(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
28 July 2016 (28.07.2016)

WIPO | PCT

(10) International Publication Number
WO 2016/118444 A1

(51) International Patent Classification:
C22C 23/06 (2006.01) *B22D 21/00* (2006.01)
C22C 23/04 (2006.01) *B32B 15/00* (2006.01)

(21) International Application Number:
PCT/US2016/013784

(22) International Filing Date:
18 January 2016 (18.01.2016)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
62/106,975 23 January 2015 (23.01.2015) US

(71) Applicant: **UNIVERSITY OF FLORIDA RESEARCH FOUNDATION, INC.** [US/US]; 233 Grinter Hall, P.O. Box 115500, Gainesville, Florida 32611-5500 (US).

(72) Inventors: **MANUEL, Michele Viola**; 2506 SW 9th Drive, Gainesville, FL 32601 (US). **HENDERSON, Hunter B.**; 3706 SW 2nd Place, Gainesville, FL 32607 (US). **JORDAN, Kelly A.**; 1424 NW 14th Avenue, Gainesville, FL 32605 (US).

(74) Agent: **RODRIGUES, David E.**; Cantor Colburn LLP, 20 Church Street, 22nd Floor, Hartford, Connecticut 06103 (US).

(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:

— *as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))*

— *as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(iii))*

Published:

— *with international search report (Art. 21(3))*

— *before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments (Rule 48.2(h))*

WO 2016/118444 A1

(54) Title: RADIATION SHIELDING AND MITIGATING ALLOYS, METHODS OF MANUFACTURE THEREOF AND ARTICLES COMPRISING THE SAME

(57) Abstract: Disclosed herein is a first composition comprising magnesium; where the magnesium is present in an amount of 50 to 99.5 wt%; based on the total weight of the composition; and gadolinium. Disclosed herein too is a second composition comprising magnesium; where the magnesium is present in an amount of 50 to 99.5 wt%; based on the total weight of the composition; and one or more metals; where the metals are aluminum, boron, manganese, scandium, lithium, yttrium, zinc, calcium or zirconium; and where the composition is devoid of gadolinium.

RADIATION SHIELDING AND MITIGATING ALLOYS, METHODS OF MANUFACTURE THEREOF AND ARTICLES COMPRISING THE SAME

STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH

[0001] This invention was made with government support under Contract Number NNX14AL04A awarded by NASA. The government has certain rights in the invention.

BACKGROUND

[0002] This disclosure relates to a radiation shielding and mitigating alloys, to methods of manufacture thereof and to articles comprising the same.

[0003] Articles used in outer space interplanetary applications are subjected to high energy protons. These high energy protons interact with the articles producing neutron radiation that is harmful to living beings that occupy the article. It is therefore desirable to produce articles that are used in outer space in interplanetary applications that can either absorb the neutrons, resist absorption of high energy protons, or accomplish both.

SUMMARY

[0004] Disclosed herein is a first composition comprising magnesium; where the magnesium is present in an amount of 50 to 99.5 wt%; based on the total weight of the composition; and gadolinium.

[0005] Disclosed herein too is a second composition comprising magnesium; where the magnesium is present in an amount of 50 to 99.5 wt%; based on the total weight of the composition; and one or more metals; where the metals are aluminum, boron, manganese, scandium, lithium, yttrium, zinc, calcium or zirconium; and where the composition is devoid of gadolinium.

[0006] Disclosed herein is a method comprising molding a composition comprising magnesium and gadolinium; where the magnesium is present in an amount of 50 to 99.5 wt%; based on the total weight of the composition.

[0007] Disclosed herein is a method comprising molding a composition comprising magnesium; where the magnesium is present in an amount of 50 to 99.5 wt%; based on the total weight of the composition; and one or more metals; where the metals are aluminum, boron, manganese, scandium, lithium, yttrium, zinc, calcium or zirconium; and where the composition is devoid of gadolinium.

DETAILED DESCRIPTION

[0008] Disclosed herein is are compositions that comprise magnesium and that are less likely (than existing aluminum, iron, and titanium-based metals) to interact ultra-high-energy cosmic rays (UHECR) (e.g., high energy protons having a kinetic energy greater than 10^{18} eV), reducing the production of damaging additional neutrons or that can absorb the ultra-high-energy cosmic rays and also absorb any additional neutrons that are produced or absorb neutrons in low energy neutron environments such as near nuclear reactors. The compositions therefore comprise magnesium and other light weight elements that result in light weight alloys having structural integrity and high strength.

[0009] This disclosure contains two type of compositions-a first composition that comprises magnesium and gadolinium, where the composition is used primarily to absorb low energy neutrons (also referred to herein as slow neutrons) that are generated from the irradiation of the high energy protons. This composition could also be used as shielding in other neutron environments, such as, but not limited to: upper atmosphere aerospace applications, nuclear reactors, nuclear warheads, and nuclear accident robotics.

[0010] The second composition contains magnesium and other elements such as magnesium, aluminum, boron, manganese, scandium, lithium, yttrium, zinc, and zirconium. This second composition is devoid of gadolinium. The second composition is used for reducing the absorption of ultra-high-energy cosmic rays (UHECR) (e.g., super high energy protons having a kinetic energy greater than 10^{18} eV), compared to existing structural materials like aluminum and titanium alloys and steels. Less interaction with UHECRs will result in lower levels of damaging secondary neutron production.

[0011] The compositions disclosed herein have a number of advantages. As the lightest structural metal, magnesium can contribute to weight savings over conventional steel, titanium, and aluminum alloys. The combination of these factors leads to a lightweight, neutron radiation resistant structural material. These compositions would be particularly well-suited to space missions outside of low earth orbit (LEO), where galactic cosmic rays (GCR) interact with spacecraft and produce a cascade of neutrons. These neutrons, in turn, present a significant risk to the health of crew members and the reliability of sensitive electronic components. The disclosed compositions would significantly reduce the neutron dose to the interior of spacecraft.

[0012] In one embodiment, the first composition contains magnesium and gadolinium. Magnesium is the lightest weight structural metal (i.e., a metal that has a high tensile strength) and hence is used as the base material in the composition. The use of magnesium imparts structural integrity as well as light weight to the alloys. The magnesium is used in an amount 50 to 99.5 weight percent (wt%), preferably 70 to 95 wt%, and more preferably 75 to 90 wt%, based on the total weight of the first composition.

[0013] Gadolinium possesses the largest neutron absorption cross section of any element by nearly an order of magnitude, making it the most efficient element to use in a neutron shielding material. In addition, magnesium alloys that contain substantial amounts of gadolinium produce highly refined and optimally oriented precipitates when heat treated. Additionally, as the lightest structural metal, Mg can contribute to weight savings over conventional steel, titanium, and aluminum alloys.

[0014] Gadolinium is used in amounts of 0.5 to 50 wt%, preferably 5 to 30 wt% and more preferably 10 to 25 wt%, based on the total weight of the first composition. The first composition may effectively be used to absorb thermal and slow neutrons, produced not exclusively by interaction of material with ultra-high-energy cosmic rays. The first composition may also be used in situations where it is desirable to generate very few high speed neutrons.

[0015] In an embodiment, the second composition may comprise one or more metals, where the metals are aluminum, boron, manganese, scandium, lithium, yttrium, zinc, calcium or zirconium. The second composition may use aluminum in an amount of up to 40 wt%, boron in an amount of up to 50 wt%, manganese in an amount of up to 3 wt%, scandium in an amount of up to 30 wt%, lithium in an amount of up to 11 wt%, yttrium in an amount of up to 36 wt%, zinc in an amount of up to 50 wt%, calcium in an amount of up to 40 wt%, and zirconium in an amount of up to 4 wt%. All weight percents are based on the total weight of the first composition. Combinations of the foregoing metals may also be used in the first composition.

[0016] The second composition comprises magnesium as a base metal and is devoid of gadolinium. The use of magnesium imparts structural integrity as well as light weight to the alloys. The magnesium is used in an amount 50 to 99.5 weight percent, preferably 70 to 97 wt%, and more preferably 80 to 95 wt%, based on the total weight of the first composition.

[0017] The second composition may comprise one or more of aluminum, boron, manganese, scandium, lithium, yttrium, zinc, calcium and zirconium.

[0018] In an embodiment, the second composition may further comprises aluminum in an amount of up to 40 wt%, preferably 0.5 to 5 wt% and more preferably 1 to 3 wt%, based on the total weight of the composition.

[0019] In another embodiment, the second composition may further comprise boron in an amount of up to 50 wt%, preferably 0.5 to 5 wt% and more preferably 1 to 3 wt%, based on the total weight of the composition.

[0020] In yet another embodiment, the second composition may further comprise manganese in an amount of up to 3 wt%, preferably 0.5 to 2 wt% and more preferably 0.7 to 1.5 wt%, based on the total weight of the composition.

[0021] In yet another embodiment, the second composition may further comprise scandium in an amount of up to 30 wt%, preferably 0.5 to 5 wt% and more preferably 1 to 3 wt%, based on the total weight of the composition.

[0022] In yet another embodiment, the second composition may further comprise lithium in an amount of up to 11 wt%, preferably 0.5 to 5 wt% and more preferably 1 to 3 wt%, based on the total weight of the composition.

[0023] In yet another embodiment, the second composition may further comprise yttrium in an amount of up to 36 wt%, preferably 0.5 to 5 wt% and more preferably 1 to 3 wt%, based on the total weight of the composition.

[0024] In yet another embodiment, the second composition may further comprise zinc in an amount of up to 50 wt%, preferably 0.5 to 5 wt% and more preferably 1 to 3 wt%, based on the total weight of the composition.

[0025] In yet another embodiment, the second composition may further comprise calcium in an amount of up to 40 wt%, preferably 0.5 to 5 wt% and more preferably 1 to 3 wt%, based on the total weight of the composition.

[0026] In yet another embodiment, the second composition may further comprise zirconium in an amount of up to 4 wt%, preferably 0.5 to 2 wt% and more preferably 0.7 to 1.5 wt%, based on the total weight of the composition. Combinations of aluminum, boron, manganese, scandium, lithium, yttrium, zinc, calcium and zirconium may also be used in conjunction with magnesium.

[0027] The first and second compositions both display numerous advantages. They are light weight and are structurally strong and versatile. They can be used for shielding in nuclear reactors, aerospace vehicles, and spacecraft. The spacecraft may be used on space missions outside of low earth orbit.

[0028] In one method of manufacturing the first composition or the second composition, the ingredients can be mixed together following which they are melted and poured into a mold. The mold is cooled and the molded object removed. The molded object may be used "as-is" or it may be subjected to additional finishing processes such as grinding, welding, polishing, adhesion, extrusion, or rolling to form articles for commercial use.

[0029] In another method of manufacturing the molded object may be ground into a powder and re-cast or sintered to form the article. The article may be subjected to the finishing processes listed above to form a commercial article.

[0030] In yet another method of manufacturing, the ingredients in powder (prior to molding) form may be sintered under pressure together to form an article. The article may be subjected to the finishing processes listed above to form a commercial article.

[0031] In one embodiment, the first composition and the second composition may be used in a multilayered article. For example, the first composition may be used in a first layer while the second composition is used in a second layer that is disposed parallel to the first layer. In one embodiment, the first layer and the second layer are in direct contact with each other.

[0032] It is to be noted that all ranges detailed herein include the endpoints. Numerical values from different ranges are combinable.

[0033] The transition term comprising encompasses the transition terms "consisting of" and "consisting essentially of".

[0034] The term "and/or" includes both "and" as well as "or". For example, "A and/or B" is interpreted to be A, B, or A and B.

[0035] While the invention has been described with reference to some embodiments, it will be understood by those skilled in the art that various changes may be made and equivalents may be substituted for elements thereof without departing from the scope of the invention. In addition, many modifications may be made to adapt a particular situation or material to the teachings of the invention without departing from essential scope thereof. Therefore, it is intended that the invention not be limited to the particular embodiments disclosed as the best mode contemplated for carrying out this invention, but that the invention will include all embodiments falling within the scope of the appended claims.

[0036] What is claimed is:

CLAIMS

1. A first composition comprising:

magnesium; where the magnesium is present in an amount of 50 to 99.5 wt%; based on the total weight of the composition; and

gadolinium.

2. The composition of Claim 1, where the first composition further comprises one or more metals, where the metals are aluminum, boron, manganese, scandium, lithium, yttrium, zinc, calcium or zirconium.

3. The composition of Claim 1, where the first composition comprises aluminum in an amount of up to 40 wt%, boron in an amount of up to 50 wt%, manganese in an amount of up to 3 wt%, scandium in an amount of up to 30 wt%, lithium in an amount of up to 11 wt%, yttrium in an amount of up to 36 wt%, zinc in an amount of up to 50 wt%, calcium in an amount of up to 40 wt%, and/or zirconium in an amount of up to 4 wt%.

4. An article comprising the composition of Claim 1.

5. The article of Claim 4, where the article comprises multiple layers.

6. A second composition comprising

magnesium; where the magnesium is present in an amount of 50 to 99.5 wt%; based on the total weight of the composition; and

one or more metals; where the metals are aluminum, boron, manganese, scandium, lithium, yttrium, zinc, calcium or zirconium; and where the composition is devoid of gadolinium.

7. The composition of Claim 6, where the aluminum is present in an amount of up to 40 wt%, boron is present in an amount of up to 50 wt%, manganese is present in an amount of up to 3 wt%, scandium is present in an amount of up to 30 wt%, lithium is present in an amount of up to 11 wt%, yttrium is present in an amount of up to 36 wt%, zinc is present in an amount of up to 50 wt%, calcium is present in an amount of up to 40 wt%, and/or zirconium is present in an amount of up to 4 wt%; where all weight percents are based on the total weight of the composition.

8. The composition of Claim 7, where the aluminum, boron, manganese, scandium, lithium, yttrium, zinc, calcium and/or zirconium is present in an amount of 0.5 to 3 wt%, based on the total weight of the composition.

9. An article comprising the composition of Claim 6.

10. The article of Claim 9, where the article comprises multiple layers.

11. A method comprising:

molding a composition comprising magnesium and gadolinium; where the magnesium is present in an amount of 50 to 99.5 wt%; based on the total weight of the composition.

12. A method comprising:

molding a composition comprising magnesium; where the magnesium is present in an amount of 50 to 99.5 wt%; based on the total weight of the composition; and one or more metals; where the metals are aluminum, boron, manganese, scandium, lithium, yttrium, zinc, calcium or zirconium; and where the composition is devoid of gadolinium.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 16/13784

A. CLASSIFICATION OF SUBJECT MATTER
IPC(8) - C22C 23/06; C22C 23/04; B22D 21/00; B32B 15/00 (2016.01)
CPC - C22C 23/06; C22C 23/04; B22D 21/00; B22D 21/007; B32B 15/00
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC - C22C 23/06; C22C 23/04; B22D 21/00; B32B 15/00 (2016.01)
CPC - C22C 23/06; C22C 23/04; B22D 21/00; B22D 21/007; B32B 15/00

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
USPC - 420/406, 420/405, 164/47, 428/649
Patents and NPL (classification, keyword; search terms below)

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
Pub West (US EP JP WO), Pat Base (AU BE BR CA CH CN DE DK EP ES FI FR GB IN JP KR SE TH TW US WO), Google Patent, Google Scholar, Free Patents Online; search terms: magnesium, gadolinium, Mg, Gd, alloy, layer, multilayer, mold, mould, cast, radiation, irradiate, cosmic, neutron, shield, absorb

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2013/0199677 A1 (VENKATESAN et al.) 08 August 2013 (08.08.2013) para [0062], [0106]	1-4, 6-9, 11-12
X	US 2012/0148871 A1 (STOERMER et al.) 14 June 2012 (14.06.2012) para [0013], [0015], [0025], [0035], [0040], [0041], Fig 2, Table 1	1-7, 9-10
X	US 2014/0373982 A1 (CHEN et al.) 25 December 2014 (25.12.2014) the entire document	1-4, 11
X	US 2013/0144290 A1 (SCHIFFL et al.) 06 June 2013 (06.06.2013) the entire document	1-4, 6-9, 11-12
X	US 2010/0310409 A1 (GIBSON et al.) 09 December 2010 (09.12.2010) the entire document	1-4, 6-9, 11-12
X	US 2009/0175754 A1 (WILKS et al.) 09 July 2009 (09.07.2009) the entire document	1-4
X	US 2008/0152532 A1 (NAKATA et al.) 26 June 2008 (26.06.2008) the entire document	1-4, 6-9,11-12
X	US 2007/0169859 A1 ((KAWAMURA et al.) 26 July 2007 (26.07.2007) the entire document	1-4, 6-9,11-12
X	HE, SM. et al. Comparison of the microstructure and mechanical properties of a ZK60 alloy with and without 1.3 wt.% gadolinium addition. Matls. Sci. and Engng. A. October 2006, Vol 433, pages 175-181	1-4, 6-9,11-12
X	ANYANWU, IA et al. Creep properties of Mg-Gd-Y-Zr Alloys. Materials Transactions July 2001, 42(7), pages 1212-1218	1-4, 6-9,11-12

☐ Further documents are listed in the continuation of Box C. ☐

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
10 May 2016 (10.05.2016)	10 JUN 2016

Name and mailing address of the ISA/US	Authorized officer:
Mail Stop PCT, Attn: ISA/US, Commissioner for Patents P.O. Box 1450, Alexandria, Virginia 22313-1450 Facsimile No. 571-273-8300	Lee W. Young PCT Helpdesk: 571-272-4300 PCT OSP: 571-272-7774

Form PCT/ISA/210 (second sheet) (January 2015)