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

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CPC **C22F 1/06** (2013.01); **C22C 1/02** (2013.01); **C22C 23/02** (2013.01); **C22C 23/00** (2013.01)

(58) **Field of Classification Search**

CPC ... **C22F 1/06**; **C22C 23/02**; **C22C 1/02**; **C22C 23/00**

See application file for complete search history.

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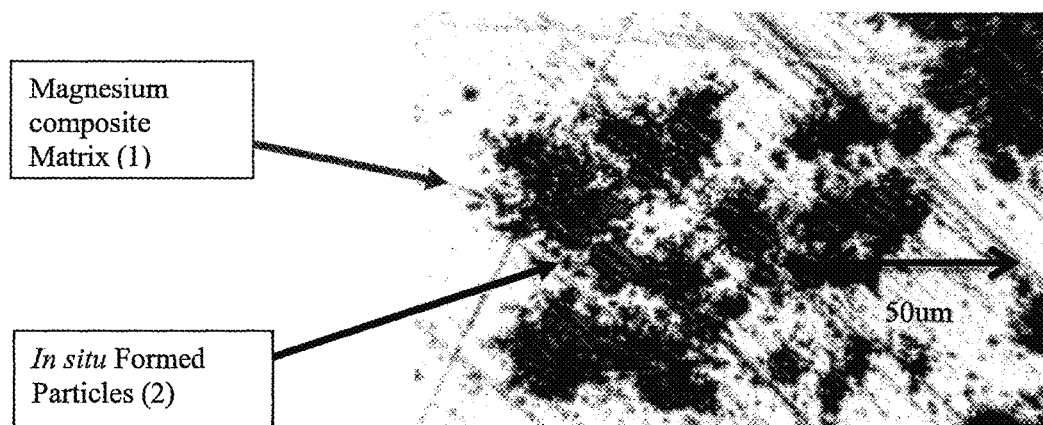
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(57) **ABSTRACT**

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.

78 Claims, 4 Drawing Sheets



Magnesium
composite
Matrix (1)

In situ Formed
Particles (2)

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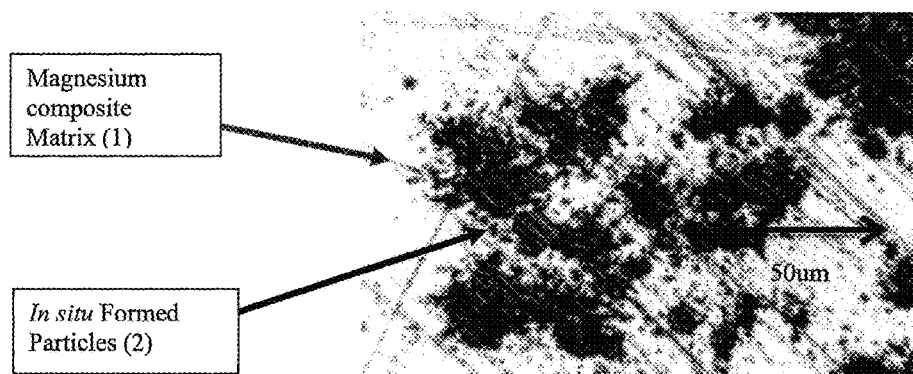


FIG 1.

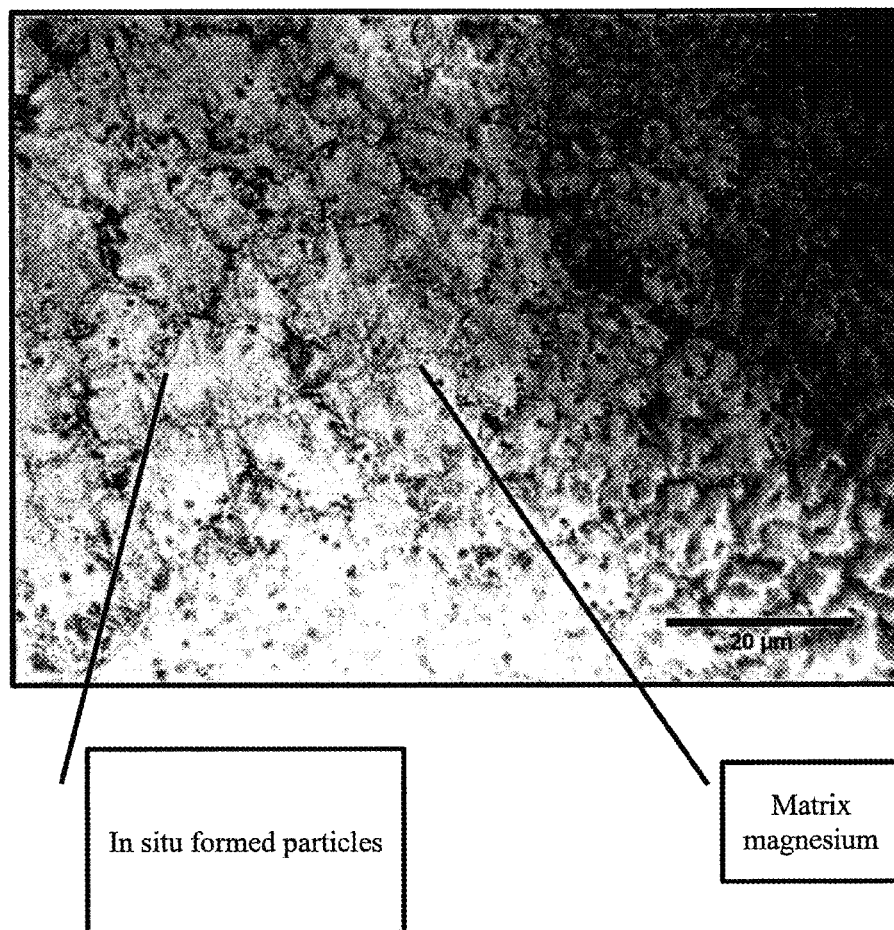
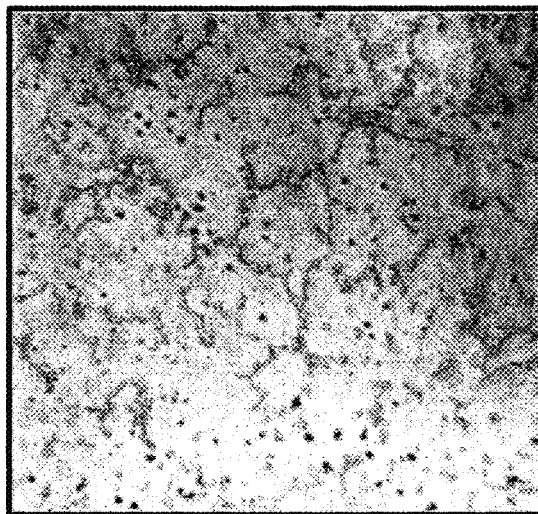


FIG. 2



Highlighted In Situ Formed Particles

FIG. 3

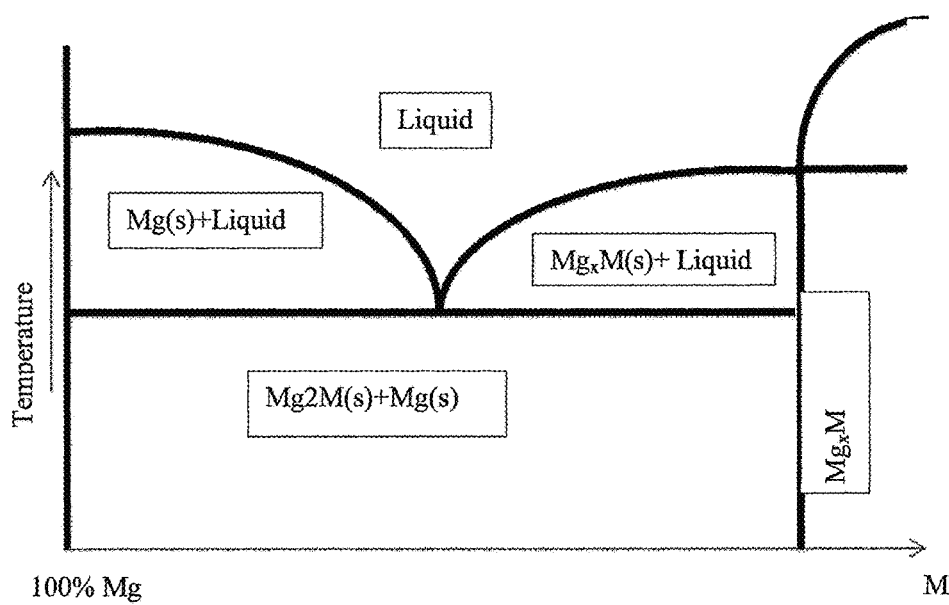


FIG. 4

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

The present invention is a divisional of U.S. patent application Ser. No. 14/689,295 filed Apr. 17, 2015, which in turn claims priority on U.S. Provisional Patent Application Ser. No. 61/981,425 filed Apr. 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

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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. % to 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. % to 95 wt. % of the magnesium composite, and typically the magnesium or magnesium alloy constitutes about 70 wt. % to 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

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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.

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 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 through 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.

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

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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 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 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 values or ranges therebetween) is added to the magnesium or magnesium alloy to form intermetallic Mg₂Ni 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 than the melting point of the nickel. Throughout

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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 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

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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

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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.

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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 anyone 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 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 anyone 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 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 of the molten magnesium or magnesium alloy is less than the melting point of the nickel. During the mixing process, solid particles of Mg₂Ni are formed. Once the mixing process is complete, the mixture of molten magnesium or magnesium alloy, solid particles of Mg₂Ni, and any unalloyed nickel particles are cooled and an in situ precipitate of solid particles of Mg₂Ni and any unalloyed nickel particles are formed in the solid magne-

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 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

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 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°

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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 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.

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 though 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, 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 least 0.05 wt. % $MgNi_2$ with the magnesium or magnesium alloy and solutionizing the resultant metal at a temperature within a range of 100-500° 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 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 100-500° C. for a period of 0.25-50 hours, the magnesium composite being characterized by higher tensile and yield strengths than magnesium base alloys 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

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magnesium composite being characterized by higher dissolution rates than metal without copper additions subjected to the said aging treatment.

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 wt. % and copper is added to form in situ precipitation of at least 0.05 wt. % $MgCu_2$ 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 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.

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 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 Mg_2Si 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 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 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 though 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, 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 least 0.05 wt. % $MgNi_2$ with the magnesium or magnesium alloy and solutionizing the resultant metal at a temperature within a range of 100-500° 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 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

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the resultant metal at a temperature at about 100-500° C. for a period of 0.25-50 hours, the magnesium composite being characterized by higher tensile and yield strengths than magnesium base alloys 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. % MgCu₂ 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.

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 wt. % 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 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.

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 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 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.

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.

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.

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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.

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 magnesium alloy having 9 wt. % aluminum, 1 wt. % zinc and 90 wt. % magnesium, b) melting the AZ91 D 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 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 11 ksi. 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 325 mg/cm²-hr. in a 3% KCl solution at 90° C. The cast material can be subjected to extrusion with a 11:1 reduction area. The extruded cast material exhibits a tensile strength of 40 ksi, 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 100 mg/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 48 ksi, an elongation to failure of 5%, and a shear strength of 25 ksi. The aged extruded cast material dissolves at a rate of 110 mg/cm²-hr in 3% KCl solution at 90° C. and 1 mg/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 84 mg/cm²-hr in 3% KCl solution at 90° C., and about 0.8 mg/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 17 ksi. The cast material has a dissolve rate of about 45 mg/cm²-min in

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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 325 mg/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 yield strength of 35 ksi, 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 50 mg/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 48 ksi, an elongation to failure of 5%, and a shear strength of 25 ksi.

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 11 ksi. 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 50 Ksi, an elongation to failure of 5%, and a shear strength of 25 ksi. The aged cast material dissolved at a rate of 40 mg/cm²-hr in 3% KCl solution at 90° C. and 0.5 mg/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

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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

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 11 ksi. 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 21° C. The material dissolved at a rate of 325 mg/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 45 ksi, an Ultimate tensile strength of 50 ksi and an elongation to failure of 8%. The material has a dissolve rate of 0.8 mg/cm²-min. in a 3% KCl solution at 20° C. The material dissolved at a rate of 100 mg/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 48 ksi and elongation to failure of 5% and a shear strength of 25 ksi. The material dissolved at a rate of 110 mg/cm²-hr. in 3% KCl solution at 90° C. and 1 mg/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.-200° C. The alloy exhibited a tensile strength of 34 ksi and

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elongation to failure of 11% and a shear strength of 18 Ksi. The material dissolved at a rate of 84 mg/cm²-hr. in 3% KCl solution at 90° C. and 0.8 mg/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 11 ksi. 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 50 ksi and elongation to failure of 5% and a shear strength of 25 ksi. The material dissolved at a rate of 40 mg/cm²-hr. in 3% KCl solution at 90° C. and 0.5 mg/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 magnesium composite that includes in situ precipitation of galvanically-active intermetallic phases to enable controlled dissolution of said magnesium composite, said magnesium composite comprising a mixture of magnesium or a magnesium alloy and an additive material, said additive material having a greater melting point temperature than a solidus temperature of said magnesium, said additive material constituting about 0.05 wt. %-45 wt. % of said mixture, said additive material forming precipitant in said magnesium composite, said additive material includes one or more metals selected from the group consisting of copper, nickel,

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iron, and cobalt, said magnesium composite has a dissolution rate of at least 5 mg/cm²/hr. in 3 wt. % KCl water mixture at 90° C.

2. The magnesium composite 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.

3. The magnesium composite 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 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. %.

4. The magnesium composite as defined in claim 1, wherein said additive material includes nickel, said nickel constitutes about 0.05-35 wt. % of said magnesium composite, said nickel forms galvanically-active in situ precipitate in said magnesium composite.

5. The magnesium composite as defined in claim 1, wherein said additive material includes copper, said copper constitutes about 0.05-35 wt. % of said magnesium composite, said copper forms galvanically-active in situ precipitate in said magnesium composite.

6. The magnesium composite as defined in claim 1, wherein said additive material includes cobalt, said cobalt constitutes about 0.05-35 wt. % of said magnesium composite, said cobalt forms galvanically-active in situ precipitate in said magnesium composite.

7. The magnesium composite as defined in claim 1, where said magnesium composite is subjected to a deformation processing 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.

8. The magnesium composite as defined in claim 1, 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.

9. The magnesium composite as defined in claim 1, wherein a dissolution rate of said magnesium composite is about 5-325 mg/cm²/hr. in 3 wt. % KCl water mixture at 90° C.

10. The magnesium composite as defined in claim 1, 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.

11. The magnesium composite as defined in claim 1, wherein said additive material is a metal or metal alloy.

12. A magnesium composite that includes in situ precipitation of galvanically-active intermetallic phases to enable controlled dissolution of said magnesium composite comprising a mixture of a magnesium or a magnesium alloy and an additive material, said additive material having a greater melting point temperature than a solidus temperature of said magnesium, said composite including greater than 50 wt. % magnesium, said additive material constituting about 0.05-45 wt. % of said magnesium composite, said additive material having a melting point temperature that is 100° C.

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greater than a melting temperature of said magnesium or magnesium alloy, said additive material including one or more metals selected from the group consisting of copper, nickel, cobalt, titanium, and iron, at least a portion of said additive material remaining unalloyed additive material, said magnesium composite including in situ precipitation of galvanically-active intermetallic phases that includes said unalloyed additive material, said magnesium composite has a dissolution rate of at least 5 mg/cm²/hr. in 3 wt. % KCl water mixture at 90° C.

13. The magnesium composite as defined in claim 12, wherein said additive material is added to said magnesium or magnesium alloy while said magnesium or magnesium alloy is at a temperature that is above said solidus temperature of said magnesium and a temperature that is less than a melting point of said additive material to form said mixture.

14. The magnesium composite as defined in claim 13, 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 an amount of about 0.4-0.7 wt. %.

15. The magnesium composite as defined in claim 14, wherein said additive material includes nickel, said nickel constitutes about 0.05-35 wt. % of said magnesium composite, said nickel forms galvanically-active in situ precipitate in said magnesium composite.

16. The magnesium composite as defined in claim 15, wherein said additive material includes nickel, said nickel constitutes about 3-7 wt. % of said magnesium composite.

17. The magnesium composite as defined in claim 15, wherein said additive material includes nickel, said nickel constitutes about 7-10 wt. % of said magnesium composite.

18. The magnesium composite as defined in claim 15, wherein a dissolution rate of said magnesium composite is at least 45 mg/cm²/hr. in 3 wt. % KCl water mixture at 90° C. and up to 325 mg/cm²/hr. in 3 wt. % KCl water mixture at 90° C.

19. The magnesium composite as defined in claim 12, 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 an amount of about 0.4-0.7 wt. %.

20. The magnesium composite as defined in claim 12, said additive material includes nickel, said nickel constitutes about 0.05-35 wt. % of said magnesium composite, said nickel forms galvanically-active in situ precipitate in said magnesium composite.

21. The magnesium composite as defined in claim 20, wherein said additive material includes nickel, said nickel constitutes about 3-7 wt. % of said magnesium composite.

22. The magnesium composite as defined in claim 20, wherein said additive material includes nickel, said nickel constitutes about 7-10 wt. % of said magnesium composite.

23. The magnesium composite as defined in claim 12, wherein a dissolution rate of said magnesium composite is at least 45 mg/cm²/hr. in 3 wt. % KCl water mixture at 90° C. and up to 325 mg/cm²/hr. in 3 wt. % KCl water mixture at 90° C.

24. The magnesium composite as defined in claim 12, wherein said additive material is a metal or metal alloy.

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25. A dissolvable magnesium alloy composite for use in a ball or other tool component in a well drilling or completion operation, said dissolvable magnesium alloy composite comprising at least 85 wt. % magnesium; one or more metals selected from the group consisting of 0.5-10 wt. % aluminum, 0.05-6 wt. % zinc, 0.01-3 wt. % zirconium, and 0.15-2 wt. % manganese; and about 0.05-45 wt. % of a secondary metal to form a galvanically-active intermetallic particle that promotes corrosion of said dissolvable magnesium alloy composite, said secondary metal including one or more metals selected from the group consisting of copper, nickel, cobalt, titanium and iron, said magnesium alloy composite has a dissolution rate of at least 5 mg/cm²/hr. in 3 wt. % KCl water mixture at 90° C.

26. The dissolvable magnesium alloy composite as defined in claim 25, wherein a dissolution rate of said magnesium alloy composite is 100-325 mg/cm²/hr. in 3 wt. % KCl water mixture at 90° C.

27. The dissolvable magnesium composite as defined in claim 25, wherein said secondary metal includes nickel, said nickel forms galvanically-active in situ precipitate in said magnesium composite.

28. The dissolvable magnesium alloy composite as defined in claim 25, wherein said additive material is a metal or metal alloy.

29. A dissolvable magnesium alloy composite for use in a ball or other tool component in a well drilling or completion operation, said dissolvable magnesium alloy composite comprising 60-95 wt. % magnesium; 0.01-1 wt. % zirconium; and about 0.05-45 wt. % of a secondary metal to form a galvanically-active intermetallic particle that promotes corrosion of said dissolvable magnesium alloy composite, said secondary metal including one or more metals selected from the group consisting of copper, nickel, cobalt, titanium and iron, said magnesium alloy composite has a dissolution rate of at least 5 mg/cm²/hr. in 3 wt. % KCl water mixture at 90° C.

30. The dissolvable magnesium alloy composite as defined in claim 29, wherein a dissolution rate of said magnesium alloy composite is 5-325 mg/cm²/hr. in 3 wt. % KCl water mixture at 90° C.

31. The dissolvable magnesium composite as defined in claim 29, wherein said secondary metal includes nickel, said nickel forms galvanically-active in situ precipitate in said magnesium composite.

32. The dissolvable magnesium alloy composite as defined in claim 29, wherein said additive material is a metal or metal alloy.

33. A dissolvable magnesium alloy composite for use in a ball or other tool component in a well drilling or completion operation, said dissolvable magnesium alloy composite comprising 60-95 wt. % magnesium; 0.5-10 wt. % aluminum; 0.05-6 wt. % zinc; 0.15-2 wt. % manganese; and about 0.05-45 wt. % of a secondary metal to form a galvanically-active intermetallic particle that promotes corrosion of said dissolvable magnesium alloy composite, said secondary metal including one or more metals selected from the group consisting of copper, nickel, cobalt, titanium and iron, said magnesium alloy composite has a dissolution rate of at least 5 mg/cm²/hr. in 3 wt. % KCl water mixture at 90° C.

34. The dissolvable magnesium alloy composite as defined in claim 33, wherein a dissolution rate of said magnesium alloy composite is 5-325 mg/cm²/hr. in 3 wt. % KCl water mixture at 90° C.

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35. The dissolvable magnesium composite as defined in claim 33, wherein said secondary metal includes nickel, said nickel forms galvanically-active in situ precipitate in said magnesium composite.

36. The dissolvable magnesium alloy composite as defined in claim 33, wherein said additive material is a metal or metal alloy.

37. A dissolvable magnesium alloy composite for use in a ball or other tool component in a well drilling or completion operation, said dissolvable magnesium alloy composite comprising 60-95 wt. % magnesium; 0.05-6 wt. % zinc; 0.01-1 wt. % zirconium; and about 0.05-45 wt. % of a secondary metal to form a galvanically-active intermetallic particle that promotes corrosion of said dissolvable magnesium alloy composite, said secondary metal including one or more metals selected from the group consisting of copper, nickel, cobalt, titanium and iron, said magnesium alloy composite has a dissolution rate of at least 5 mg/cm²/hr. in 3 wt. % KCl water mixture at 90° C.

38. The dissolvable magnesium alloy composite as defined in claim 37, wherein a dissolution rate of said magnesium alloy composite is 5-325 mg/cm²/hr. in 3 wt. % KCl water mixture at 90° C.

39. The dissolvable magnesium composite as defined in claim 37, wherein said secondary metal includes nickel, said nickel forms galvanically-active in situ precipitate in said magnesium composite.

40. The dissolvable magnesium alloy composite as defined in claim 37, wherein said additive material is a metal or metal alloy.

41. A dissolvable magnesium alloy composite for use in a ball or other tool component in a well drilling or completion operation, said dissolvable magnesium alloy composite comprising over 50 wt. % magnesium; one or more metals selected from the group consisting of 0.5-10 wt. % aluminum, 0.1-2 wt. % zinc, 0.01-1 wt. % zirconium, and 0.15-2 wt. % manganese; and about 0.05-45 wt. % of a secondary metal to form a galvanically-active intermetallic particle that promotes corrosion of said dissolvable magnesium alloy composite, said secondary metal including one or more metals selected from the group consisting of copper, nickel and cobalt, said magnesium alloy composite has a dissolution rate of at least 5 mg/cm²/hr. in 3 wt. % KCl water mixture at 90° C.

42. The dissolvable magnesium alloy composite as defined in claim 41, wherein a dissolution rate of said magnesium alloy composite is 5-325 mg/cm²/hr. in 3 wt. % KCl water mixture at 90° C.

43. The dissolvable magnesium composite as defined in claim 41, wherein said secondary metal includes nickel, said nickel forms galvanically-active in situ precipitate in said magnesium composite.

44. The dissolvable magnesium alloy composite as defined in claim 41, wherein said additive material is a metal or metal alloy.

45. A dissolvable magnesium alloy composite for use in a ball or other tool component in a well drilling or completion operation, said dissolvable magnesium alloy composite comprising over 50 wt. % magnesium; one or more metals selected from the group consisting of 0.1-3 wt. % zinc, 0.01-1 wt. % zirconium, 0.05-1 wt. % manganese, 0.0002-0.04 wt. % boron, and 0.4-0.7 wt. % bismuth; and about 0.05-45 wt. % of a secondary metal to form a galvanically-active intermetallic particle that promotes corrosion of said dissolvable magnesium alloy composite, said secondary metal including one or more metals selected from the group consisting of copper, nickel, and cobalt, said magnesium

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alloy composite has a dissolution rate of at least 5 mg/cm²/hr. in 3 wt. % KCl water mixture at 90° C.

46. The dissolvable magnesium alloy composite as defined in claim 45, wherein a dissolution rate of said magnesium alloy composite is 5-325 mg/cm²/hr. in 3 wt. % KCl water mixture at 90° C.

47. The dissolvable magnesium composite as defined in claim 45, wherein said secondary metal includes nickel, said nickel forms galvanically-active in situ precipitate in said magnesium composite.

48. The dissolvable magnesium alloy composite as defined in claim 45, wherein said additive material is a metal or metal alloy.

49. A magnesium composite that includes in situ precipitation of galvanically-active intermetallic phases to enable controlled dissolution of said magnesium composite, said magnesium composite comprising a mixture of magnesium or a magnesium alloy and an additive material, said additive material constituting about 0.05-45 wt. % of said mixture, said additive material includes one or more metals selected from the group consisting of copper, nickel, titanium, iron, and cobalt, said magnesium composite including in situ precipitation of galvanically-active intermetallic phases that include said additive material, said additive material located in sufficient quantities in said galvanically-active intermetallic phases so as to obtain a composition and morphology of said galvanically-active intermetallic phases such that a galvanic corrosion rate along said galvanically-active intermetallic phases causes said magnesium composite to have a dissolution rate of at least at least 5 mg/cm²/hr. in 3 wt. % KCl water mixture at 90° C.

50. The magnesium composite as defined in claim 49, wherein said additive material includes one or more metals selected from the group consisting of copper, nickel, and cobalt.

51. The magnesium composite as defined in claim 49, wherein said additive material includes particles having an average particle diameter size of about 0.1-500 microns.

52. The magnesium composite as defined in claim 49, 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.

53. The magnesium composite as defined in claim 49, 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 an 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 an amount of about 0.0002-0.04 wt. %, and bismuth in amount of about 0.4-0.7 wt. %.

54. The magnesium composite as defined in claim 49, 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 an 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 an amount of about 0.0002-0.04 wt. %, and bismuth in an amount of about 0.4-0.7 wt. %.

55. The magnesium composite as defined in claim 49, wherein said magnesium alloy includes at least 85 wt. % magnesium, and one or more metals selected from the group consisting of 0.5-10 wt. % aluminum, 0.05-6 wt. % zinc, 0.01-3 wt. % zirconium, and 0.15-2 wt. % manganese.

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56. The magnesium composite as defined in claim 49, wherein said magnesium alloy includes 60-95 wt. % magnesium and 0.01-1 wt. % zirconium.

57. The magnesium composite as defined in claim 56, wherein said magnesium alloy further includes 0.05-6 wt. % zinc.

58. The magnesium composite as defined in claim 49, wherein said magnesium alloy includes 60-95 wt. % magnesium, 0.5-10 wt. % aluminum, 0.05-6 wt. % zinc, and 0.15-2 wt. % manganese.

59. The magnesium composite as defined in claim 49, wherein said magnesium alloy includes over 50 wt. % magnesium and one or more metals selected from the group consisting of 0.5-10 wt. % aluminum, 0.1-2 wt. % zinc, 0.01-1 wt. % zirconium, and 0.15-2 wt. % manganese.

60. The magnesium composite as defined in claim 49, wherein said magnesium alloy includes over 50 wt. % magnesium, and one or more metals selected from the group consisting of 0.1-3 wt. % zinc, 0.01-1 wt. % zirconium, 0.05-1 wt. % manganese, 0.0002-0.04 wt. % boron, and 0.4-0.7 wt. % bismuth.

61. The magnesium composite as defined in claim 49, wherein said additive material includes nickel, said nickel constitutes about 0.05-35 wt. % of said magnesium composite, said nickel forms galvanically-active in situ precipitate in said magnesium composite.

62. The magnesium composite as defined in claim 61, wherein said nickel constitutes about 3-7 wt. % of said magnesium composite.

63. The magnesium composite as defined in claim 61, wherein said nickel constitutes about 7-10 wt. % of said magnesium composite.

64. The magnesium composite as defined in claim 49, wherein said additive material includes copper, said copper constitutes about 0.05-35 wt. % of said magnesium composite, said copper forms the galvanically-active in situ precipitate in said magnesium composite.

65. The magnesium composite as defined in claim 49, wherein said additive material includes cobalt, said cobalt constitutes about 0.05-35 wt. % of said magnesium composite, said cobalt forms the galvanically-active in situ precipitate in said magnesium composite.

66. The magnesium composite as defined in claim 49, wherein a dissolution rate of said magnesium composite is about 5-325 mg/cm²/hr. in 3 wt. % KCl water mixture at 90° C.

67. The magnesium composite as defined in claim 49, wherein a dissolution rate of said magnesium composite is at least 45 mg/cm²/hr. in 3 wt. % KCl water mixture at 90° C. and up to 325 mg/cm²/hr. in 3 wt. % KCl water mixture at 90° C.

68. The magnesium composite as defined in claim 49, wherein a dissolution rate of said magnesium composite is up to 1 mg/cm²/hr. in 3 wt. % KCl water mixture at 21° C.

69. The magnesium composite as defined in claim 49, wherein said additive material has a melting point temperature that is 100° C. greater than a melting temperature of said magnesium or magnesium alloy.

70. The magnesium composite as defined in claim 49, wherein said magnesium composite is at least partially included in a down hole well component, said down hole well component including one or more components selected from the group consisting of a sleeve, frac ball, hydraulic actuating tooling, tube, valve, valve component, or plug.

71. The magnesium composite as defined in claim 49, wherein at least a portion of said additive material remains unalloyed additive material in said magnesium composite.

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72. The magnesium composite as defined in claim 49, wherein said additive material is a metal or metal alloy.

73. A dissolvable magnesium composite for use in a ball or other tool component in a well drilling or completion operation, said dissolvable magnesium composite includes in situ precipitation of galvanically-active intermetallic phases to enable controlled dissolution of said magnesium composite, said magnesium composite comprising a mixture of magnesium or a magnesium alloy and an additive material, said additive material constituting about 0.05 wt. % of said mixture, said additive material is a metal or metal alloy, said additive material includes one or more metals selected from the group consisting of copper, nickel, titanium, iron, silicon, and cobalt, said magnesium composite including in situ precipitation of galvanically-active intermetallic phases that include said additive material, said additive material located in sufficient quantities in said galvanically-active intermetallic phases so as to obtain a composition and morphology of said galvanically-active intermetallic phases such that a galvanic corrosion rate along said galvanically-active intermetallic phases causes said magnesium composite to have a dissolution rate of at least at least 5 mg/cm²/hr. in 3 wt. % KCl water mixture at 90° C.

74. A dissolvable magnesium composite for use in a ball or other tool component in a well drilling or completion operation, said dissolvable magnesium composite includes in situ precipitation of galvanically-active intermetallic

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phases to enable controlled dissolution of said magnesium composite, said magnesium composite comprising a mixture of magnesium or a magnesium alloy and an additive material, said additive material constituting at least 0.1 wt. % of said mixture, said magnesium in said magnesium composite constituting at least 85 wt. %, said additive material is a metal material selected from the group consisting of copper, nickel and cobalt, said magnesium composite including in situ precipitation of galvanically-active intermetallic phases that include said additive material, said magnesium composite has a dissolution rate of 84-325 mg/cm²/hr. in 3 wt. % KCl water mixture at 90° C.

75. The magnesium composite as defined in claim 74, wherein said magnesium alloy is an AZ91D magnesium alloy that includes aluminum and zinc.

76. The magnesium composite as defined in claim 74, wherein said additive material includes nickel, a content of said nickel in said magnesium composite is at least 0.3 wt. %.

77. The magnesium composite as defined in claim 74, wherein said additive material includes nickel, a content of said nickel in said magnesium composite is at least 7 wt. %.

78. The magnesium composite as defined in claim 74, wherein said additive material includes nickel, a content of said nickel in said magnesium composite is at least 10 wt. %.

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