(19) DANMARK

(10) **DK/EP 3175010 T3**

Patent- og Varemærkestyrelsen

(12) Oversættelse af europæisk patentskrift

(51) Int.Cl.: *C 22 C 23/00 (2006.01)* *B 22 D 21/00 (2006.01)* *B 22 D 21/04 (2006.01)* *C 22 C 23/02 (2006.01)* *C 22 C 23/04 (2006.01)* *C 22 C 23/06 (2006.01)* *E 21 B 33/12 (2006.01)* *E 21 B 34/06 (2006.01)*

(45) Oversættelsen bekendtgjort den: **2020-06-02**

(80) Dato for Den Europæiske Patentmyndigheds bekendtgørelse om meddelelse af patentet: **2020-03-25**

(86) Europæisk ansøgning nr.: **15744320.1**

(86) Europæisk indleveringsdag: **2015-07-28**

(87) Den europæiske ansøgnings publiceringsdag: **2017-06-07**

(86) International ansøgning nr.: **GB2015052169**

(87) Internationalt publikationsnr.: **WO2016016628**

(30) Prioritet: **2014-07-28 GB 201413327**

(84) Designerede stater: **AL AT BE BG CH CY CZ DE DK EE ES FI FR GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO RS SE SI SK SM TR**

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(54) Benævnelse: **Borehulsartikel, der kan korrodere**

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DESCRIPTION

[0001] This invention relates to a corrodible downhole article comprising a magnesium alloy and the use of the article.

Background

[0002] The oil and gas industries utilise a technology known as hydraulic fracturing or "fracking". This normally involves the pressurisation with water of a system of boreholes in oil and/or gas bearing rocks in order to fracture the rocks to release the oil and/or gas.

[0003] In order to achieve this pressurisation, valves may be used to separate different sections of a borehole system. These valves are referred to as downhole valves, the word downhole being used in the context of the invention to refer to an article that is used in a well or borehole.

[0004] One way of forming such valves involves the use of spheres of material known as fracking balls to seal off parts of a borehole. Fracking balls may be made from aluminium, magnesium, polymers or composites.

[0005] A problem with the use of fracking balls relates to how they are removed once the fracking operation has been completed in order to allow fluid to flow through the well or borehole. One way of doing this is to drill through the fracking ball. However, this type of drilling process can hamper production, as well as being expensive, difficult and therefore undesirable.

[0006] One proposed solution to this problem has been to form the fracking ball from a material that will dissolve or corrode under the conditions in the well or borehole. An issue that needs to be considered in relation to such corrodible articles is ensuring that they corrode at a rate which allows them to remain useable for the time period during which they are required to perform their function, but that allows them to corrode or dissolve afterwards.

[0007] Degradable polymers have been used in order to provide a corrodible article for use in such methods. However, these polymers do not generally have particularly high mechanical strength.

[0008] An alternative corrodible article is described in US patent no 8,425,651 in the name of Xu et al. This document describes a powder metal composite comprising a nanomatrix, preferably made of Al or Ni or a combination thereof, in which are dispersed a plurality of first particles, a plurality of second particles and a solid-state bond layer. The first particles comprise Mg, Al, Zn or Mn, or a combination thereof, and the second particles comprise carbon nanoparticles. The composite may be produced by forming a powder mixture of the required components and then applying temperature and pressure to the powder to sinter and deform (but not melt) the composite in order to form a powder composite. A problem with such powder metallurgical methods is that they are complicated and expensive.

[0009] A further corrodible article is described in US patent application publication no 2012/0318513 in the name of Mazyar et al. In this document, the corrodible article is described as having a corrodible core and a metallic layer covering the core. The core material is described as being a magnesium alloy. However, it appears that the combination of magnesium and one or more other materials in a form which is not an alloy is also intended to be covered by the use of the term "alloy" in Mazyar et al. For example, this document refers to alloys of magnesium with tungsten, whereas it is actually not technically feasible to form a magnesium-tungsten alloy. Similarly, Mazyer et al also mentions powders of magnesium coated with a metal oxide as being useful for forming the core, which again would not be magnesium "alloys". Thus, Mazyar et al appears to utilise the term "magnesium alloy" to mean any way in which magnesium and another metal are combined. The metallic layer is described as including aluminium or nickel.

[0010] A dissolvable wellbore isolation device is described in US patent application publication no 2014/0124216 in the name of Halliburton Energy Services, Inc.. Although there is minimal description on how the device is made, it appears that again a powder composite is formed instead of an "alloy". In addition, this document only mentions magnesium as one of a large list of components, with magnesium not being one of the preferred components. The device also requires the presence of an "electrolytic compound" which dissolves in the fluid in the wellbore. Similarly, related US patent application publication no 2014/0190705, also in the name of Halliburton Energy Services, Inc., only mentions magnesium as one of a large list of components, with magnesium not being one of the preferred components. This document also requires the presence of an "electrolytic compound" which dissolves in the fluid in the wellbore.

[0011] Although casting, forging and machining are described in Mazyar et al, these are only mentioned in very general terms (eg method steps and heating temperatures are not stated) and the structure of the resulting materials is not described. In addition, the preferred method of forming the corrodible article is by compressing the powder into the desired shape, for example by cold compression using a isostatic press. As noted above, such powder metallurgical methods are complicated and expensive. In addition, the resulting powder composites can have poor mechanical properties.

[0012] CN 103 343 271 A discloses a light and pressure-proof fast-decomposed cast magnesium alloy which can be used as a tripping ball material for a multi-stage sliding sleeve staged-fracturing technique. CN 101 392 345 A discloses a nickel-containing heat resisting magnesium-rare earth alloy. S. GONZÃLEZ et al., "Influence of processing route on microstructure and mechanical properties of two Mg Ni Y RE alloys", MATERIALS CHARACTERIZATION vol. 64, pages 53-61 (2012, ISSN: 1044-5803, DOI: 10.1016/J.MATCHAR.2011.12.001) discloses Mg-Ni-Y-CeMM alloys. D. V. LOUZGUINE at al. "Influence of Ni, Cu, Zn and Al Additions on Glass-Forming Ability and Mechanical Properties of

Mg-Y-Mm (Mm=Mischmetal) Alloys", MATERIALS SCIENCE FORUM, vol. 350-351, pages 123-130 (2000, DOI: 10.4028/ www.scientific.net/MSF.350-351.123) discloses Mg-Y-Mm-(Ni, Cu, Zn or Al) alloys. J. F. KING, P. LYON, K. SAVAGE "Influence of rare earth elements and minor additions on properties and performance of magnesium-yttrium alloys in critical aerospace applications", ANNUAL WORLD MAGNESIUM CONFERENCE, PROCEEDINGS, 59TH, MONTREAL, QC, CANADA, MAY 19-21, CODEN: 69DIZX CODEN: 69DIZX, 1 January 2002 (2002-01-01), pages 15-21, discloses alloys WE54 and WE43.

[0013] Thus, there is a need in the oil and gas industries to provide a corrodible article which provides the desired corrosion characteristics, whilst also having improved mechanical properties, and at a lower cost than can currently be achieved. It is also advantageous for the corrodible article to have a relatively low density (for example, compared to metals in general). This invention seeks to ameliorate these problems.

Statement of invention

[0014] The invention is defined in the appended claims. This invention relates to a corrodible downhole article comprising a magnesium alloy, the magnesium alloy comprising:

1. (a) 0.01-10wt% of one or more of Ni, Co, Ir, Au, Pd or Cu,
2. (b) 1-10wt% Y,
3. (c) 1-15wt% of at least one rare earth metal other than Y, and
4. (d) 0-1wt% Zr,

wherein the remainder of the alloy is magnesium and incidental impurities, and wherein the alloy has a corrosion rate of at least 50mg/cm^2/day in 15% KCl at 93°C and a 0.2% proof strength of at least 50MPa when tested using standard tensile test method ASTM B557-10.

[0015] In relation to this invention, the term "alloy" is used to mean a composition made by mixing and fusing two or more metallic elements by melting them together, mixing and re-solidifying them.

[0016] The term "rare earth metals" is used in relation to the invention to refer to the fifteen lanthanide elements, as well as Sc and Y.

[0017] The magnesium alloy comprises one or more of Ni, Co, Ir, Au, Pd or Cu. In some embodiments, Ni is preferred. These metallic elements promote the corrosion of the alloy. In all embodiments, the alloy comprises one or more of Ni, Co, Ir, Au, Pd or Cu, more preferably Ni, in an amount of between 0.01% and 10% by weight (wt%), and in some embodiments more preferably between 0.1% and 10% by weight, even more preferably between 0.2 % by weight and 8% by weight.

[0018] Particularly preferred combinations of metals in the magnesium alloy include Mg-Y-RE-

Zr. These additional elements can be included by forming an alloy of magnesium with those elements, and then adding a corrosion promoting metallic element (ie Ni, Co, Ir, Au, Pd and/or Cu) to the molten alloy.

[0019] In a first embodiment of the disclosure, which corresponds to the invention, the magnesium alloy comprises (a) 0.01-10wt% of one or more of Ni, Co, Ir, Au, Pd or Cu, (b) 1-10wt% Y, (c) 1-15wt% of at least one rare earth metal other than Y, and (d) 0-1wt% Zr.

[0020] In the first embodiment, the magnesium alloy comprises one or more rare earth metals other than Y in an amount of 1-15wt%, more preferably in an amount of 1-10wt%, even more preferably in an amount of 1.5-5.0wt%. A preferred rare earth metal other than Y is Nd. A particularly preferred amount of Nd in the alloy is 1.7-2.5wt%, more preferably 2.0-2.3wt%.

[0021] In the first embodiment, the magnesium alloy comprises Y in an amount of 1-10wt%, preferably in an amount of 2.0-6.0wt%, more preferably in an amount of 3.0-5.0wt%, even more preferably in an amount of 3.3-4.3wt% or 3.7-4.3wt%.

[0022] In the first embodiment, the magnesium alloy comprises Zr in an amount of up to 1wt%. In some embodiments, the magnesium alloy comprises Zr in an amount of 0.05-1.0wt%, more preferably in an amount of 0.2-1.0wt%, even more preferably in an amount of 0.3-0.6wt%. In some embodiments, the magnesium alloy comprises Zr in an amount of up to 0.6wt%, preferably up to 0.3wt%, more preferably up to 0.15wt%. In some embodiments, the magnesium alloy is substantially free of Zr (eg the magnesium alloy comprises less than 0.05wt% Zr).

[0023] For the first embodiment, the remainder of the alloy is magnesium and incidental impurities.

[0024] A particularly preferred composition of the first embodiment is a magnesium alloy comprising 3.3-4.3wt% Y, 0.2-1.0wt% Zr, 2.0-2.5wt% Nd and optionally 0.3-1.0wt% other rare earths with Ni as the corrosion promoting metallic element. An alternative preferred composition of the first embodiment is a magnesium alloy comprising 3.3-4.3wt% Y, up to 0.2wt% Zr, 1.7-2.5wt% Nd and optionally 0.3-1.0wt% other rare earths with Ni as the corrosion promoting metallic element.

[0025] In the first embodiment, the magnesium alloy preferably comprises Ni in an amount of between 0.01% and 10% by weight, more preferably between 0.1% and 8% by weight, even more preferably between 0.2% by weight and 7% by weight. A further particularly preferred composition is a magnesium alloy comprising 3.3-4.3wt% Y, 0.2-1.0wt% Zr, 2.0-2.5wt% Nd and 0.2-7wt% Ni. An alternative further particularly preferred composition is a magnesium alloy comprising 3.3-4.3wt% Y, 0.2wt% or less Zr, 1.7-2.5wt% Nd and 0.2-7wt% Ni. It is preferred that the remainder of the alloy is magnesium and incidental impurities.

[0026] Also described (but not claimed) is a second magnesium alloy comprising (a) 0.01-

10wt% of one or more of Ni, Co, Ir, Au, Pd or Cu, (b) 1-15wt% Al, (c) 0.1-1wt% Mn, and (d) optionally one or more of Ca, Sn and Zn.

[0027] In the second alloy, the magnesium alloy comprises 1-15wt% Al, preferably 2-12wt% Al, more preferably 2.5-10wt% Al.

[0028] In the second alloy, the magnesium alloy comprises 0.1-1wt% Mn, preferably 0.1-0.8wt% Mn, more preferably 0.2-0.6wt% Mn.

[0029] In the second alloy, the magnesium alloy optionally comprises one or more of Ca, Sn and Zn. When the alloy comprises Sn, it is preferably in an amount of 2-6wt%, more preferably 3-5wt%. When the alloy comprises Zn, it is preferably in an amount of 0.1-3wt%, more preferably 0.2-2.5wt%. In some alloys, the alloy comprises both Sn and Zn. When the alloy comprises Ca, it is preferably in an amount of 1-10wt%, more preferably 2-6wt%.

[0030] In the second alloy, the magnesium alloy preferably comprises Ni in an amount of between 0.01% and 10% by weight, more preferably between 0.01% and 5% by weight, even more preferably between 0.1% by weight and 3% by weight.

[0031] In addition, described (but not claimed) is a third magnesium alloy comprising (a) 0.01-15wt% of one or more of Ni, Co, Ir, Au, Pd or Cu, (b) 1-9wt% Zn, and (c) optionally one or more of Mn and Zr.

[0032] In the third alloy, the magnesium alloy comprises 1-9wt% Zn, preferably 5-8wt% Zn, more preferably 6-7wt% Zn.

[0033] In the third alloy, when the alloy comprises Mn it is preferably in an amount of 0.1-1wt%, more preferably 0.5-1.0wt%, even more preferably 0.7-0.9wt%.

[0034] In the third alloy, the magnesium alloy preferably comprises Ni in an amount of between 0.01% and 10% by weight, more preferably between 0.01% and 7% by weight, even more preferably between 0.1% by weight and 5% by weight.

[0035] In the third alloy, the magnesium alloy may also comprise Cu, preferably in an amount of 0.1-5wt%, more preferably 0.5-3wt%, even more preferably 1-2wt%. In some alloys, the alloy comprises both Mn and Cu.

[0036] In the third alloy, when the magnesium alloy comprises Zr it is preferably in an amount of up to 1wt%, more preferably in an amount of 0.05-1.0wt%, even more preferably in an amount of 0.2-1.0wt%, more preferably in an amount of 0.3-0.7wt%.

[0037] In the second and third alloys, preferably the remainder of the alloy is magnesium and incidental impurities. It is preferred that the content of Mg in the magnesium alloy is preferably at least 80wt%, more preferably at least 85wt%, even more preferably at least 87wt%.

[0038] It is preferred that the corrosion promoting metallic element (ie Ni, Co, Ir, Au, Pd and/or Cu) has a solubility of at least 0.1% by weight in molten magnesium at 850°C. Preferably, the corrosion promoting metallic element has a solubility of at least 0.5% by weight in molten magnesium at 850°C, more preferably at least 1% by weight. In some embodiments, it is preferred that the corrosion promoting metallic element has a solubility of at least 1% by weight in the molten magnesium alloy to which it is to be added at 850°C. In relation to the molten material, the term "solubility" is used to mean that the corrosion promoting metallic element dissolves in the molten magnesium or magnesium alloy.

[0039] Preferably, the corrosion promoting metallic element has a solubility of less than 0.1% by weight, more preferably less than 0.01% by weight, in solid magnesium at 25°C. In some embodiments, it is preferred that the corrosion promoting metallic element has a solubility of less than 0.1% by weight, more preferably less than 0.01% by weight, in the solid magnesium alloy to which it is to be added at 25°C. In relation to the solid material, the term "solubility" is used to mean that atoms of the corrosion promoting metallic element are randomly distributed throughout the alloy in a single phase (ie rather than forming a separate phase).

[0040] The magnesium alloy preferably has a corrosion rate of at least 50mg/cm^2/day, preferably at least 75mg/cm^2/day, even more preferably at least 100mg/cm^2/day, in 3% KCl at 38°C (100F). It is preferred that the magnesium alloy has a corrosion rate of at least 75mg/cm^2/day, preferably at least 250mg/cm^2/day, even more preferably at least 500mg/cm^2/day, in 15% KCl at 93°C (200F). It is preferred that the corrosion rate, in 3% KCl at 38°C or in 15% KCl at 93°C (200F), is less than 15,000mg/cm^2/day.

[0041] It is preferred that the magnesium alloy has a 0.2% proof strength of at least 75MPa, more preferably at least 100MPa, even more preferably at least 150MPa, when tested using standard tensile test method ASTM B557-10. It is preferred that the 0.2% proof strength is less than 700MPa. The proof strength of a material is the stress at which material strain changes from elastic deformation to plastic deformation, causing the material to deform permanently.

[0042] It is preferred that the 0.2% proof strength of the magnesium alloy when the one or more of Ni, Co, Ir, Au, Pd or Cu has been added is at least 80%, more preferably at least 90%, of the 0.2% proof strength of the base alloy. The term "base alloy" is used to mean the magnesium alloy without one or more of Ni, Co, Ir, Au, Pd or Cu having been added. Even more preferably, the 0.2% proof strength of the magnesium alloy when Ni has been added is at least 80%, more preferably at least 90%, of the 0.2% proof strength of the base alloy.

[0043] This invention relates to a corrodible downhole article, such as a downhole tool, comprising the magnesium alloy described above. In some embodiments, the corrodible downhole article is a fracking ball, plug, packer or tool assembly. The fracking ball is preferably substantially spherical in shape. In some embodiments, the fracking ball consists essentially of the magnesium alloy described above.

[0044] Also described (but not claimed) is a method for producing a magnesium alloy suitable for use as a corrodible downhole article comprising the steps of:

1. (a) melting magnesium or a magnesium alloy,
2. (b) adding one or more of Ni, Co, Ir, Au, Pd or Cu to the molten magnesium or magnesium alloy such that the one or more of Ni, Co, Ir, Au, Pd or Cu melts,
3. (c) mixing the resulting molten magnesium alloy, and
4. (d) casting the magnesium alloy.

[0045] Preferably the method is for producing a magnesium alloy as defined above. It is preferred that the melting step is carried out at a temperature of 650°C (ie the melting point of pure magnesium) or more, preferably less than 1090°C (the boiling point of pure magnesium). A preferred temperature range is 650°C to 850°C, more preferably 700°C to 800°C, most preferably about 750°C.

[0046] The casting step normally involves pouring the molten magnesium alloy into a mould, and then allowing it to cool and solidify. The mould may be a die mould, a permanent mould, a sand mould, an investment mould, a direct chill casting (DC) mould, or other mould.

[0047] After step (c), the method may comprise one or more of the following additional steps: (d) extruding, (e) forging, (f) rolling, (g) machining.

[0048] It is preferred that step (a) comprises melting a magnesium alloy. Preferably the magnesium alloy of step (a) comprises one or more of Al, Zn, Mn, Zr, Y, rare earth metals, Cu, Nd, Gd, Ca, Sn and/or Ag. Particularly preferred magnesium alloys for step (a) include Mg-Al-Zn-Mn, Mg-Al-Mn, Mg-Zn-Zr, Mg-Y-RE-Zr, Mg-Zn-Cu-Mn, Mg-Nd-Gd-Zr, Mg-Ag-RE-Zr, Mg-Zn-RE-Zr, Mg-Gd-Y-Zr, Mg-Al-Ca-Mn and Mg-Al-Sn-Zn-Mn. As noted above, these additional elements can be included by forming an alloy of magnesium with those elements, and then adding the corrosion promoting metallic element to the molten alloy.

[0049] In a first embodiment, the magnesium alloy comprises 1-10wt% Y, 1-15wt% rare earths other than Y and up to 1wt% Zr. A particularly preferred magnesium alloy comprises 3.3-4.3wt% Y, up to 1wt% Zr, 2.0-2.5wt% Nd and optionally 0.3-1.0wt% rare earths. In this alloy, Zr may be present in an amount of 0.05-1.0wt%, or the alloy may comprise less than 0.05wt% Zr. Ni is preferably added in an amount of between 0.2% and 7% by weight. It is preferred that the remainder of the alloy is magnesium and incidental impurities.

[0050] Also described (but not claimed) is a second magnesium alloy comprising 1-15wt% Al and up to 2wt% in total of Zn and/or Mn. The alloy preferably comprises 2-12wt% Al. Preferably, the alloy comprises 0.2-1.2wt% in total of Zn and/or Mn. Ni is preferably added in an amount of 0.1-3wt%.

[0051] In addition, described (but not claimed) is a third magnesium alloy comprising 1-9wt% Zn and optionally one or more of Mn and Zr. The alloy preferably comprises 5-8wt% Zn. Ni is preferably added in an amount of 0.1-5wt%.

[0052] The composition of the magnesium alloy, in particular those of the first embodiment, can be tailored to achieve a desired corrosion rate falling in a particular range. The desired corrosion rate in 15% KCl at 93°C can be in any of the following particular ranges: 50-100mg/cm^2/day; 100-250mg/cm^2/day; 250-500mg/cm^2/day; 500-1000mg/cm^2/day; 1000-3000mg/cm^2/day; 3000-4000 mg/cm^2/day; 4000-5000mg/cm^2/day; 5000-10,000mg/cm^2/day; 10,000-15,000 mg/cm^2/day.

[0053] The method of producing the alloy may also comprise tailoring compositions of the magnesium alloys, in particular of the first embodiment, such that the cast magnesium alloys achieve desired corrosion rates in 15% KCl at 93°C falling in at least two of the following ranges: 50 to 100mg/cm^2/day; 100-250mg/cm^2/day; 250-500mg/cm^2/day; 500-1000mg/cm^2/day; 1000-3000mg/cm^2/day; 3000-4000 mg/cm^2/day; 4000-5000mg/cm^2/day; 5000-10,000mg/cm^2/day; and 10,000-15,000 mg/cm^2/day.

[0054] It is preferred that the corrosion promoting metallic element (ie Ni, Co, Ir, Au, Pd and/or Cu) has a solubility of at least 0.1% by weight in molten magnesium at 850°C. Preferably, the corrosion promoting metallic element has a solubility of at least 0.5% by weight in molten magnesium at 850°C, more preferably at least 1% by weight. In some embodiments, it is preferred that the corrosion promoting metallic element has a solubility of at least 1% by weight in the molten magnesium or magnesium alloy to which it is added.

[0055] Preferably the corrosion promoting metallic element (ie Ni, Co, Ir, Au, Pd and/or Cu) has a solubility of less than 0.1% by weight, more preferably less than 0.01% by weight, in solid magnesium at 25°C. In some embodiments, it is preferred that the corrosion promoting metallic element has a solubility of less than 0.1% by weight, more preferably less than 0.01% by weight, in the molten magnesium or magnesium alloy to which it is added once it has been cooled to 25°C and solidified.

[0056] The corrosion promoting metallic element is one or more of Ni, Co, Ir, Au, Pd or Cu. In some embodiments, Ni is preferred. In relation to compositions of the first embodiment, the corrosion promoting metallic element is added in an amount of between 0.01% and 10% by weight, more preferably between 0.1% and 8% by weight, even more preferably between 0.2% and 7% by weight. In relation to compositions of the second alloy, the corrosion promoting metallic element is preferably added in an amount of between 0.01% and 15% by weight, more preferably between 0.01% and 5% by weight, even more preferably between 0.1% and 3% by weight. In relation to compositions of the third alloy, the corrosion promoting metallic element is preferably added in an amount of between 0.01% and 10% by weight, more preferably 0.01% and 7% by weight, even more preferably between 0.1% and 5% by weight.

[0057] A particularly preferred method comprises melting in step (a) a magnesium alloy comprising 3.3-4.3wt% Y, 0.2-1.0wt% Zr, 2.0-2.5wt% Nd and optionally 0.3-1.0wt% rare earths, and adding in step (b) Ni as the corrosion promoting metallic element. It is preferred that in step (b) Ni is added in an amount of between 0.01% and 10% by weight, more preferably between 0.1% by weight and 8% by weight.

[0058] Also described (but not claimed) is a magnesium alloy suitable for use as a corrodible downhole article which is obtainable by the method described above.

[0059] In addition, described (but not claimed) is a magnesium alloy as described above for use as a corrodible downhole article.

[0060] This invention also relates to a method of hydraulic fracturing comprising the use of a corrodible downhole article comprising the magnesium alloy as described above, or a downhole tool as described above. Preferably, the method comprises forming an at least partial seal in a borehole with the corrodible downhole article. The method may then comprise removing the at least partial seal by permitting the corrodible downhole article to corrode. This corrosion can occur at a desired rate with certain alloy compositions of the disclosure as discussed above. It is preferred that the corrodible downhole article is a fracking ball, plug, packer or tool assembly. The fracking ball is preferably substantially spherical in shape. In some embodiments, the fracking ball consists essentially of the magnesium alloy described above.

[0061] This invention will be further described by reference to the following Figures which is not intended to limit the scope of the invention claimed, in which:

Figure 1 shows a microstructure of sample DF9905D of Example 1,

Figure 2 shows a graph of % loss in proof stress against Ni addition (wt%) for the alloys of Examples 3A, 3B and 3C,

Figure 3 shows a graph of proof stress against Ni addition (wt%) for the alloys of Examples 3A, 3B and 3C, and

Figure 4 shows a graph of corrosion rate against Ni addition (wt%) for the alloys of Examples 3A, 3B and 3C.

Examples

Example 1 - Magnesium Aluminium Alloy (not of the invention)

[0062] A base magnesium alloy consisting of the commercial alloy AZ80A which has a typical chemical composition of 8.5wt% Al, 0.5wt% Zn and 0.3wt% Mn, was melted by heating to 750°C and nickel was added to it in amounts ranging between 0.01% wt to 1% wt. The product was then cast into a billet and extruded into a rod.

[0063] In order to simulate the mild and extreme corrosion performance in a well, the material was corrosion tested by measuring weight loss in an aqueous solution of 3wt% potassium chloride at a constant temperature of 38°C (100F) and 15wt% potassium chloride aqueous solution at a constant temperature of 93°C (200F).

[0064] The corrosion rates are shown in Table 1 below. The samples comprise the standard alloy (ie AZ80A without nickel added), and two samples with different amounts of nickel added.

Table 1

Sample ID	Nickel concentration Wt%	Corrosion rate in 3% KCL at 38°C (100F) $Mg/cm^2/day$	Corrosion rate in 15% KCL at 93°C (200F) $Mg/cm^2/day$
Standard alloy	<0.005	<0.5	<0.5
DF9905B	0.016	113	449
DF9905D	0.61	161	1328

[0065] The data in Table 1 clearly shows the increased corrosion level achieved in the samples to which nickel has been added, with a higher nickel content resulting in a higher corrosion rate.

[0066] The mechanical properties of the samples were also tested using standardised tension tests (ie ASTM B557-10), and the results are shown in Table 2 below.

Table 2

Sample ID	Nickel concentration Wt%	0.2% Proof Strength MPa	UTS MPa	Elongation %
Standard alloy	<0.005	219	339	9
DF9905B	0.016	238	334	11
DF9905D	0.61	219	309	14

[0067] Figure 1 shows a microstructure of sample DF9905D (ie 0.61wt% nickel). The dark area of the microstructure, labelled "1", is the α-Mg phase (ie the phase comprising magnesium in solid solution with the other alloying elements). The light area of the microstructure, an example of which is labelled "2", is the phase comprising the corrosion promoting element (ie nickel in this case) and magnesium.

Example 2 - Magnesium Yttrium Rare Earth Alloy

[0068] The procedure of Example 1 was repeated, but with the base magnesium alloy AZ80A being replaced by commercial alloy Elektron 43. A WE43C alloy was used with a composition of 3.7-4.3wt% Y, 0.2-1.0wt% Zr, 2.0-2.5wt% Nd and 0.3-1.0wt% rare earths.

[0069] The corrosion rates are shown in Table 3 below. The samples comprise the standard alloy (ie WE43C without nickel added), and five samples with different amounts of nickel added.

Table 3

Sample ID	Nickel concentration Wt %	Corrosion rate in 3% KCl at 38°C (100F) $Mg/cm^2/day$	Corrosion rate in 15% KCl at 93°C (200F) $Mg/cm^2/day$
Standard alloy	<0.005	<0.5	<0.5
DF9911D	0.1	<0.5	94
DF9912A	0.2	78	308
DF9912B	0.4	199	643
DF9912C	0.62	203	929
DF9915C	0.65	302	1075
DF9915D	1.43	542	1811

[0070] The data in Table 3 clearly shows the increased corrosion level achieved in the samples to which nickel has been added, with a higher nickel content resulting in a higher corrosion rate.

[0071] The mechanical properties of these samples were also tested using standardised tension tests, and the results are shown in Table 4 below.

Table 4

Sample ID	Nickel concentration Wt%	0.2% Proof Strength MPa	UTS MPa	Elongation %
Standard alloy	<0.005	186	301	15
DF9911D	0.1	197	302	17
DF9912A	0.2	234	337	15
DF9912B	0.4	238	331	14
DF9912C	0.62	230	311	11
DF9915C	0.65	224	305	21

Sample ID	Nickel concentration Wt%	0.2% Proof Strength MPa	UTS MPa	Elongation %
DF9915D	1.43	229	321	20

[0072] The data in Table 4 shows that alloys of the invention have improved mechanical properties, in particular 0.2% proof strength, when compared to prior art compositions.

Example 3A - Magnesium Aluminium Alloys (not of the invention)

[0073] Further magnesium alloy compositions were prepared by combining the components in the amounts listed in Table 5 below (the balance being magnesium). These compositions were then melted by heating at 750°C. The product was then cast into a billet and extruded to a rod.

Table 5

Mg-Al	Alloy Additions (wt%, balance magnesium)					
Sample ID	Al	Ca	Sn	Zn	Mn	Ni
A1	8.4			0.4	0.2	0.00
A2	8.4			0.4	0.2	0.02
A3	8.4			0.4	0.2	0.15
A4	8.4			0.4	0.2	1.50
A5	6.5			0.7	0.3	0.00
A6	6.5			0.7	0.3	0.05
A7	6.5			0.7	0.3	0.15
A8	6.5			0.7	0.3	0.30
A9	6.5			0.7	0.3	0.60
A10	6.5			0.7	0.3	1.20
A11	3.0			0.7	0.3	0.00
A12	3.0			0.7	0.3	0.05
A13	3.0			0.7	0.3	0.15
A14	3.0			0.7	0.3	0.30
A15	3.0			0.7	0.3	0.60
A16	3.0			0.7	0.3	1.20
A17	3.5	3.0		0.0	0.3	0.00
A18	4.0	5.0		0.0	0.5	0.15
A19	4.0	3.6		0.0	0.4	0.50
A20	3.5	3.0		0.0	0.3	2.00
A21	8.0		4.0	2.0	0.3	0.00

Mg-Al	Alloy Additions (wt%, balance magnesium)					
Sample ID	Al	Ca	Sn	Zn	Mn	Ni
A22	8.0		4.0	2.0	0.3	0.15

[0074] The mechanical properties of these samples were also tested using the same standardised tension tests, and the results are shown in Table 6 below.

Table 6

Alloy class: Mg-Al			
Sample ID	0.2 % Proof Strength (MPa)	Percentage Proof Strength remaining (%)	Corrosion Rate in 15% KCl at 93°C (200F) ($mg/cm^2/day$)
A1	219	100	0
A2	239	109	449
A3	235	107	1995
A4	220	101	1328
A5	199	100	0
A6	197	99	2078
A7	203	102	2531
A8	198	99	2800
A9	197	99	2574
A10	199	100	2494
A11	211	100	0
A12	196	93	1483
A13	192	91	1853
A14	194	92	1854
A15	197	94	1969
A16	194	92	1877
A17	321	100	0
A18	329	102	3299
A19	312	97	4851
A20	309	96	2828
A21	258	100	0
A22	256	99	1205

[0075] This data shows that the addition of nickel to these magnesium-aluminium alloys significantly increases the corrosion rate of the alloys. Advantageously, for these alloys this increase in corrosion rate is provided whilst maintaining the mechanical properties of the alloy (as exemplified by the 0.2% proof strength). Thus, the alloys tested in this example can find use as components in downhole tools due to their combination of high corrosion rates and good mechanical properties.

Example 3B - Magnesium Yttrium Rare Earth Alloys

[0076] Further magnesium alloy compositions were prepared by combining the components in the amounts listed in Table 7 below. These compositions were then melted by heating at 750°C. The product was then cast into a billet and extruded to a rod.

Table 7

Mg-Y-RE	Alloy Additions (wt%, balance Mg)			
Sample ID	Y	Nd	Zr	Ni
R1	4.0	2.2	0.5	0.0
R2	3.6	2.1	0.5	0.4
R3	3.6	2.1	0.5	0.6
R4	3.6	2.1	0.5	1.4
R5	3.5	2.1	0.4	1.8
R6	3.5	2.1	0.4	3.5
R7	3.5	2.1	0.4	5.0
R8	3.5	2.1	0.4	6.1
R9	3.7	2.1	0.0	0.4
R10	3.7	2.1	0.0	0.6
R11	3.6	2.1	0.1	1.5
R12	3.9	2.0	0.0	1.1
R13	3.5	1.8	0.0	2.2

[0077] The mechanical properties of these samples were tested using standardised tension tests, and the results are shown in Table 8 below.

Table 8

Alloy Class: Mg-Y-RE			
Sample ID	0.2 % Proof Strength (MPa)	Percentage Proof Strength remaining (%)	Corrosion Rate in 15% KCl at 93°C (200F) (mg/cm^2/day)
R1	241	100	0.0
R2	229	95	198.6
R3	235	97	578.5
R4	234	97	1302.3

Alloy Class: Mg-Y-RE			
Sample ID	0.2 % Proof Strength (MPa)	Percentage Proof Strength remaining (%)	Corrosion Rate in 15% KCl at 93°C (200F) ($mg/cm^2/day$)
R5	238	99	2160.0
R6	263	109	6060.8
R7	253	105	7175.7
R8	232	96	7793.1
R9	221	92	636.0
R10	217	90	937.0
R11	206	85	1115.0
R12	209	87	1118.0
R13	256	106	3401.0

[0078] This data shows that, as for the magnesium-aluminium alloys, the addition of nickel to these magnesium-yttrium-rare earth alloys significantly increases the corrosion rate of the alloy. Advantageously, for these alloys this increase in corrosion rate is provided whilst maintaining the mechanical properties of the alloy (as exemplified by the 0.2% proof strength). However, in addition to these advantageous properties, for these alloys the increase in corrosion rate is substantially proportional to the amount of added nickel. This can provide the further feature that the corrosion rate of these alloys is therefore "tunable" and alloys with specific desirable corrosion rates, or ranges of particular corrosion rates, can be produced. Thus, the alloys tested in this example can find use as components in downhole tools due to their combination of high corrosion rates and good mechanical properties.

Example 3C - Magnesium Zinc Alloys (not of the invention)

[0079] Magnesium alloy compositions were prepared by combining the components in the amounts listed in Table 9 below. These compositions were then melted by heating at 750°C. The product was then cast into a billet and extruded to a rod.

Table 9

Mg-Zn	Alloy Additions (wt%, balance Mg)				
Sample ID	Zn	Cu	Mn	Zr	Ni
Z1	6.5	1.5	0.8		0.00
Z2	6.5	1.5	0.8		1.00
Z3	6.5	1.5	0.8		2.00
Z4	6.5	1.5	0.8		4.00
Z5	6.5			0.5	0.00

Mg-Zn	Alloy Additions (wt%, balance Mg)				
Sample ID	Zn	Cu	Mn	Zr	Ni
Z6	6.5				0.15
Z7	6.5				0.30
Z8	6.5				1.00

[0080] The mechanical properties of these samples were tested using standardised tension tests, and the results are shown in Table 10 below.

Table 10

Alloy Class: Mg-Zn			
Sample ID	0.2 % Proof Strength (MPa)	Percentage Proof Strength remaining (%)	Corrosion Rate in 15% KCl at 93°C (200F) ($mg/cm^2/day$)
Z1	312	100	50
Z2	229	73	315
Z3	229	73	5474
Z4	216	69	9312
Z5	223	100	1
Z6	133	59	565
Z7	137	62	643
Z8	142	63	905

[0081] This data shows that, as for the magnesium-aluminium and magnesium-yttrium-rare earth alloys, the addition of nickel to these magnesium-zinc alloys significantly increases their corrosion rate. Magnesium-zinc alloys are known in the art to have high strength values and it is shown in the disclosure that the addition of nickel also increases their corrosion rate. However, the data demonstrates that the mechanical properties of these alloys (as exemplified by the 0.2% proof strength) decrease with increasing nickel content.

[0082] This example shows that not all magnesium alloys provide the mechanical strength required for certain uses of the invention when nickel is added to them, and that it is in fact difficult to predict how the properties of a particular alloy will be altered when a corrosion promoting element such as nickel is added.

[0083] In Figures 2, 3 and 4 the mechanical properties of the alloys of Examples 3A, 3B and 3C, have been plotted against the Ni addition (wt%).

[0084] Figure 2 in particular shows that for the magnesium-zinc alloys of Example 3C ("Mg-Zn", where zinc is the major strengthening element), between 20% and 40% of the strength is lost when nickel is added. In contrast, the strength of the magnesium-aluminium ("Mg-Al") and magnesium-yttrium-rare earth (Mg-Y-RE) alloys (Examples 3A and 3B) is maintained. Figure 3 is a plot showing the absolute proof strength values (MPa) against Ni addition (wt%).

[0085] Figure 4 is a plot of corrosion rate against Ni addition (wt%). For the magnesium-yttrium-rare earth alloys, a line has been drawn through the data points which demonstrates the correlation between corrosion rate and Ni addition for these alloys. This shows that the magnesium-yttrium rare earth alloys advantageously can be tailored to achieve a desired specific corrosion rate or range of corrosion rates.

REFERENCES CITED IN THE DESCRIPTION

Patent documents cited in the description

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- US20120318513 [0009]
- US20140124216 [0010]
- US20140190705 [0010]
- CN103343271A [0012]
- CN101392345A [0012]

Non-patent literature cited in the description

- **S. GONZÃLEZ et al.**Influence of processing route on microstructure and mechanical properties of two Mg Ni Y RE alloysMATERIALS CHARACTERIZATION, 2012, vol. 64, 1044-580353-61 [0012]
- **D. V. LOUZGUINE**Influence of Ni, Cu, Zn and Al Additions on Glass-Forming Ability and Mechanical Properties of Mg-Y-Mm (Mm=Mischmetal) AlloysMATERIALS SCIENCE FORUM, 2000, vol. 350, 351123-130 [0012]
- **J. F. KINGP. LYONK. SAVAGE**Influence of rare earth elements and minor additions on properties and performance of magnesium-yttrium alloys in critical aerospace applicationsANNUAL WORLD MAGNESIUM CONFERENCE, PROCEEDINGS, 2002, 15-

21 [0012]

PATENTKRAV

1. En borehulsartikel, der kan korrodere, omfattende en magnesiumbelægning, magnesiumbelægningen omfatter:
   (a) 0,01-10 wt% af en eller flere af Ni, Co, Ir, Au, Pd eller Cu,
   (b) 1-10 wt% Y,
   (c) 1-15 wt% af mindst et andet sjældent jordartmetal end Y, og
   (d) 0-1 wt% Zr,

   hvor resten af belægningen er magnesium og tilfældige urenheder, og hvor belægningen har en korrosionsrate på mindst 50 mg/cm^2/dag i 15 % KCl ved 93 °C og en 0,2 % blivende forlængelse på mindst 50 MPa ved test ved hjælp af standard-træktestmetoden ASTM B557-10.

2. En borehulsartikel, der kan korrodere, ifølge krav 1, hvor magnesiumbelægningen har en korrosionsrate på mindst 75 mg/cm^2/dag i 15 % KCl ved 93 °C.

3. En borehulsartikel, der kan korrodere, ifølge enten krav 1 eller krav 2, hvor magnesiumbelægningen har en 0,2 % blivende forlængelse på mindst 150 MPa ved test ved hjælp af standard-træktestmetoden ASTM B557-10.

4. En borehulsartikel, der kan korrodere, ifølge ethvert af foregående krav, hvor magnesiumbelægningen omfatter 0,1-8 wt % Ni.

5. En borehulsartikel, der kan korrodere, ifølge ethvert af foregående krav, hvor magnesiumbelægningen omfatter Y i en mængde på 2,0-6,0 wt%, helst 3,0-5,0 wt%.

6. En borehulsartikel, der kan korrodere, ifølge ethvert af foregående krav, hvor magnesiumbelægningen mindst omfatter et andet sjældent jordartmetal end Y i en mængde på 1,5-5,0 wt%.

7. En borehulsartikel, der kan korrodere, ifølge ethvert af foregående krav, hvor mindst et andet sjældent jordartmetal end Y er Nd.

8. En borehulsartikel, der kan korrodere, ifølge krav 7, hvor magnesiumbelægningen omfatter Nd i en mængde på 1,7-2,5 wt%.

9. En borehulsartikel, der kan korrodere, ifølge ethvert af foregående krav, hvor magnesiumbelægningen omfatter Zr i en mængde på op til 0,3 wt%.

10. En borehulsartikel, der kan korrodere, ifølge krav 1, hvor magnesiumbelægningen omfatter 3,3-4,3 wt% Y, op til 0,2 wt% Zr og 1,7-2,5 wt% Nd og eventuelt 0,3-1,0 wt% andre sjældne jordarter.

11. En borehulsartikel, der kan korrodere, ifølge ethvert af foregående krav, hvor borehulsartiklen, der kan korrodere, er et borehulsværktøj.

12. En borehulsartikel, der kan korrodere, ifølge krav 11, hvor borehulsværktøjet er en fracking-kugle, plug, packer eller værktøjsanordning.

13. En metode til hydraulisk fracking omfattende anvendelsen af et borehulsværktøj ifølge enten krav 11 eller krav 12.

DRAWINGS

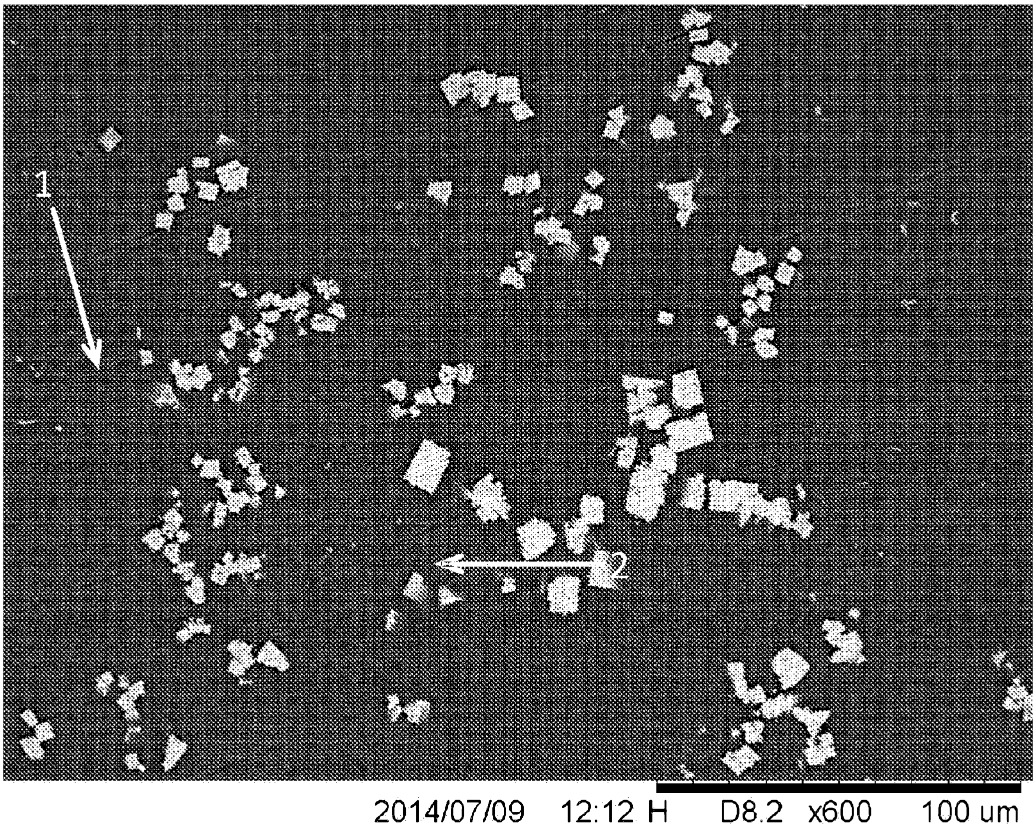
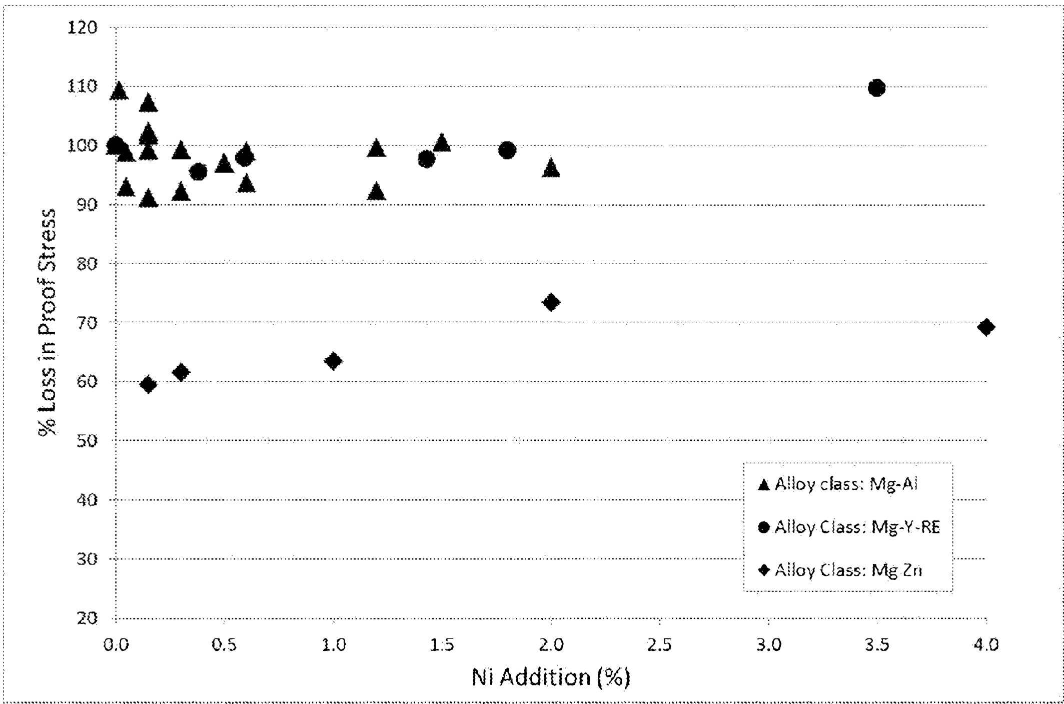


Figure 1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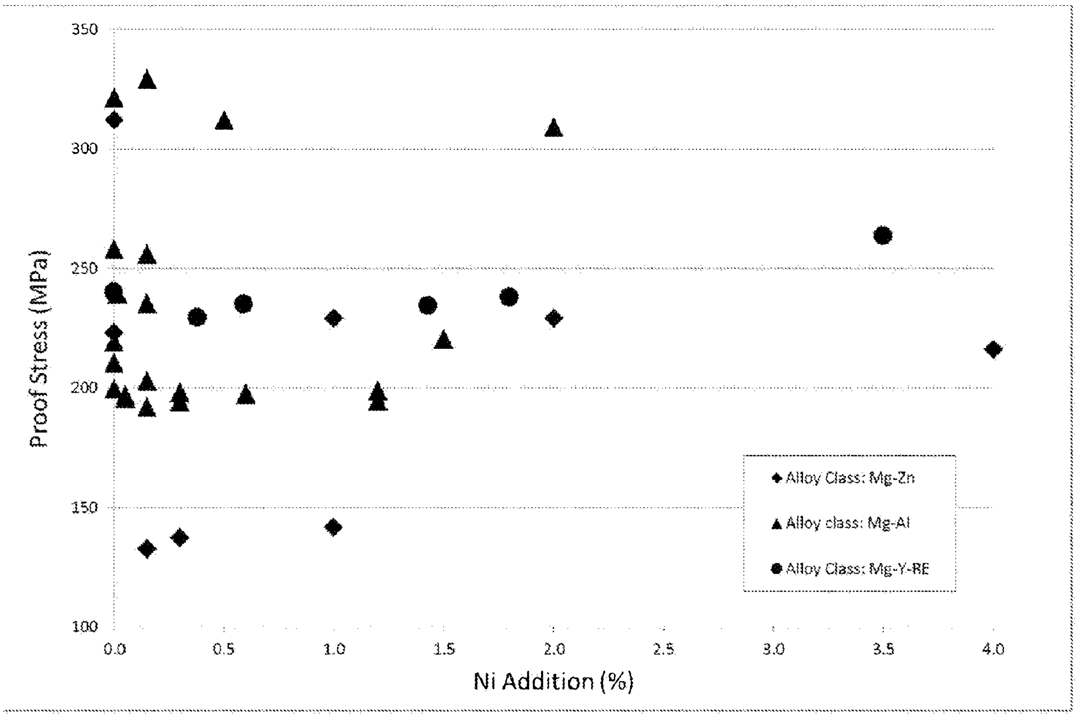
Ni Addition (%)
Alloy class: Mg-Al
Alloy Class: Mg-Y-RE
Alloy Class: Mg Zn

Figure 2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Proof Stress (MPa)
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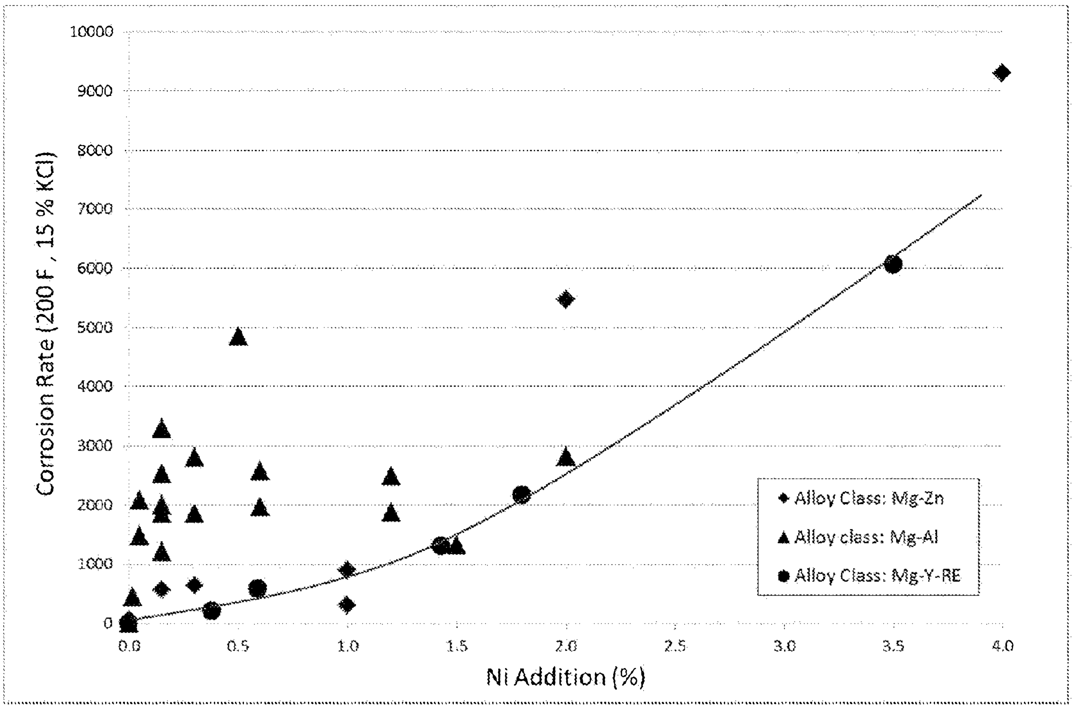
3.5
4.0
Ni Addition (%)
Alloy Class: Mg-Zn
Alloy class: Mg-Al
Alloy Class: Mg-Y-RE

Figure 3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5000
4000
3000
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1000
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Corrosion Rate (200 F , 15 % KCl)
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1.0
1.5
2.0
2.5
3.0
3.5
4.0
Ni Addition (%)
Alloy Class: Mg-Zn
Alloy class: Mg-Al
Alloy Class: Mg-Y-RE

Figure 4