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(12) EX PARTE REEXAMINATION CERTIFICATE (12052nd)**United States Patent****Doud et al.****(10) Number: US 10,329,653 C1****(45) Certificate Issued: *May 10, 2022****(54) GALVANICALLY-ACTIVE IN SITU FORMED PARTICLES FOR CONTROLLED RATE DISSOLVING TOOLS****(71) Applicant: Terves Inc., Euclid, OH (US)****(72) Inventors: Brian P. Doud, Cleveland Heights, OH (US); Nicholas J. Farkas, Euclid, OH (US); Andrew J. Sherman, Mentor, OH (US)****(73) Assignee: WI-LAN INC., Ottawa (CA)****Reexamination Request:**

No. 90/014,795, Jul. 6, 2021

Reexamination Certificate for:Patent No.: **10,329,653**Issued: **Jun. 25, 2019**Appl. No.: **15/641,439**Filed: **Jul. 5, 2017****(*) Notice:** This patent is subject to a terminal disclaimer.**Related U.S. Application Data****(62)** Division of application No. 14/689,295, filed on Apr. 17, 2015, now Pat. No. 9,903,010.**(60)** Provisional application No. 61/981,425, filed on Apr. 18, 2014.**(51) Int. Cl.**
C22F 1/06 (2006.01)
C22C 1/02 (2006.01)**C22C 23/02** (2006.01)**C22C 23/00** (2006.01)**(52) U.S. Cl.**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**

None

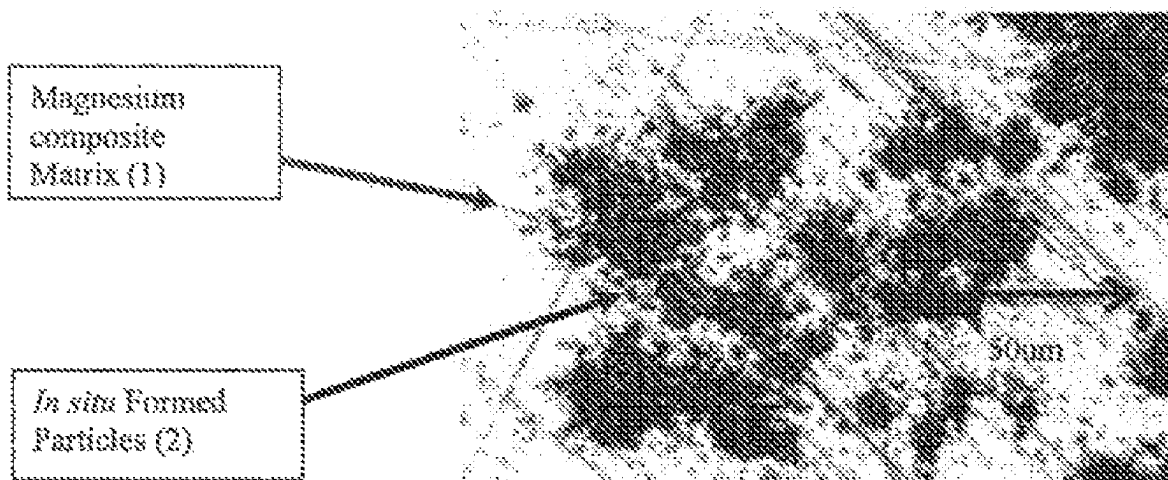
See application file for complete search history.

(56) References Cited

To view the complete listing of prior art documents cited during the proceeding for Reexamination Control Number 90/014,795, please refer to the USPTO's public Patent Application Information Retrieval (PAIR) system under the Display References tab.

Primary Examiner — Sean E Vincent**(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.



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EX PARTE REEXAMINATION CERTIFICATE

THE PATENT IS HEREBY AMENDED AS
INDICATED BELOW.

Matter enclosed in heavy brackets [] appeared in the patent, but has been deleted and is no longer a part of the patent; matter printed in italics indicates additions made to the patent.

ONLY THOSE PARAGRAPHS OF THE
SPECIFICATIONS AFFECTED BY
AMENDMENT ARE PRINTED HEREIN.

Column 14, lines 10-51:

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]hr. 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 an 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]hr. 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.

Column 14, line 52-column 15, line 14:

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.

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% zinc and 90 wt. % magnesium, b) melting the AZ91D magnesium alloy to a temperature above 800° C., c) adding up to about 1 wt. % nickel to the melted AZ91D magnesium alloy at a temperature that is less than the melting point of nickel, d) mixing the nickel with the melted AZ91D magnesium alloy and dispersing the nickel in the melted alloy using chemical mixing agents while maintaining the temperature below the melting point of nickel, and e) cooling and casting the melted mixture in a steel mold. The cast material has a tensile strength of about 18 ksi, and an elongation of about 5% and a shear strength of 17ksi. The cast material has a dissolve rate of about 45 mg/cm²-[min]hr. in a 3% KCl solution at 90° C. The cast material dissolves at a rate of 0.5 mg/cm²-hr. in a 3% KCl solution at 21° C. The cast material dissolves at a rate of 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 [yeild] 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]hr. 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.

Column 17, lines 30-41:

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]hr. 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.

Column 17, lines 45-52:

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.]hr. 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.

AS A RESULT OF REEXAMINATION, IT HAS BEEN DETERMINED THAT:

The patentability of claims 1-5, 7-9, 11, 25-33, 35-50, 52-62, 64, 66, and 70-76 is confirmed.

Claims 12, 18, 23, 34, 67 and 69 are determined to be patentable as amended.

Claims 13-16, 19-21 and 24, dependent on an amended claim, are determined to be patentable.

New claims 79-126 are added and determined to be patentable.

Claims 6, 10, 17, 22, 51, 63, 65, 68, 77, and 78 were not reexamined.

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.] C 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.

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.] C and up to 325 mg/cm²/hr. in 3 wt. % KCl water mixture at 90° C.

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.] C and up to 325 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.] 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.] C and up to 325 mg/cm²/hr. in 3 wt. % KCl water mixture at 90° C.

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

79. The magnesium composite as defined in claim 1, wherein said magnesium constitutes at least 85 wt. % of said magnesium composite.

80. The magnesium composite as defined in claim 1, further including aluminum, a content of said aluminum is 0.5-10 wt. % of said magnesium composite.

81. The magnesium composite as defined in claim 79, further including aluminum, a content of said aluminum is 0.5-10 wt. % of said magnesium composite.

82. The magnesium composite as defined in claim 12, wherein said magnesium constitutes at least 85 wt. % of said magnesium composite.

83. The magnesium composite as defined in claim 12, further including aluminum, a content of said aluminum is 0.5-10 wt. % of said magnesium composite.

84. The magnesium composite as defined in claim 82, further including aluminum, a content of said aluminum is 0.5-10 wt. % of said magnesium composite.

85. The magnesium composite as defined in claim 25, further including aluminum, a content of said aluminum is 0.5-10 wt. % of said magnesium composite.

86. The magnesium composite as defined in claim 29, wherein said magnesium constitutes at least 85 wt. % of said magnesium composite.

87. The magnesium composite as defined in claim 29, further including aluminum, a content of said aluminum is 0.5-10 wt. % of said magnesium composite.

88. The magnesium composite as defined in claim 86, further including aluminum, a content of said aluminum is 0.5-10 wt. % of said magnesium composite.

89. The magnesium composite as defined in claim 33, wherein said magnesium constitutes at least 85 wt. % of said magnesium composite.

90. The magnesium composite as defined in claim 37, wherein said magnesium constitutes at least 85 wt. % of said magnesium composite.

91. The magnesium composite as defined in claim 41, wherein said magnesium constitutes at least 85 wt. % of said magnesium composite.

92. The magnesium composite as defined in claim 41, further including aluminum, a content of said aluminum is 0.5-10 wt. % of said magnesium composite.

93. The magnesium composite as defined in claim 91, further including aluminum, a content of said aluminum is 0.5-10 wt. % of said magnesium composite.

94. The magnesium composite as defined in claim 45, wherein said magnesium constitutes at least 85 wt. % of said magnesium composite.

95. The magnesium composite as defined in claim 49, wherein said magnesium constitutes at least 85 wt. % of said magnesium composite.

96. The magnesium composite as defined in claim 49, further including aluminum, a content of said aluminum is 0.5-10 wt. % of said magnesium composite.

97. The magnesium composite as defined in claim 95, further including aluminum, a content of said aluminum is 0.5-10 wt. % of said magnesium composite.

98. The magnesium composite as defined in claim 73, wherein said magnesium constitutes at least 85 wt. % of said magnesium composite.

99. The magnesium composite as defined in claim 73, further including aluminum, a content of said aluminum is 0.5-10 wt. % of said magnesium composite.

100. The magnesium composite as defined in claim 98, further including aluminum, a content of said aluminum is 0.5-10 wt. % of said magnesium composite.

101. The magnesium composite as defined in claim 74, further including aluminum, a content of said aluminum is 0.5-10 wt. % of said magnesium composite.

102. The magnesium composite as defined in claim 80, wherein additive material includes i) 0.01-5 wt. % nickel, ii) 0.01-5 wt. % copper, or iii) 0.01-5 wt. % nickel and 0.01-5 wt. % copper.

103. The magnesium composite as defined in claim 81, wherein additive material includes i) 0.01-5 wt. % nickel, ii) 0.01-5 wt. % copper, or iii) 0.01-5 wt. % nickel and 0.01-5 wt. % copper.

104. The magnesium composite as defined in claim 83, wherein additive material includes i) 0.01-5 wt. % nickel, ii) 0.01-5 wt. % copper, or iii) 0.01-5 wt. % nickel and 0.01-5 wt. % copper.

105. The magnesium composite as defined in claim 84, wherein additive material includes i) 0.01-5 wt. % nickel, ii) 0.01-5 wt. % copper, or iii) 0.01-5 wt. % nickel and 0.01-5 wt. % copper.

106. The magnesium composite as defined in claim 85, wherein secondary metal includes i) 0.01-5 wt. % nickel, ii) 0.01-5 wt. % copper, or iii) 0.01-5 wt. % nickel and 0.01-5 wt. % copper.

116. The magnesium composite as defined in claim 99, wherein said additive material includes i) up to 5 wt. % nickel, ii) up to 5 wt. % copper, or iii) up to 5 wt. % nickel and up to 5 wt. % copper.

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126. The magnesium composite as defined in claim 98, wherein said additive material includes i) up to 5 wt. % nickel, ii) up to 5 wt. % copper, or iii) up to 5 wt. % nickel and up to 5 wt. % copper.

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