

GALVANICALLY-ACTIVE *IN SITU* FORMED PARTICLES FOR CONTROLLED RATE DISSOLVING TOOLS

The present invention claims priority on United States Provisional Patent Application
Serial No. 61/981,425 filed April 18, 2014, which is incorporated herein by reference.

FIELD OF THE INVENTION

The present invention is directed to a novel magnesium composite for use as a
dissolvable component in oil drilling.

BACKGROUND OF THE INVENTION

The ability to control the dissolution of a down hole well component in a variety of
solutions is very important to the utilization of non-drillable completion tools, such as sleeves,
frac balls, hydraulic actuating tooling, and the like. Reactive materials for this application,
which dissolve or corrode when exposed to acid, salt, and/or other wellbore conditions, have
been proposed for some time. Generally, these components consist of materials that are
engineered to dissolve or corrode. Dissolving polymers and some powder metallurgy metals
have been disclosed, and are also used extensively in the pharmaceutical industry for controlled
release of drugs. Also, some medical devices have been formed of metals or polymers that
dissolve in the body.

While the prior art well drill components have enjoyed modest success in reducing well
completion costs, their consistency and ability to specifically control dissolution rates in specific
solutions, as well as other drawbacks such as limited strength and poor reliability, have impacted
their ubiquitous adoption. Ideally, these components would be manufactured by a process that is
low cost, scalable, and produces a controlled corrosion rate having similar or increased strength
as compared to traditional engineering alloys such as aluminum, magnesium, and iron. Ideally,
traditional heat treatments, deformation processing, and machining techniques could be used on
the components without impacting the dissolution rate and reliability of such components.

SUMMARY OF THE INVENTION

The present invention is directed to a novel magnesium composite for use as a
dissolvable component in oil drilling and will be described with particular reference to such
application. As can be appreciated, the novel magnesium composite of the present invention can

be used in other applications (e.g., non-oil wells, etc.). In one non-limiting embodiment, the present invention is directed to a ball or other tool component in a well drilling or completion operation such as, but not limited to, a component that is seated in a hydraulic operation that can be dissolved away after use so that no drilling or removal of the component is necessary. Tubes, valves, valve components, plugs, frac balls, and other shapes and components can also be formed of the novel magnesium composite of the present invention. For purposes of this invention, primary dissolution is measured for valve components and plugs as the time the part removes itself from the seat of a valve or plug arrangement or can become free floating in the system. For example, when the part is a plug in a plug system, primary dissolution occurs when the plug has degraded or dissolved to a point that it can no longer function as a plug and thereby allows fluid to flow about the plug. For purposes of this invention, secondary dissolution is measured in the time the part is fully dissolved into sub-mm particles. As can be appreciated, the novel magnesium composite of the present invention can be used in other well components that also desire the function of dissolving after a period of time. In one non-limiting aspect of the present invention, a galvanically-active phase is precipitated from the novel magnesium composite composition and is used to control the dissolution rate of the component; however, this is not required. The novel magnesium composite is generally castable and/or machinable, and can be used in place of existing metallic or plastic components in oil and gas drilling rigs including, but not limited to, water injection and hydraulic fracturing. The novel magnesium composite can be heat treated as well as extruded and/or forged.

In one non-limiting aspect of the present invention, the novel magnesium composite is used to form a castable, moldable, or extrudable component. Non-limiting magnesium composites in accordance with the present invention include at least 50 wt% magnesium. One or more additives are added to a magnesium or magnesium alloy to form the novel magnesium composite of the present invention. The one or more additives can be selected and used in quantities so that galvanically-active intermetallic or insoluble precipitates form in the magnesium or magnesium alloy while the magnesium or magnesium alloy is in a molten state and/or during the cooling of the melt; however, this is not required. The one or more additives typically are added in a weight percent that is less than a weight percent of said magnesium or

magnesium alloy. Typically, the magnesium or magnesium alloy constitutes about 50.1 wt%-99.9 wt% of the magnesium composite and all values and ranges therebetween. In one non-limiting aspect of the invention, the magnesium or magnesium alloy constitutes about 60 wt%-95 wt% of the magnesium composite, and typically the magnesium or magnesium alloy constitutes about 70 wt%-90 wt% of the magnesium composite. The one or more additives are typically added to the molten magnesium or magnesium alloy at a temperature that is less than the melting point of the one or more additives. The one or more additives generally have an average particle diameter size of at least about 0.1 microns, typically no more than about 500 microns (e.g., 0.1 microns, 0.1001 microns, 0.1002 microns ... 499.9998 microns, 499.9999 microns, 500 microns) and including any value or range therebetween, more typically about 0.1 to 400 microns, and still more typically about 10 to 50 microns. During the process of mixing the one or more additives in the molten magnesium or magnesium alloy, the one or more additives are typically not caused to fully melt in the molten magnesium or magnesium alloy. As can be appreciated, the one or more additives can be added to the molten magnesium or magnesium alloy at a temperature that is greater than the melting point of the one or more additives. In such a method of forming the magnesium composite, the one or more additives form secondary metallic alloys with the magnesium and/or other metals in the magnesium alloy, said secondary metallic alloys having a melting point that is greater than the magnesium and/or other metals in the magnesium alloy. As the molten metal cools, these newly formed secondary metallic alloys begin to precipitate out of the molten metal and form the *in situ* phase to the matrix phase in the cooled and solid magnesium composite. After the mixing process is completed, the molten magnesium or magnesium alloy and the one or more additives that are mixed in the molten magnesium or magnesium alloy are cooled to form a solid component. Generally, the temperature of the molten magnesium or magnesium alloy is at least about 10°C less than the melting point of the additive added to the molten magnesium or magnesium alloy during the addition and mixing process, typically at least about 100°C less than the melting point of the additive added to the molten magnesium or magnesium alloy during the addition and mixing process, more typically about 100°C-1000°C (and any value or range therebetween) less than the melting point of the additive added to the molten magnesium or magnesium alloy during the addition and mixing

process; however, this is not required. The never melted particles and/or the newly formed secondary metallic alloys are referred to as *in situ* particle formation in the molten magnesium composite. Such a process can be used to achieve a specific galvanic corrosion rate in the entire magnesium composite and/or along the grain boundaries of the magnesium composite.

5 The invention adopts a feature that is usually a negative in traditional casting practices wherein a particle is formed during the melt processing that corrodes the alloy when exposed to conductive fluids and is imbedded in eutectic phases, the grain boundaries, and/or even within grains with precipitation hardening. This feature results in the ability to control where the galvanically-active phases are located in the final casting, as well as the surface area ratio of the
10 *in situ* phase to the matrix phase, which enables the use of lower cathode phase loadings as compared to a powder metallurgical or alloyed composite to achieve the same dissolution rates. The *in situ* formed galvanic additives can be used to enhance mechanical properties of the magnesium composite such as ductility, tensile strength, and/or shear strength. The final magnesium composite can also be enhanced by heat treatment as well as deformation processing
15 (such as extrusion, forging, or rolling) to further improve the strength of the final composite over the as-cast material; however, this is not required. The deformation processing can be used to achieve strengthening of the magnesium composite by reducing the grain size of the magnesium composite. Further enhancements, such as traditional alloy heat treatments (such as solutionizing, aging and/or cold working) can be used to enable control of dissolution rates
20 though precipitation of more or less galvanically-active phases within the alloy microstructure while improving mechanical properties; however, this is not required. Because galvanic corrosion is driven by both the electro potential between the anode and cathode phase, as well as the exposed surface area of the two phases, the rate of corrosion can also be controlled through adjustment of the *in situ* formed particles size, while not increasing or decreasing the volume or
25 weight fraction of the addition, and/or by changing the volume/weight fraction without changing the particle size. Achievement of *in situ* particle size control can be achieved by mechanical agitation of the melt, ultrasonic processing of the melt, controlling cooling rates, and/or by performing heat treatments. *In situ* particle size can also or alternatively be modified by secondary processing such as rolling, forging, extrusion and/or other deformation techniques.

In another non-limiting aspect of the invention, a cast structure can be made into almost any shape. During formation, the active galvanically-active *in situ* phases can be uniformly dispersed throughout the component and the grain or the grain boundary composition can be modified to achieve the desired dissolution rate. The galvanic corrosion can be engineered to affect only the grain boundaries and/or can affect the grains as well (based on composition); however, this is not required. This feature can be used to enable fast dissolutions of high-strength lightweight alloy composites with significantly less active (cathode) *in situ* phases as compared to other processes.

In still another and/or alternative non-limiting aspect of the invention, ultrasonic processing can be used to control the size of the *in situ* formed galvanically-active phases; however, this is not required.

In yet another and/or alternative non-limiting aspect of the invention, the *in situ* formed particles can act as matrix strengtheners to further increase the tensile strength of the material compared to the base alloy without the additive; however, this is not required.

In still yet another and/or alternative non-limiting aspect of the invention, there is provided a method of controlling the dissolution properties of a metal selected from the class of magnesium and/or magnesium alloy comprising of the steps of a) melting the magnesium or magnesium alloy to a point above its solidus, b) introducing an additive material and/or phase to the magnesium or magnesium alloy in order to achieve *in situ* precipitation of galvanically-active intermetallic phases, and c) cooling the melt to a solid form. The additive material is generally added to the magnesium or magnesium alloy when the magnesium or magnesium alloy is in a molten state and at a temperature that is less than the melting point of the additive material. The galvanically-active intermetallic phases can be used to enhance the yield strength of the alloy; however, this is not required. The size of the *in situ* precipitated intermetallic phase can be controlled by a melt mixing technique and/or cooling rate; however, this is not required. The method can include the additional step of subjecting the magnesium composite to intermetallic precipitates to solutionizing of at least about 300°C to improve tensile strength and/or improve ductility; however, this is not required. The solutionizing temperature is less than the melting point of the magnesium composite. Generally, the solutionizing temperature is less than 50°C-

200°C (the melting point of the magnesium composite) and the time period of solutionizing is at least 0.1 hours. In one non-limiting aspect of the invention, the magnesium composite can be subjected to a solutionizing temperature for about 0.5-50 hours (e.g., 1-15 hours, etc.) at a temperature of 300°C-620°C (e.g., 300°C -500°C, etc.). The method can include the additional
5 step of subjecting the magnesium composite to intermetallic precipitates and to artificially age the magnesium composite at a temperature at least about 90°C to improve the tensile strength; however, this is not required. The artificially aging process temperature is typically less than the solutionizing temperature and the time period of the artificially aging process temperature is typically at least 0.1 hours. Generally, the artificially aging process is less than 50°C-400°C (the
10 solutionizing temperature). In one non-limiting aspect of the invention, the magnesium composite can be subjected to aging treatment for about 0.5-50 hours (e.g., 1-16 hours, etc.) at a temperature of 90°C -300°C (e.g., 100°C -200°C).

In another and/or alternative non-limiting aspect of the invention, there is provided a magnesium composite that is over 50 wt% magnesium and about 0.05-35 wt% nickel (and all
15 values or ranges therebetween) is added to the magnesium or magnesium alloy to form intermetallic Mg_2Ni as a galvanically-active *in situ* precipitate. In one non-limiting arrangement, the magnesium composite includes about 0.05-23.5 wt% nickel, 0.01-5 wt % nickel, 3-7 wt% nickel, 7-10 wt% nickel, or 10-24.5 wt% nickel. The nickel is added to the magnesium or magnesium alloy while the temperature of the molten magnesium or magnesium alloy is less
20 than the melting point of the nickel. Throughout the mixing process, the temperature of the molten magnesium or magnesium alloy is less than the melting point of the nickel. During the mixing process, solid particles of Mg_2Ni are formed. Once the mixing process is complete, the mixture of molten magnesium or magnesium alloy, solid particles of Mg_2Ni , and any unalloyed nickel particles are cooled and an *in situ* precipitate of solid particles of Mg_2Ni and any
25 unalloyed nickel particles are formed in the solid magnesium or magnesium alloy. Generally, the temperature of the molten magnesium or magnesium alloy is at least about 200°C less than the melting point of the nickel added to the molten magnesium or magnesium alloy during the addition and mixing process.

In still another and/or alternative non-limiting aspect of the invention, there is provided a magnesium composite that is over 50 wt% magnesium and about 0.05-35 wt% copper (and all values or ranges therebetween) is added to the magnesium or magnesium alloy to form intermetallic CuMg_2 as the galvanically-active *in situ* precipitate. In one non-limiting arrangement, the magnesium composite includes about 0.01-5 wt% copper, about 0.5-15 wt% copper, about 15-35 wt% copper, or about 0.01-20 wt%. The copper is added to the magnesium or magnesium alloy while the temperature of the molten magnesium or magnesium alloy is less than the melting point of the copper. Throughout the mixing process, the temperature of the molten magnesium or magnesium alloy is less than the melting point of the copper. During the mixing process, solid particles of CuMg_2 are formed. Once the mixing process is complete, the mixture of molten magnesium or magnesium alloy, solid particles of CuMg_2 , and any unalloyed copper particles are cooled and an *in situ* precipitate of solid particles of CuMg_2 and any unalloyed copper particles are formed in the solid magnesium or magnesium alloy. Generally, the temperature of the molten magnesium or magnesium alloy is at least about 200°C less than the melting point of the copper added to the molten magnesium or magnesium alloy.

In yet another and/or alternative non-limiting aspect of the invention, there is provided a magnesium composite that is over 50 wt% magnesium and about 0.05-20% by weight cobalt is added to the magnesium or magnesium alloy to form an intermetallic CoMg_2 as the galvanically-active *in situ* precipitate. The cobalt is added to the magnesium or magnesium alloy while the temperature of the molten magnesium or magnesium alloy is less than the melting point of the cobalt. Throughout the mixing process, the temperature of the molten magnesium or magnesium alloy is less than the melting point of the cobalt. During the mixing process, solid particles of CoMg_2 are formed. Once the mixing process is complete, the mixture of molten magnesium or magnesium alloy, solid particles of CoMg_2 , and any unalloyed cobalt particles are cooled and an *in situ* precipitate of solid particles of CoMg_2 and any unalloyed cobalt particles are formed in the solid magnesium or magnesium alloy. Generally, the temperature of the molten magnesium or magnesium alloy is at least about 200°C less than the melting point of the cobalt added to the molten magnesium or magnesium alloy.

In yet another and/or alternative non-limiting aspect of the invention, there is provided a magnesium composite that is over 50 wt% magnesium and cobalt is added to the magnesium or magnesium alloy which forms an intermetallic Mg_xCo as the galvanically-active particle *in situ* precipitate. The cobalt is added to the magnesium or magnesium alloy while the temperature of the molten magnesium or magnesium alloy is less than the melting point of the cobalt. Throughout the mixing process, the temperature of the molten magnesium or magnesium alloy is less than the melting point of the cobalt. During the mixing process, solid particles of $CoMg_x$ are formed. Once the mixing process is complete, the mixture of molten magnesium or magnesium alloy, solid particles of $CoMg_x$, and any unalloyed cobalt particles are cooled and an *in situ* precipitate of solid particles of $CoMg_x$ and any unalloyed cobalt particles are formed in the solid magnesium or magnesium alloy. Generally, the temperature of the molten magnesium or magnesium alloy is at least about 200°C less than the melting point of the cobalt added to the molten magnesium or magnesium alloy.

In still yet another and/or alternative non-limiting aspect of the invention, there is provided a magnesium composite that is over 50 wt% magnesium and about 0.5-35% by weight of secondary metal (SM) is added to the magnesium or magnesium alloy to form a galvanically-active intermetallic particle when compared to magnesium or a magnesium alloy in the remaining casting where the cooling rate between the liquidus to the solidus is faster than 1°C per minute. The secondary metal is added to the magnesium or magnesium alloy while the temperature of the molten magnesium or magnesium alloy is less than the melting point of the secondary metal. Throughout the mixing process, the temperature of the molten magnesium or magnesium alloy is less than the melting point of the secondary metal. During the mixing process, solid particles of $SMMg_x$ are formed. Once the mixing process is complete, the mixture of molten magnesium or magnesium alloy, solid particles of $SMMg_x$, and any unalloyed secondary metal particles are cooled and an *in situ* precipitate of solid particles of $SMMg_x$ and any unalloyed secondary metal particles are formed in the solid magnesium or magnesium alloy. Generally, the temperature of the molten magnesium or magnesium alloy is at least about 200°C less than the melting point of the secondary metal added to the molten magnesium or magnesium

alloy. As can be appreciated, one or more secondary metals can be added to the molten magnesium or magnesium alloy.

In another and/or alternative non-limiting aspect of the invention, there is provided a magnesium composite that is over 50 wt% magnesium and about 0.5-35% by weight of secondary metal (SM) is added to the magnesium or magnesium alloy to form a galvanically-active intermetallic particle when compared to magnesium or a magnesium alloy in the remaining casting where the cooling rate between the liquidus to the solidus is slower than 1°C per minute. The secondary metal is added to the magnesium or magnesium alloy while the temperature of the molten magnesium or magnesium alloy is less than the melting point of the secondary metal. Throughout the mixing process, the temperature of the molten magnesium or magnesium alloy is less than the melting point of the secondary metal. During the mixing process, solid particles of $SMMg_x$ are formed. Once the mixing process is complete, the mixture of molten magnesium or magnesium alloy, solid particles of $SMMg_x$, and any unalloyed secondary metal particles are cooled and an *in situ* precipitate of solid particles of $SMMg_x$ and any unalloyed secondary metal particles are formed in the solid magnesium or magnesium alloy. Generally, the temperature of the molten magnesium or magnesium alloy is at least about 200°C less than the melting point of the secondary metal added to the molten magnesium or magnesium alloy. As can be appreciated, one or more secondary metals can be added to the molten magnesium or magnesium alloy.

In still another and/or alternative non-limiting aspect of the invention, there is provided a magnesium composite that is over 50 wt% magnesium and about 0.05-35 wt% of secondary metal (SM) is added to the magnesium or magnesium alloy to form a galvanically-active intermetallic particle when compared to magnesium or a magnesium alloy in the remaining casting where the cooling rate between the liquidus to the solidus is faster than 0.01°C per min and slower than 1°C per minute. The secondary metal is added to the magnesium or magnesium alloy while the temperature of the molten magnesium or magnesium alloy is less than the melting point of the secondary metal. Throughout the mixing process, the temperature of the molten magnesium or magnesium alloy is less than the melting point of the secondary metal. During the mixing process, solid particles of $SMMg_x$ are formed. Once the mixing process is

complete, the mixture of molten magnesium or magnesium alloy, solid particles of SMMg_x and any unalloyed secondary metal particles are cooled and an *in situ* precipitate of solid particles of SMMg_x , and any unalloyed secondary metal particles are formed in the solid magnesium or magnesium alloy. Generally, the temperature of the molten magnesium or magnesium alloy is at least about 200°C less than the melting point of the secondary metal added to the molten magnesium or magnesium alloy. As can be appreciated, one or more secondary metals can be added to the molten magnesium or magnesium alloy.

In yet another and/or alternative non-limiting aspect of the invention, there is provided a magnesium composite that is over 50 wt% magnesium and about 0.05-35 wt% of secondary metal (SM) is added to the magnesium or magnesium alloy to form a galvanically-active intermetallic particle when compared to magnesium or a magnesium alloy in the remaining casting where the cooling rate between the liquidus to the solidus is faster than 10°C per minute. The secondary metal is added to the magnesium or magnesium alloy while the temperature of the molten magnesium or magnesium alloy is less than the melting point of the secondary metal. Throughout the mixing process, the temperature of the molten magnesium or magnesium alloy is less than the melting point of the secondary metal. During the mixing process, solid particles of SMMg_x were formed. Once the mixing process was completed, the mixture of molten magnesium or magnesium alloy, solid particles of SMMg_x , and any unalloyed secondary metal particles are cooled and an *in situ* precipitate of solid particles of SMMg_x and any unalloyed secondary metal particles are formed in the solid magnesium or magnesium alloy. Generally, the temperature of the molten magnesium or magnesium alloy is at least about 200°C less than the melting point of the secondary metal added to the molten magnesium or magnesium alloy. As can be appreciated, one or more secondary metals can be added to the molten magnesium or magnesium alloy.

In still yet another and/or alternative non-limiting aspect of the invention, there is provided magnesium composite that is over 50 wt% magnesium and about 0.5-35 wt% of secondary metal (SM) is added to the magnesium or magnesium alloy to form a galvanically-active intermetallic particle when compared to magnesium or a magnesium alloy in the remaining casting where the cooling rate between the liquidus to the solidus is slower than 10°C

per minute. The secondary metal is added to the magnesium or magnesium alloy while the temperature of the molten magnesium or magnesium alloy is less than the melting point of the secondary metal. Throughout the mixing process, the temperature of the molten magnesium or magnesium alloy is less than the melting point of the secondary metal. During the mixing process, solid particles of SMMg_x are formed. Once the mixing process is complete, the mixture of molten magnesium or magnesium alloy, solid particles of SMMg_x , and any unalloyed secondary metal particles are cooled and an *in situ* precipitate of solid particles of SMMg_x and any unalloyed secondary metal particles are formed in the solid magnesium or magnesium alloy. Generally, the temperature of the molten magnesium or magnesium alloy is at least about 200°C less than the melting point of the secondary metal added to the molten magnesium or magnesium alloy. As can be appreciated, one or more secondary metals can be added to the molten magnesium or magnesium alloy.

In another and/or alternative non-limiting aspect of the invention, there is provided a magnesium alloy that includes over 50 wt% magnesium and includes at least one metal selected from the group consisting of aluminum in an amount of about 0.5-10 wt%, zinc in amount of about 0.05-6 wt%, zirconium in an amount of about 0.01-3 wt%, and/or manganese in an amount of about 0.15-2 wt%. In one non-limiting formulation, the magnesium alloy that includes over 50 wt% magnesium and includes at least one metal selected from the group consisting of zinc in amount of about 0.05-6 wt%, zirconium in an amount of about 0.05-3 wt%, manganese in an amount of about 0.05-0.25 wt%, boron in an amount of about 0.0002-0.04 wt%, and bismuth in an amount of about 0.4-0.7 wt%. The magnesium alloy can then be heated to a molten state and one or more secondary metal (SM) (e.g., copper, nickel, cobalt, titanium, silicon, iron, etc.) can be added to the molten magnesium alloy which forms an intermetallic galvanically-active particle *in situ* precipitate. The galvanically-active particle can be SMMg_x , SMAl_x , SMZn_x , SMZr_x , SMMn_x , SMB_x , SMBi_x , SM in combination with any one of B, Bi, Mg, Al, Zn, Zr, and Mn.

In still another and/or alternative non-limiting aspect of the invention, there is provided a magnesium composite that is over 50 wt% magnesium and at least one metal selected from the group consisting of zinc in an amount of about 0.05-6 wt%, zirconium in amount of about 0.05-3

wt%, manganese in an amount of about 0.05-0.25 wt%, boron in an amount of about 0.0002-0.04 wt%, and/or bismuth in an amount of about 0.4-0.7 wt% is added to the magnesium or magnesium alloy to form a galvanically-active intermetallic particle in the magnesium or magnesium alloy. The magnesium alloy can then be heated to a molten state and one or more
 5 secondary metal (SM) (e.g., copper, nickel, cobalt, titanium, iron, etc.) can be added to the molten magnesium alloy which forms an intermetallic galvanically-active particle *in situ* precipitate. The galvanically-active particle can be SMMg_x , SMZn_x , SMZr_x , SMMn_x , SMB_x , SMBi_x , SM in combination with any one of Mg, Zn, Zr, Mn, B and/or Bi.

In yet another and/or alternative non-limiting aspect of the invention, there is provided a
 10 magnesium or magnesium alloy that is over 50 wt% magnesium and nickel in an amount of about 0.01-5 wt% is added to the magnesium or magnesium alloy to form a galvanically-active intermetallic particle in the magnesium or magnesium alloy. The nickel is added to the magnesium or magnesium alloy while the temperature of the molten magnesium or magnesium alloy is less than the melting point of the nickel. Throughout the mixing process, the temperature
 15 of the molten magnesium or magnesium alloy is less than the melting point of the nickel. During the mixing process, solid particles of Mg_2Ni are formed. Once the mixing process is complete, the mixture of molten magnesium or magnesium alloy, solid particles of Mg_2Ni , and any unalloyed nickel particles are cooled and an *in situ* precipitate of solid particles of Mg_2Ni and any unalloyed nickel particles are formed in the solid magnesium or magnesium alloy.
 20 Generally, the temperature of the molten magnesium or magnesium alloy is at least about 200°C less than the melting point of the nickel added to the molten magnesium or magnesium alloy during the addition and mixing process.

In still yet another and/or alternative non-limiting aspect of the invention, there is provided a magnesium composite that is over 50 wt% magnesium and nickel in an amount of
 25 from about 0.3-7 wt% is added to the magnesium or magnesium alloy to form a galvanically-active intermetallic particle in the magnesium or magnesium alloy. The nickel is added to the magnesium or magnesium alloy while the temperature of the molten magnesium or magnesium alloy is less than the melting point of the nickel. Throughout the mixing process, the temperature of the molten magnesium or magnesium alloy is less than the melting point of the nickel. During

the mixing process, solid particles of Mg_2Ni are formed. Once the mixing process is complete, the mixture of molten magnesium or magnesium alloy, solid particles of Mg_2Ni , and any unalloyed nickel particles are cooled and an *in situ* precipitate of solid particles of Mg_2Ni and any unalloyed nickel particles are formed in the solid magnesium or magnesium alloy. Generally, the temperature of the molten magnesium or magnesium alloy is at least about 200°C less than the melting point of the nickel added to the molten magnesium or magnesium alloy during the addition and mixing process.

In another and/or alternative non-limiting aspect of the invention, there is provided a magnesium composite that is over 50 wt% magnesium and nickel in an amount of about 7-10 wt% is added to the magnesium or magnesium alloy to form a galvanically-active intermetallic particle in the magnesium or magnesium alloy. The nickel is added to the magnesium or magnesium alloy while the temperature of the molten magnesium or magnesium alloy is less than the melting point of the nickel. Throughout the mixing process, the temperature of the molten magnesium or magnesium alloy is less than the melting point of the nickel. During the mixing process, solid particles of Mg_2Ni are formed. Once the mixing process was completed, the mixture of molten magnesium or magnesium alloy, solid particles of Mg_2Ni , and any unalloyed nickel particles are cooled and an *in situ* precipitate of solid particles of Mg_2Ni and any unalloyed nickel particles are formed in the solid magnesium or magnesium alloy. Generally, the temperature of the molten magnesium or magnesium alloy is at least about 200°C less than the melting point of the nickel added to the molten magnesium or magnesium alloy during the addition and mixing process.

In still another and/or alternative non-limiting aspect of the invention, there is provided a magnesium composite that is over 50 wt% magnesium and nickel in an amount of about 10-24.5 wt% is added to the magnesium or magnesium alloy to form a galvanically-active intermetallic particle in the magnesium or magnesium alloy. The nickel is added to the magnesium or magnesium alloy while the temperature of the molten magnesium or magnesium alloy is less than the melting point of the nickel. Throughout the mixing process, the temperature of the molten magnesium or magnesium alloy is less than the melting point of the nickel. During the mixing process, solid particles of Mg_2Ni are formed. Once the mixing process is complete, the

5 mixture of molten magnesium or magnesium alloy, solid particles of Mg_2Ni , and any unalloyed nickel particles are cooled and an *in situ* precipitate of solid particles of Mg_2Ni and any unalloyed nickel particles are formed in the solid magnesium or magnesium alloy. Generally, the temperature of the molten magnesium or magnesium alloy is at least about 200°C less than the melting point of the nickel added to the molten magnesium or magnesium alloy during the addition and mixing process.

10 In yet another and/or alternative non-limiting aspect of the invention, there is provided a magnesium composite that is over 50 wt% magnesium and copper in an amount of about 0.01-5 wt% is added to the magnesium or magnesium alloy to form a galvanically-active intermetallic particle in the magnesium or magnesium alloy. The copper is added to the magnesium or magnesium alloy while the temperature of the molten magnesium or magnesium alloy is less than the melting point of the copper. Throughout the mixing process, the temperature of the molten magnesium or magnesium alloy is less than the melting point of the copper. During the mixing process, solid particles of Mg_2Cu are formed. Once the mixing process is complete, the mixture of molten magnesium or magnesium alloy, solid particles of Mg_2Cu , and any unalloyed nickel particles are cooled and an *in situ* precipitate of solid particles of Mg_2Cu and any unalloyed copper particles are formed in the solid magnesium or magnesium alloy. Generally, the temperature of the molten magnesium or magnesium alloy is at least about 200°C less than the melting point of the copper added to the molten magnesium or magnesium alloy during the addition and mixing process.

20 In still yet another and/or alternative non-limiting aspect of the invention, there is provided a magnesium composite that is over 50 wt% magnesium and includes copper in an amount of about 0.5-15 wt% is added to the magnesium or magnesium alloy to form a galvanically-active intermetallic particle in the magnesium or magnesium alloy. The copper is added to the magnesium or magnesium alloy while the temperature of the molten magnesium or magnesium alloy is less than the melting point of the copper. Throughout the mixing process, the temperature of the molten magnesium or magnesium alloy is less than the melting point of the copper. During the mixing process, solid particles of Mg_2Cu are formed. Once the mixing process is complete, the mixture of molten magnesium or magnesium alloy, solid particles of

Mg₂Cu, and any unalloyed nickel particles are cooled and an *in situ* precipitate of solid particles of Mg₂Cu and any unalloyed copper particles are formed in the solid magnesium or magnesium alloy. Generally, the temperature of the molten magnesium or magnesium alloy is at least about 200°C less than the melting point of the copper added to the molten magnesium or magnesium alloy during the addition and mixing process.

In another and/or alternative non-limiting aspect of the invention, there is provided a magnesium composite that is over 50 wt% magnesium and includes copper in an amount of about 15-35 wt% is added to the magnesium or magnesium alloy to form a galvanically-active intermetallic particle in the magnesium or magnesium alloy. The copper is added to the magnesium or magnesium alloy while the temperature of the molten magnesium or magnesium alloy is less than the melting point of the copper. Throughout the mixing process, the temperature of the molten magnesium or magnesium alloy is less than the melting point of the copper. During the mixing process, solid particles of Mg₂Cu are formed. Once the mixing process is complete, the mixture of molten magnesium or magnesium alloy, solid particles of Mg₂Cu, and any unalloyed nickel particles are cooled and an *in situ* precipitate of solid particles of Mg₂Cu and any unalloyed copper particles are formed in the solid magnesium or magnesium alloy. Generally, the temperature of the molten magnesium or magnesium alloy is at least about 200°C less than the melting point of the copper added to the molten magnesium or magnesium alloy during the addition and mixing process.

In still another and/or alternative non-limiting aspect of the invention, there is provided a magnesium composite that is over 50 wt% magnesium and includes copper in an amount of about 0.01-20 wt% is added to the magnesium or magnesium alloy to form a galvanically-active intermetallic particle in the magnesium or magnesium alloy. The copper is added to the magnesium or magnesium alloy while the temperature of the molten magnesium or magnesium alloy is less than the melting point of the copper. Throughout the mixing process, the temperature of the molten magnesium or magnesium alloy is less than the melting point of the copper. During the mixing process, solid particles of Mg₂Cu are formed. Once the mixing process is complete, the mixture of molten magnesium or magnesium alloy, solid particles of Mg₂Cu, and any unalloyed nickel particles are cooled and an *in situ* precipitate of solid particles

of Mg_2Cu and any unalloyed copper particles are formed in the solid magnesium or magnesium alloy. Generally, the temperature of the molten magnesium or magnesium alloy is at least about 200°C less than the melting point of the copper added to the molten magnesium or magnesium alloy during the addition and mixing process.

5 In yet another and/or alternative non-limiting aspect of the invention, there is provided a magnesium composite that is subjected to heat treatments such as solutionizing, aging and/or cold working to be used to control dissolution rates through precipitation of more or less galvanically-active phases within the alloy microstructure while improving mechanical properties. The aging process (when used) can be for at least about 1 hour, for about 1-50 hours,
10 for about 1-20 hours, or for about 8-20 hours. The solutionizing (when used) can be for at least about 1 hour, for about 1-50 hours, for about 1-20 hours, or for about 8-20 hours.

In still yet another and/or alternative non-limiting aspect of the invention, there is provided a method for controlling the dissolution rate of the magnesium composite wherein the magnesium content is at least about 75% and nickel is added to form *in situ* precipitation of at
15 least 0.05 wt MgNi_2 with the magnesium or magnesium alloy and solutionizing the resultant metal at a temperature within a range of $100\text{-}500^\circ\text{C}$ for a period of 0.25-50 hours, the magnesium composite being characterized by higher dissolution rates than metal without nickel additions subjected to the said aging treatment.

In another and/or alternative non-limiting aspect of the invention, there is provided a
20 method for improving the physical properties of the magnesium composite wherein the magnesium content is at least about 85% and nickel is added to form *in situ* precipitation of at least 0.05 wt% MgNi_2 with the magnesium or magnesium alloy and solutionizing the resultant metal at a temperature at about $100\text{-}500^\circ\text{C}$ for a period of 0.25-50 hours, the magnesium composite being characterized by higher tensile and yield strengths than magnesium base alloys
25 of the same composition, but not including the amount of nickel.

In still another and/or alternative non-limiting aspect of the invention, there is provided a method for controlling the dissolution rate of the magnesium composite wherein the magnesium content in the alloy is at least about 75% and copper is added to form *in situ* precipitation of at least about 0.05 wt% MgCu_2 with the magnesium or magnesium alloy and solutionizing the

resultant metal at a temperature within a range of 100-500°C for a period of 0.25-50 hours, the magnesium composite being characterized by higher dissolution rates than metal without copper additions subjected to the said aging treatment.

5 In yet another and/or alternative non-limiting aspect of the invention, there is provided a method for improving the physical properties of the magnesium composite wherein the total content of magnesium in the magnesium or magnesium alloy is at least about 85% and copper is added to form *in situ* precipitation of at least 0.05 wt% MgCu₂ with the magnesium or magnesium composite and solutionizing the resultant metal at a temperature of about 100-500°C for a period of 0.25-50 hours, the magnesium composite is characterized by higher tensile and
10 yield strengths than magnesium base alloys of the same composition, but not including the amount of copper.

In still yet another and/or alternative non-limiting aspect of the invention, there is provided a magnesium composite for use as a dissolvable ball or frac ball in hydraulic fracturing and well drilling.

15 In another and/or alternative non-limiting aspect of the invention, there is provided a magnesium composite for use as a dissolvable tool for use in well drilling and hydraulic control as well as hydraulic fracturing.

In still another and/or alternative non-limiting aspect of the invention, there is provided a magnesium composite that includes secondary institute formed reinforcements that are not
20 galvanically-active to the magnesium or magnesium alloy matrix to increase the mechanical properties of the magnesium composite. The secondary institute formed reinforcements include a Mg₂Si phase as the *in situ* formed reinforcement.

In yet another and/or alternative non-limiting aspect of the invention, there is provided a magnesium composite that is subjected to a faster cooling rate from the liquidus to the solidus
25 point to create smaller *in situ* formed particles.

In still yet another and/or alternative non-limiting aspect of the invention, there is provided a magnesium composite that is subjected to a slower cooling rate from the liquidus to the solidus point to create larger *in situ* formed particles.

In another and/or alternative non-limiting aspect of the invention, there is provided a magnesium composite that is subjected to mechanical agitation during the cooling rate from the liquidus to the solidus point to create smaller *in situ* formed particles.

5 In still another and/or alternative non-limiting aspect of the invention, there is provided a magnesium composite that is subjected to chemical agitation during the cooling rate from the liquidus to the solidus point to create smaller *in situ* formed particles.

In yet another and/or alternative non-limiting aspect of the invention, there is provided a magnesium composite that is subjected to ultrasonic agitation during the cooling rate from the liquidus to the solidus point to create smaller *in situ* formed particles.

10 In still yet another and/or alternative non-limiting aspect of the invention, there is provided a magnesium composite that is subjected to deformation or extrusion to further improve dispersion of the *in situ* formed particles.

In another and/or alternative non-limiting aspect of the invention, there is provided a method for forming a novel magnesium composite including the steps of a) selecting an AZ91D
15 magnesium alloy having 9 wt% aluminum, 1 wt% zinc and 90 wt% magnesium, b) melting the AZ91D magnesium alloy to a temperature above 800°C, c) adding up to about 7 wt% nickel to the melted AZ91D magnesium alloy at a temperature that is less than the melting point of nickel, d) mixing the nickel with the melted AZ91D magnesium alloy and dispersing the nickel in the melted alloy using chemical mixing agents while maintaining the temperature below the melting
20 point of nickel, and e) cooling and casting the melted mixture in a steel mold. The cast material has a tensile strength of about 14 ksi, and an elongation of about 3% and a shear strength of 11ksi. The cast material has a dissolve rate of about 75 mg/cm²-min in a 3% KCl solution at 90°C. The cast material dissolves at a rate of 1 mg/cm²-hr in a 3% KCl solution at 21°C. The cast material dissolves at a rate of 325mg/cm²-hr. in a 3% KCl solution at 90°C. The cast
25 material can be subjected to extrusion with a 11:1 reduction area. The extruded cast material exhibits a tensile strength of 40ksi, and an elongation to failure of 12%. The extruded cast material dissolves at a rate of 0.8 mg/cm²-min in a 3% KCl solution at 20°C. The extruded cast material dissolves at a rate of 100mg/cm²-hr in a 3% KCl solution at 90°C. The extruded cast material can be subjected to an artificial T5 age treatment of 16 hours between 100°C-200°C.

The aged extruded cast material exhibits a tensile strength of 48Ksi, an elongation to failure of 5%, and a shear strength of 25Ksi. The aged extruded cast material dissolves at a rate of 110mg/cm²-hr in 3% KCl solution at 90°C and 1mg/cm²-hr in 3% KCl solution at 20°C. The cast material can be subjected to a solutionizing treatment T4 for about 18 hours between 400°C-500°C and then subjected to an artificial T6 age treatment for about 16 hours between 100°C-200°C. The aged and solutionized cast material exhibits a tensile strength of about 34 Ksi, an elongation to failure of about 11%, and a shear strength of about 18 Ksi. The aged and solutionized cast material dissolves at a rate of about 84mg/cm²-hr in 3% KCl solution at 90°C, and about 0.8mg/cm²-hr in 3% KCl solution at 20°C.

In another and/or alternative non-limiting aspect of the invention, there is provided a method for forming a novel magnesium composite including the steps of a) selecting an AZ91D magnesium alloy having 9 wt% aluminum, 1 wt% zinc and 90 wt% magnesium, b) melting the AZ91D magnesium alloy to a temperature above 800°C, c) adding up to about 1 wt% nickel to the melted AZ91D magnesium alloy at a temperature that is less than the melting point of nickel, d) mixing the nickel with the melted AZ91D magnesium alloy and dispersing the nickel in the melted alloy using chemical mixing agents while maintaining the temperature below the melting point of nickel, and e) cooling and casting the melted mixture in a steel mold. The cast material has a tensile strength of about 18 ksi, and an elongation of about 5% and a shear strength of 17ksi. The cast material has a dissolve rate of about 45 mg/cm²-min in a 3% KCl solution at 90°C. The cast material dissolves at a rate of 0.5 mg/cm²-hr in a 3% KCl solution at 21°C. The cast material dissolves at a rate of 325mg/cm²-hr. in a 3% KCl solution at 90°C. The cast material was then subjected to extrusion with a 20:1 reduction area. The extruded cast material exhibits a tensile yeild strength of 35ksi, and an elongation to failure of 12%. The extruded cast material dissolves at a rate of 0.8 mg/cm²-min in a 3% KCl solution at 20°C. The extruded cast material dissolves at a rate of 50mg/cm²-hr in a 3% KCl solution at 90°C. The extruded cast material can be subjected to an artificial T5 age treatment of 16 hours between 100°C-200°C. The aged extruded cast material exhibits a tensile strength of 48Ksi, an elongation to failure of 5%, and a shear strength of 25Ksi.

In still another and/or alternative non-limiting aspect of the invention, there is provided a method for forming a novel magnesium composite including the steps of a) selecting an AZ91D magnesium alloy having about 9 wt% aluminum, 1 wt% zinc and 90 wt% magnesium, b) melting the AZ91D magnesium alloy to a temperature above 800°C, c) adding about 10 wt% copper to the melted AZ91D magnesium alloy at a temperature that is less than the melting point of copper, d) dispersing the copper in the melted AZ91D magnesium alloy using chemical mixing agents at a temperature that is less than the melting point of copper, and e) cooling casting the melted mixture in a steel mold. The cast material exhibits a tensile strength of about 14 ksi, an elongation of about 3%, and shear strength of 11ksi. The cast material dissolves at a rate of about 50 mg/cm²-hr in a 3% KCl solution at 90°C. The cast material dissolves at a rate of 0.6 mg/cm²-hr in a 3% KCl solution at 21°C. The cast material can be subjected to an artificial T5 age treatment for about 16 hours at a temperature of 100-200°C. The aged cast material exhibits a tensile strength of 50Ksi, an elongation to failure of 5%, and a shear strength of 25Ksi. The aged cast material dissolved at a rate of 40mg/cm²-hr in 3% KCl solution at 90°C and 0.5mg/cm²-hr in 3% KCl solution at 20°C.

These and other objects, features and advantages of the present invention will become apparent in light of the following detailed description of preferred embodiments thereof, as illustrated in the accompanying drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

Figs. 1-3 show a typical cast microstructure with galvanically-active *in situ* formed intermetallic phase wetted to the magnesium matrix; and,

Fig. 4 shows a typical phase diagram to create *in situ* formed particles of an intermetallic Mg_x(M) where M is any element on the periodic table or any compound in a magnesium matrix and wherein M has a melting point that is greater than the melting point of Mg.

DETAILED DESCRIPTION OF THE INVENTION

The present invention is directed to a novel magnesium composite that can be used to form a castable, moldable, or extrudable component. The magnesium composite includes at least 50 wt% magnesium. Generally, the magnesium composite includes over 50 wt% magnesium and less than about 99.5 wt% magnesium and all values and ranges therebetween. One or more

additives are added to a magnesium or magnesium alloy to form the novel magnesium composite of the present invention. The one or more additives can be selected and used in quantities so that galvanically-active intermetallic or insoluble precipitates form in the magnesium or magnesium alloy while the magnesium or magnesium alloy is in a molten state and/or during the cooling of the melt; however, this is not required. The one or more additives are added to the molten magnesium or magnesium alloy at a temperature that is less than the melting point of the one or more additives. During the process of mixing the one or more additives in the molten magnesium or magnesium alloy, the one or more additives are not caused to fully melt in the molten magnesium or magnesium alloy. After the mixing process is completed, the molten magnesium or magnesium alloy and the one or more additives that are mixed in the molten magnesium or magnesium alloy are cooled to form a solid component. Such a formation in the melt is called *in situ* particle formation as illustrated in Figs. 1-3. Such a process can be used to achieve a specific galvanic corrosion rate in the entire magnesium composite and/or along the grain boundaries of the magnesium composite. This feature results in the ability to control where the galvanically-active phases are located in the final casting, as well as the surface area ratio of the *in situ* phase to the matrix phase, which enables the use of lower cathode phase loadings as compared to a powder metallurgical or alloyed composite to achieve the same dissolution rates. The *in situ* formed galvanic additives can be used to enhance mechanical properties of the magnesium composite such as ductility, tensile strength, and/or shear strength. The final magnesium composite can also be enhanced by heat treatment as well as deformation processing (such as extrusion, forging, or rolling) to further improve the strength of the final composite over the as-cast material; however, this is not required. The deformation processing can be used to achieve strengthening of the magnesium composite by reducing the grain size of the magnesium composite. Further enhancements, such as traditional alloy heat treatments (such as solutionizing, aging and/or cold working) can be used to enable control of dissolution rates though precipitation of more or less galvanically-active phases within the alloy microstructure while improving mechanical properties; however, this is not required. Because galvanic corrosion is driven by both the electro potential between the anode and cathode phase, as well as the exposed surface area of the two phases, the rate of corrosion can also be controlled through

adjustment of the *in situ* formed particles size, while not increasing or decreasing the volume or weight fraction of the addition, and/or by changing the volume/weight fraction without changing the particle size. Achievement of *in situ* particle size control can be achieved by mechanical agitation of the melt, ultrasonic processing of the melt, controlling cooling rates, and/or by performing heat treatments. *In situ* particle size can also or alternatively be modified by secondary processing such as rolling, forging, extrusion and/or other deformation techniques. A smaller particle size can be used to increase the dissolution rate of the magnesium composite. An increase in the weight percent of the *in situ* formed particles or phases in the magnesium composite can also or alternatively be used to increase the dissolution rate of the magnesium composite. A phase diagram for forming *in situ* formed particles or phases in the magnesium composite is illustrated in Fig. 4.

In accordance with the present invention, a novel magnesium composite is produced by casting a magnesium metal or magnesium alloy with at least one component to form a galvanically-active phase with another component in the chemistry that forms a discrete phase that is insoluble at the use temperature of the dissolvable component. The *in situ* formed particles and phases have a different galvanic potential from the remaining magnesium metal or magnesium alloy. The *in situ* formed particles or phases are uniformly dispersed through the matrix metal or metal alloy using techniques such as thixomolding, stir casting, mechanical agitation, chemical agitation, electrowetting, ultrasonic dispersion, and/or combinations of these methods. Due to the particles being formed *in situ* to the melt, such particles generally have excellent wetting to the matrix phase and can be found at grain boundaries or as continuous dendritic phases throughout the component depending on alloy composition and the phase diagram. Because the alloys form galvanic intermetallic particles where the intermetallic phase is insoluble to the matrix at use temperatures, once the material is below the solidus temperature, no further dispersing or size control is necessary in the component. This feature also allows for further grain refinement of the final alloy through traditional deformation processing to increase tensile strength, elongation to failure, and other properties in the alloy system that are not achievable without the use of insoluble particle additions. Because the ratio of *in situ* formed phases in the material is generally constant and the grain boundary to grain surface area is

typically consistent even after deformation processing and heat treatment of the composite, the corrosion rate of such composites remains very similar after mechanical processing.

EXAMPLE 1

5 An AZ91D magnesium alloy having 9 wt% aluminum, 1 wt% zinc and 90 wt% magnesium was melted to above 800°C and at least 200°C below the melting point of nickel. About 7 wt% of nickel was added to the melt and dispersed. The melt was cast into a steel mold. The cast material exhibited a tensile strength of about 14 ksi, an elongation of about 3%, and shear strength of 11ksi. The cast material dissolved at a rate of about 75 mg/cm²-min in a 3% KCl solution at 90°C. The material dissolved at a rate of 1 mg/cm²-hr in a 3% KCl solution at 10 21°C. The material dissolved at a rate of 325mg/cm²-hr. in a 3% KCl solution at 90°C.

EXAMPLE 2

The composite in Example 1 was subjected to extrusion with an 11:1 reduction area. The material exhibited a tensile yield strength of 45ksi, an Ultimate tensile strength of 50ksi and an elongation to failure of 8%. The material has a dissolve rate of 0.8 mg/cm²-min in a 3% KCl 15 solution at 20°C. The material dissolved at a rate of 100mg/cm²-hr in a 3% KCl solution at 90°C.

EXAMPLE 3

The alloy in Example 2 was subjected to an artificial T5 age treatment of 16 hours from 100°C-200°C. The alloy exhibited a tensile strength of 48Ksi and elongation to failure of 5% 20 and a shear strength of 25Ksi. The material dissolved at a rate of 110mg/ cm²-hr in 3% KCl solution at 90°C and 1mg/ cm²-hr in 3% KCl solution at 20°C.

EXAMPLE 4

The alloy in Example 1 was subjected to a solutionizing treatment T4 of 18 hours from 400°C-500°C and then an artificial T6 aging treatment of 16 hours from 100°C-200C. The alloy 25 exhibited a tensile strength of 34Ksi and elongation to failure of 11% and a shear strength of 18Ksi. The material dissolved at a rate of 84mg/ cm²-hr in 3% KCl solution at 90°C and 0.8mg/ cm²-hr in 3% KCl solution at 20°C.

EXAMPLE 5

An AZ91D magnesium alloy having 9 wt% aluminum, 1 wt% zinc and 90 wt% magnesium was melted to above 800°C and at least 200°C below the melting point of copper. About 10 wt% of copper alloyed to the melt and dispersed. The melt was cast into a steel mold. The cast material exhibited a tensile yield strength of about 14 ksi, an elongation of about 3%, and shear strength of 11ksi. The cast material dissolved at a rate of about 50 mg/cm²-hr in a 3% KCl solution at 90°C. The material dissolved at a rate of 0.6 mg/cm²-hr in a 3% KCl solution at 21°C.

EXAMPLE 6

The alloy in Example 5 was subjected to an artificial T5 aging treatment of 16 hours from 100°C-200°C the alloy exhibited a tensile strength of 50Ksi and elongation to failure of 5% and a shear strength of 25Ksi. The material dissolved at a rate of 40mg/ cm²-hr in 3% KCl solution at 90°C and 0.5mg/cm²-hr in 3% KCl solution at 20°C.

It will thus be seen that the objects set forth above, among those made apparent from the preceding description, are efficiently attained, and since certain changes may be made in the constructions set forth without departing from the spirit and scope of the invention, it is intended that all matter contained in the above description and shown in the accompanying drawings shall be interpreted as illustrative and not in a limiting sense. The invention has been described with reference to preferred and alternate embodiments. Modifications and alterations will become apparent to those skilled in the art upon reading and understanding the detailed discussion of the invention provided herein. This invention is intended to include all such modifications and alterations insofar as they come within the scope of the present invention. It is also to be understood that the following claims are intended to cover all of the generic and specific features of the invention herein described and all statements of the scope of the invention, which, as a matter of language, might be said to fall there between. The invention has been described with reference to the preferred embodiments. These and other modifications of the preferred embodiments as well as other embodiments of the invention will be obvious from the disclosure herein, whereby the foregoing descriptive matter is to be interpreted merely as illustrative of the

invention and not as a limitation. It is intended to include all such modifications and alterations insofar as they come within the scope of the appended claims.

What is claimed:

1. A method of controlling the dissolution properties of a magnesium or a magnesium alloy comprising of the steps of:

heating the magnesium or magnesium alloy to a point above its solidus temperature;

5 adding an additive material to said magnesium or magnesium alloy while said magnesium or magnesium alloy is above said solidus temperature of magnesium or magnesium alloy to form a mixture, said additive material having a greater melting point temperature than said solidus temperature of said magnesium or magnesium alloy, said additive material constituting about 0.05wt%-45wt% of said mixture;

10 dispersing said additive material in said mixture while said magnesium or magnesium alloy is above said solidus temperature of magnesium or magnesium alloy; and,

cooling said mixture to form a magnesium composite, said magnesium composite including *in situ* precipitation of galvanically-active intermetallic phases.

15 2. The method as defined in claim 1, including the step of controlling a size of said *in situ* precipitated intermetallic phase by controlled selection of a mixing technique during said dispersion step, controlling a cooling rate of said mixture, or combinations thereof.

20 3. The method as defined in claim 1, wherein said magnesium or magnesium alloy is heated to a temperature that is less than said melting point temperature of said additive material.

4. The method as defined in claim 2, wherein said magnesium or magnesium alloy is heated to a temperature that is less than said melting point temperature of said additive material.

25 5. The method as defined in claim 1, wherein said additive includes one or more metals selected from the group consisting of copper, silicon, nickel and cobalt.

6. The method as defined in claim 4, wherein said additive includes one or more metals selected from the group consisting of copper, silicon, nickel and cobalt.

7. The method as defined in claim 1, wherein said additive is formed of a single composition, and have an average particle diameter size of about 0.1-500 microns.

8. The method as defined in claim 6, wherein said additive is formed of a single composition, and have an average particle diameter size of about 0.1-500 microns.

9. The method as defined in claim 1, wherein said magnesium alloy includes over 50 wt% magnesium and one or more metals selected from the group consisting of aluminum, boron, bismuth, zinc, zirconium, and manganese.

10. The method as defined in claim 9, wherein said magnesium alloy includes over 50 wt% magnesium and one or more metals selected from the group consisting of aluminum in an amount of about 0.5-10 wt%, zinc in amount of about 0.1-6 wt%, zirconium in an amount of about 0.01-3 wt%, manganese in an amount of about 0.15-2 wt%; boron in amount of about 0.0002-0.04 wt%, and bismuth in amount of about 0.4-0.7 wt%.

11. The method as defined in claim 8, wherein said magnesium alloy includes over 50 wt% magnesium and one or more metals selected from the group consisting of aluminum in an amount of about 0.5-10 wt%, zinc in amount of about 0.1-3 wt%, zirconium in an amount of about 0.01-1 wt%, manganese in an amount of about 0.15-2 wt%; boron in amount of about 0.0002-0.04 wt%, and bismuth in amount of about 0.4-0.7 wt%.

12. The method as defined in claim 1, including the step of solutionizing said magnesium composite at a temperature above 300°C and below a melting temperature of said magnesium composite to improve tensile strength, ductility, or combinations thereof of said magnesium composite.

13. The method as defined in claim 11, including the step of solutionizing said magnesium composite at a temperature above 300°C and below a melting temperature of said

magnesium composite to improve tensile strength, ductility, or combinations thereof of said magnesium composite.

14. The method as defined in claim 1, including the step of aging said magnesium composite at a temperature of above 100°C and below 300°C to improve tensile strength of said magnesium composite.

15. The method as defined in claim 13, including the step of aging said magnesium composite at a temperature of above 100°C and below 300°C to improve tensile strength of said magnesium composite.

16. The method as defined in claim 1, wherein said additive metal includes about 0.05-35 wt% nickel, said nickel forms intermetallic Mg_xNi as a galvanically-active *in situ* precipitate in said magnesium composite.

17. The method as defined in claim 15, wherein said additive metal includes about 0.05-35 wt% nickel, said nickel forms intermetallic Mg_xNi as a galvanically-active *in situ* precipitate in said magnesium composite.

18. The method as defined in claim 1, wherein said additive includes about 0.05-35 wt% copper, said copper forms intermetallic $CuMg_x$ as the galvanically-active *in situ* precipitate in said magnesium composite.

19. The method as defined in claim 15, wherein said additive includes about 0.05-35 wt% copper, said copper forms intermetallic $CuMg_x$ as the galvanically-active *in situ* precipitate in said magnesium composite.

20. The method as defined in claim 1, wherein said additive includes about 0.05-35 wt% cobalt, said cobalt forms intermetallic CoMg_x as the galvanically-active *in situ* precipitate in said magnesium composite.

5 21. The method as defined in claim 15, wherein said additive includes about 0.05-35 wt% cobalt, said cobalt forms intermetallic CoMg_x as the galvanically-active *in situ* precipitate in said magnesium composite.

10 22. A magnesium composite that includes *in situ* precipitation of galvanically-active intermetallic phases comprising a magnesium or a magnesium alloy, an additive material having a greater melting point temperature than a solidus temperature of said magnesium or magnesium alloy, said additive material constituting about 0.05wt%-45wt% of said mixture, said additive material forming metal composite particles or precipitant in said magnesium composite that include said additive material and magnesium, said metal composite particles or precipitant forming said *in situ* precipitation of galvanically-active intermetallic phases.

15 23. The magnesium composite as defined in claim 22, wherein said additive includes one or more metals selected from the group consisting of copper, silicon, nickel and cobalt.

20 24. The magnesium composite as defined in claim 22, wherein said magnesium alloy includes over 50 wt% magnesium and one or more metals selected from the group consisting of aluminum, boron, bismuth, zinc, zirconium, and manganese.

25 25. The magnesium composite as defined in claim 22, wherein said magnesium alloy includes over 50 wt% magnesium and one or more metals selected from the group consisting of aluminum in an amount of about 0.5-10 wt%, zinc in amount of about 0.1-3 wt%, zirconium in an amount of about 0.01-1 wt%, manganese in an amount of about 0.15-2 wt%, boron in amount of about 0.0002-0.04 wt%, and bismuth in amount of about 0.4-0.7 wt%.

26. The magnesium composite as defined in claim 22, wherein said additive metal includes about 0.05-35 wt% nickel, said nickel forms intermetallic Mg_xNi as a galvanically-active *in situ* precipitate in said magnesium composite.

5 27. The magnesium composite as defined in claim 22, wherein said additive includes about 0.05-35 wt% copper, said copper forms intermetallic $CuMg_x$ as the galvanically-active *in situ* precipitate in said magnesium composite.

10 28. The magnesium composite as defined in claim 22, wherein said additive includes about 0.05-35 wt% cobalt, said cobalt forms intermetallic $CoMg_x$ as the galvanically-active *in situ* precipitate in said magnesium composite.

15 29. The magnesium composite as defined in claim 22, where the use of a deformation processing such as forging or extrusion is used to reduce grain size of said magnesium composite, increase tensile yield strength of said magnesium composite, increase elongation of said magnesium composite, or combinations thereof.

20 30. The magnesium composite as defined in claim 22, wherein said magnesium composite is subjected to a surface treatment to improve a surface hardness of said magnesium composite, said surface treatment including peening, heat treatment, aluminizing, or combinations thereof.

25 31. The magnesium composite as defined in claim 22, wherein a dissolution rate of said magnesium composite is about $5-300\text{mg}/\text{cm}^2/\text{hr}$ in 3 wt% KCl water mixture at 90°C .

32. The magnesium composite as defined in claim 22, wherein a dissolution rate of said magnesium composite is controlled by an amount and size of said *in situ* formed galvanically-active particles whereby smaller average sized particles of said *in situ* formed galvanically-active particles, a greater weight percent of said *in situ* formed galvanically-active

particles in said magnesium composite, or combinations thereof increases said dissolution rate of said magnesium composite.

ABSTRACT OF THE DISCLOSURE

A castable, moldable, and/or extrudable structure using a metallic primary alloy. One or more additives are added to the metallic primary alloy so that *in situ* galvanically-active reinforcement particles are formed in the melt or on cooling from the melt. The composite contain an optimal composition and morphology to achieve a specific galvanic corrosion rate in the entire composite. The *in situ* formed galvanically-active particles can be used to enhance mechanical properties of the composite, such as ductility and/or tensile strength. The final casting can also be enhanced by heat treatment, as well as deformation processing such as extrusion, forging, or rolling, to further improve the strength of the final composite over the as-cast material.

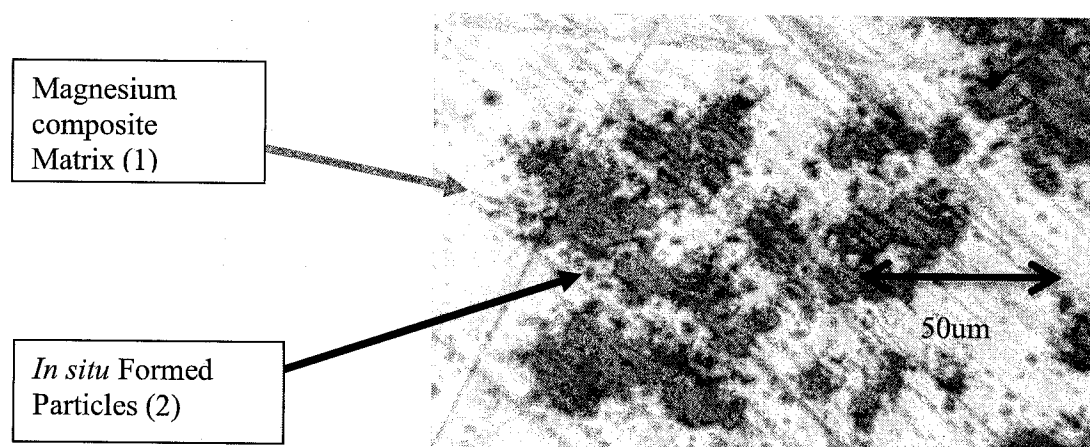


FIG 1.

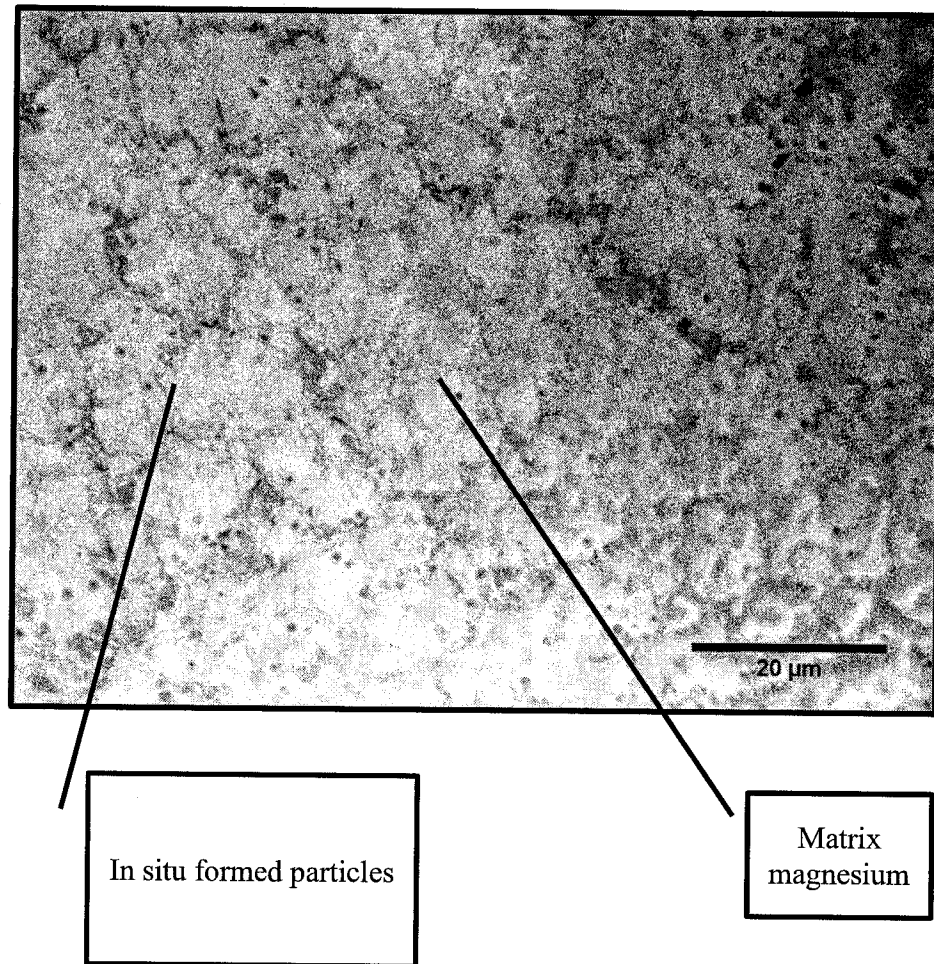
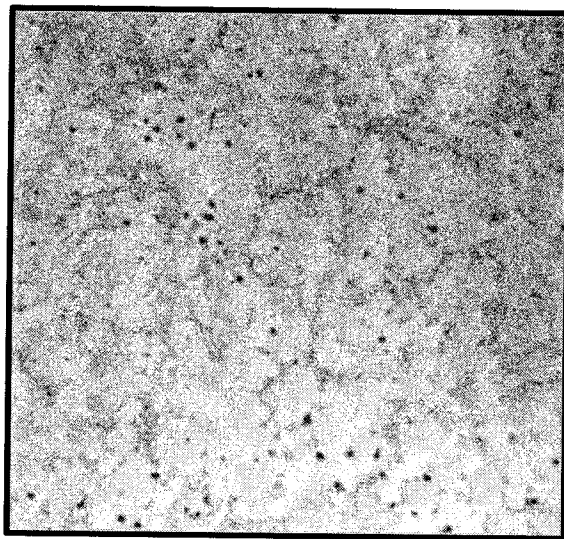


FIG. 2

3/4



Highlighted In Situ Formed Particles

FIG. 3

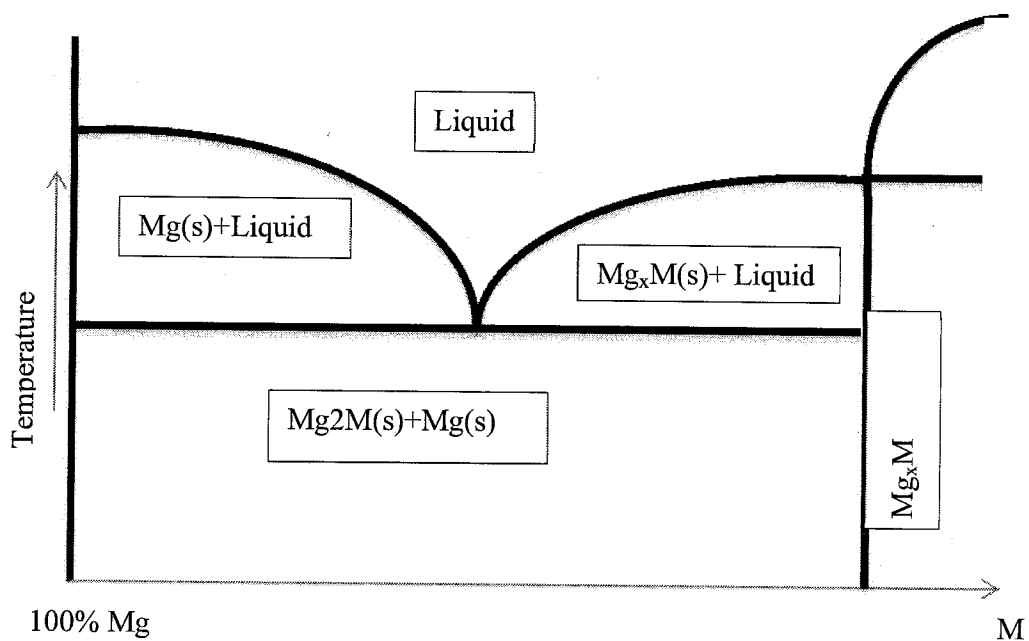


FIG. 4