein the molding step includes semisolid metal injection
molding of the metal alloy material.

33. The method of claim 32 wherein a solids content of the semisolid metal material does
not exceed about 30 percent.

34. The method of claim 32 wherein a solids content of the semisolid metal material does
not exceed about 10 percent.

35. The method of claim 32 wherein the semisolid metal injection molding includes
delivering the semisolid metal material to a mold via a hot runner system.

36. The method of claim 35 wherein a plurality of the fine grain precursors are formed
with at least 80 percent production yield.

37. The method of claim 32 wherein the semisolid metal material is injected with a screw
shot velocity of at least 1.5 m/sec.

38. The method of claim 32 wherein the molding step further includes providing argon
gas to the metal alloy material.

39. The method of claim 1 wherein the molding step further includes extruding of the
metal alloy material.

40. The method of claim 1 wherein the molding step further includes vacuum molding of
the metal alloy material.

41. The method of claim 1 further comprising, after the step of imparting plastic
deformation, the step of net shaping the ultra fine grain structured sheet to form a part.

42. The method of claim 41 further comprising the step of heat treating the net shaped
part to impart creep resistance to the net shaped part.
43. The method of claim 41 wherein the step of net shaping includes one of stamping, drawing, deep drawing and superplastic forming.

44. The method of claim 41 wherein the step of net shaping forms an automotive component.

45. An apparatus for performing the method of claim 1.

46. An article formed by the method of claim 1.

47. The method of claim 1 wherein the step of imparting plastic deformation includes die pressing of the fine grain precursor.

48. The method of claim 1 wherein the step of imparting plastic deformation includes rolling the fine grain precursor.

49. The method of claim 48 wherein the step of imparting plastic deformation further includes constraining edges of the fine grain precursor.

50. The method of claim 49 wherein the edges of the fine grain precursor are constrained by a Turks Head arrangement.

51. The method of claim 1 wherein the step of imparting plastic deformation includes rolling the fine grain precursor in a plurality of rolling passes with a plurality of respective deformation strains.

52. The method of claim 51 wherein the corresponding deformation strain of each rolling pass is at least 50 percent.

53. The method of claim 52 wherein the step of rolling includes a first rolling pass at a temperature above ambient, wherein each successive pass is at a lower temperature.

54. The method of claim 52 wherein the plurality of rolling passes are cross rolled.

55. The method of claim 1 wherein the step of imparting plastic deformation includes extrusion of the fine grain precursor.
56. The method of claim 1 wherein the step of imparting plastic deformation includes forging of the fine grain precursor.

57. The method of claim 1 wherein the step of imparting plastic deformation includes flow forming of the fine grain precursor.

58. The method of claim 1 wherein the sheet form is provided having a grain structure of less than about 2 micrometers.

59. The method of claim 1 wherein the sheet form is provided having a grain structure of less than about 1 micrometer.

60. The method of claim 1 wherein the precursor is provided having a grain structure of about 5 micrometers.

61. The method of claim 1 wherein the step of imparting plastic deformation is performed while the precursor is heated above ambient.

62. The method of claim 1 wherein the magnesium metal alloy is provided with a moisture content less than about 0.1 percent.

63. An apparatus for refining grain structure and producing ultra-fine grained metal material sheets, the apparatus comprising:
   a receptacle having an inlet, a discharge outlet remote from the inlet, and a chamber defined between the inlet and the discharge outlet;
   a feeder coupled with the inlet, the feeder configured to introduce a metal material into the chamber via the inlet;
   a heating device for transferring heat to the metal material located within the chamber such that the metal material is at a temperature above its solidus temperature;
   discharge means for discharging the metal material from the receptacle through the discharge outlet;
   forming means for forming and rapidly solidifying the discharged metal material into a fine grained precursor having a grain structure of less than 10 micrometers; and
plastic deformation means including a pair of opposing forming members for imparting deformation strain into the precursor article forming a sheet of the metal material having an ultra-fine grain size with a grain structure of less than 5 micrometers.

64. The apparatus of claim 63 wherein the opposed forming members are dies.

65. The apparatus of claim 63 wherein the opposed forming members are rolls.

66. The apparatus of claim 63 further including means for stacking a plurality of the precursor articles into a stack, and wherein the pair of opposing forming members are configured for imparting deformation strain into the stack to form the sheet of the metal material having the ultra fine grain size.

67. The apparatus of claim 63 further comprising net shaping means for shaping the sheet form of the metal material into a net-shaped article.

68. The apparatus of claim 67 wherein the shaping means is one of a drawing press and a superplastic forming machine.

69. The apparatus of claim 63 wherein the receptacle, feeder, heating means, discharge means and forming means are part of an injection molding machine.

70. The apparatus of claim 63 wherein the receptacle, feeder, heating means, discharge means and forming means are part of a semi-solid metal injection molding machine.
Fig. 5A

Fig. 5B
Fig. 6

Fig. 7
Fig. 8

Fig. 9

SSMIM AZ91D  
(5 μm grain size)

SWP AZ91D  
(700 nm grain size)
**INTERNATIONAL SEARCH REPORT**

**International application No**
PCT/US2008/055151

**A. CLASSIFICATION OF SUBJECT MATTER**

**INV. C22F1/06**

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols):
C22F C22C B22D B21D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal, WPI Data, INSPEC, COMPENDEX

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

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**D. DOCUMENTS CITED**

- Further documents are listed in the continuation of Box C
- See patent family annex.

**Date of the actual completion of the international search**
23 September 2008

**Date of mailing of the international search report**
01/10/2008

**Name and mailing address of the ISA/Authorized officer**
European Patent Office, P B. 5618 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016

**Morra, Valentina**
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