rigidity, stability, biocompatibility, tissue receptivity and resistance to corrosion would make an ideal material for orthopedic implants and applications.

Summary

In one aspect of the present disclosure, there is provided a method for producing an alloy comprising:

(a) placing alloy components in a crucible, wherein the alloy components are placed in the crucible in a multilayer arrangement;

(b) melting the alloy components at 700 °C to 850 °C;

(c) stirring the melt of step (b) at 400 rpm to 500 rpm;

(d) atomizing the melt of step (c) into millimeter size droplets using jets of inert gas; and

(e) cooling and depositing the atomized alloy melt to obtain an ingot

wherein step (a) comprises controlling the volume of the alloy components to 70% to 75% the volume of the crucible.

In one example of the present disclosure, there is provided a biodegradable alloy of Formula (I):

Mg-Zn-X -- Formula (I)

wherein:

X represents –Ca-Mn or –Dy-Sr;

Mg is magnesium, Zn is zinc, Dy is dysprosium, Sr is strontium, Ca is calcium and Mn is manganese;

wherein said alloy comprises, based on total alloy weight:

about 0.1 wt% to about 3.0 wt% Zn;
about 0.1 wt% to about 0.7 wt% Dy;
about 0.1 wt% to about 0.9 wt% Sr;
about 0.1 wt% to about 1.5 wt% Ca;
about 0.1 wt% to about 0.9 wt% Mn; and
balance of Mg and impurities.

In another example of the present disclosure, there is provided an implant comprising the alloy disclosed herein.

Advantageously, the disclosed biodegradable alloys may possess zero level cytotoxicity which allows for the effective use of the material in orthopedic, neurosurgical, cranial, maxillofacial applications and lowers the associated risks to the patients.

Low weight fractions of alloying element (e.g. zinc) may be used in the biodegradable alloys. Advantageously, this lowers the cost of the alloy. Similarly with trace additions of biocompatible elements like calcium and manganese, or rare earth elements such as strontium and dysprosium, the cost of the biodegradable alloy may be kept low with all functions and properties met.

In a further example of the present disclosure, there is provided a method for producing an alloy comprising:

(a) placing alloy components in a crucible, wherein the alloy components are placed in the crucible in a multilayer arrangement;

(b) melting the alloy components at about 700 °C to about 850 °C;
(c) stirring the melt of step (b) at about 400 rpm to about 500 rpm;
(d) atomizing the melt of step (c) into millimeter size droplets using jets of inert gas;
(e) cooling and depositing the atomized alloy melt to obtain an ingot.

In another example of the present disclosure, there is provided a method for producing an alloy of Formula (I):

Mg-Zn-X -- Formula (I)

wherein:

X represents –Ca-Mn or –Dy-Sr;

Mg is magnesium, Zn is zinc, Dy is dysprosium, Sr is strontium, Ca is calcium and Mn is manganese;

wherein said alloy comprises, based on total alloy weight:

about 0.1 wt% to about 3.0 wt% Zn;
about 0.1 wt% to about 0.7 wt% Dy;
about 0.1 wt% to about 0.9 wt% Sr;
about 0.1 wt% to about 1.5 wt% Ca;
about 0.1 wt% to about 0.9 wt% Mn; and
balance of Mg and impurities,

wherein said method comprises:

(a) placing alloy components in a crucible, wherein the alloy components are placed in the crucible in a multilayer arrangement;
(b) melting the alloy components at about 700 °C to about 850 °C;
(c) stirring the melt of step (b) at about 400 rpm to about 500 rpm;
(d) atomizing the melt of step (c) into millimeter size droplets using jets of inert gas;
(e) cooling and depositing the atomized alloy melt to obtain an ingot.

Advantageously, arranging the alloy components in this multilayer or sandwich fashion ensures the maximum capture and wettability of the alloy matrix material (which may be the first alloy component) as the alloying element(s) in the second alloy component may have different melting points as compared to the alloy matrix material. This layerwise or multilayer arrangement ensures the best possible homogenization of the alloying elements into the molten matrix metal/material.

Using the disclosed methods of the present disclosure, the disclosed biodegradable alloy can be manufactured effectively without using any toxic flux

strength retained by the material post-implantation can be assessed and the functional life cycle requirements of the implant can be determined.

Referring to Figs. 8A and 8B, Figs. 8A and 8B show the fracture morphology of the magnesium alloys after compression testing which provides insights on the mechanism of failure and the amount of energy absorbed by the implant before failure.

Detailed Disclosure of Embodiments

Magnesium is non-toxic, biocompatible, bioresorbable, of low density and possesses mechanical properties closer to that of bone. However, monolithic magnesium displays low corrosion resistance in physiological environments leading to low mechanical properties retention and possible implant failure prior to complete bone repair. Modification of magnesium using an alloying technology is crucial in order to tailor the properties to meet that of an ideal orthopedic implant material.

In the present invention, suitable alloying elements like zinc and biocompatible elements like dysprosium, strontium, calcium and manganese are used in optimized amounts in the magnesium matrix to develop unique biodegradable magnesium-based alloys with improved mechanical, degradation and cytotoxicity response.

The present disclosure relates to a biodegradable alloy of Formula (I):

Mg-Zn-X -- Formula (I)

wherein:

X represents –Ca-Mn or –Dy-Sr;

Mg is magnesium, Zn is zinc, Dy is dysprosium, Sr is strontium, Ca is calcium and Mn is manganese;

wherein said alloy comprises or consists of, based on total alloy weight:

about 0.1 wt% to about 3.0 wt% Zn;
about 0.1 wt% to about 0.7 wt% Dy;
about 0.1 wt% to about 0.9 wt% Sr;
about 0.1 wt% to about 1.5 wt% Ca;
about 0.1 wt% to about 0.9 wt% Mn; and
balance of Mg and impurities.

- Mg-Zn-Dy-Sr, wherein Zn is 2.5 wt%, Dy is 0.5 wt%, Sr is 0.8 wt% and Mg makes up the balance.

The alloy may comprise trace amounts of impurities, such as aluminum, iron, nickel, silicon or copper. Each impurity or the total amount of impurities may constitute about 20 ppm or less, or about 20 ppm, about 19 ppm, about 18 ppm, about 17 ppm, about 16 ppm, about 15 ppm, about 14 ppm, about 13 ppm, about 12 ppm, about 11 ppm, about 10 ppm, about 9 ppm, about 8 ppm, about 7 ppm, about 6 ppm, about 5 ppm, about 4 ppm, about 3 ppm, about 2 ppm, about 1 ppm, or about 0 ppm.

The alloy may advantageously not contain yttrium which is known to be cytotoxic. The inventors have surprisingly found that yttrium may be omitted from the alloy and by using trace additions of strontium, calcium, manganese and dysprosium instead, similar functional advantages may be achieved with lower risk and lower costs.

The present disclosure also relates to an implant comprising a biodegradable alloy of Formula (I):

Mg-Zn-X -- Formula (I)

wherein:

X represents –Ca-Mn or –Dy-Sr;

Mg is magnesium, Zn is zinc, Dy is dysprosium, Sr is strontium, Ca is calcium and Mn is manganese;

wherein said alloy comprises or consists of, based on total alloy weight:

about 0.1 wt% to about 3.0 wt% Zn;
about 0.1 wt% to about 0.7 wt% Dy;
about 0.1 wt% to about 0.9 wt% Sr;
about 0.1 wt% to about 1.5 wt% Ca;
about 0.1 wt% to about 0.9 wt% Mn; and
balance of Mg and impurities.

The implant may be an orthopedic, cranial, maxillofacial, neurosurgical or dental implant.

The present disclosure further relates to a method for producing an alloy comprising:

(a) placing alloy components in a crucible, wherein the alloy components are placed in the crucible in a multilayer arrangement;

(b) melting the alloy components at about 700 °C to about 850 °C;

(c) stirring the melt of step (b) at about 400 rpm to about 500 rpm;

(d) atomizing the melt of step (c) into millimeter size droplets using jets of inert gas;

(e) cooling and depositing the atomized alloy melt to obtain an ingot.

The present disclosure further relates to a method for producing an alloy of Formula (I):

Mg-Zn-X -- Formula (I)

wherein:

X represents –Ca-Mn or –Dy-Sr;

Mg is magnesium, Zn is zinc, Dy is dysprosium, Sr is strontium, Ca is calcium and Mn is manganese;

wherein said alloy comprises or consists of, based on total alloy weight:

about 0.1 wt% to about 3.0 wt% Zn;
about 0.1 wt% to about 0.7 wt% Dy;
about 0.1 wt% to about 0.9 wt% Sr;
about 0.1 wt% to about 1.5 wt% Ca;
about 0.1 wt% to about 0.9 wt% Mn; and
Balance of Mg and impurities,

wherein said method comprises:

(a) placing alloy components in a crucible, wherein the alloy components are placed in the crucible in a multilayer arrangement;
(b) melting the alloy components at about 700 °C to about 850 °C;
(c) stirring the melt of step (b) at about 400 rpm to about 500 rpm;
(d) atomizing the melt of step (c) into millimeter size droplets using jets of inert gas;
(e) cooling and depositing the atomized alloy melt to obtain an ingot.

The crucible may be a graphite or metal crucible.

Step (a) may comprise controlling the volume of the alloy components to about 70% to about 75% the volume of the crucible. The inventors have surprisingly found that when the volume of precursor material/alloy components is controlled in the range of about 70% to about 75% with respect to the volume of the crucible, the molten flow rate is regulated for the amount of material used as the raw material. This engineering control advantageously ensures the reproducibility of the deposited material into the mold. Furthermore, with the uniform molten metal flow rate, the amount of gas impinging on

the downpouring molten metal is also standardized, further regulating the heat extraction from the molten metal stream. The controlled volume of inert gas impingement into the molten metal stream standardizes the volume ratio of gas and molten metal thus advantageously ensuring reproducibility of similar microstructure evolution and mechanical properties of the deposited material.

The volume of the alloy components may be about 70%, about 71%, about 72 %, about 73%, about 74%, or about 75% the volume of the crucible.

Additionally, in step (a), the multilayer arrangement of step (a) may comprise an A-B-A arrangement, wherein A comprises or consists of a first alloy component and B comprises or consists of a second alloy component, wherein the first and second alloy components may each comprise or consist of a single alloy material or a blended alloy mixture of two or more alloy materials.

The inventors have surprisingly found that arranging the alloy components in this multilayer or sandwich fashion ensures the maximum capture and wettability of the alloy matrix material (which may be the first alloy component) as the alloying element(s) in the second alloy component may have different melting points as compared to the alloy matrix material. This layerwise or multilayer arrangement ensures the best possible homogenization of the alloying elements into the molten matrix metal/material.

In another embodiment, the multilayer arrangement of step (a) may comprise an A-B-A-B-A arrangement, wherein A comprises or consists of a first alloy component and B comprises or consists of a second alloy component, wherein the first and second alloy components may each comprise or consist of a single alloy material or a blended alloy mixture of two or more alloy materials.

Fig. 7 is a cross-section schematic of the crucible showing the multilayer arrangement. (A) refers to the first alloy component layer, and (B) refers to the second alloy component layer.

In an embodiment, A may consist of magnesium and B may consist of a blended alloy mixture of zinc and X.

In an embodiment, A may consist of magnesium and B may consist of a blended alloy mixture of zinc, calcium, and manganese.

In an embodiment, A may consist of magnesium and B may consist of a blended alloy mixture of zinc, dysprosium and strontium.

Each layer of the multilayer arrangement may be of substantially equal volume. Advantageously, this assists in uniform heating of each layer within the furnace.

The inventors have surprisingly found that arranging the alloy components in this multilayer or sandwich fashion ensures the maximum capture and wettability of the

magnesium matrix as the alloying element(s) (such as zinc, manganese, calcium, dysprosium and strontium) may have different melting points as compared to magnesium. Magnesium, in the form of turnings, may be arranged in three equal volume layers with the blended alloy layer mixture sandwiched between the magnesium layers. Post melting of magnesium, this layerwise/multilayer arrangement advantageously ensures the best possible homogenization of the alloying elements into the molten magnesium metal.

The method of the present invention is a liquid based processing methodology. Magnesium may be the matrix material, and the constituent elements (such as zinc, manganese, calcium, dysprosium and strontium) may be added to the crucible with the magnesium in a multilayer or sandwich arrangement. As the constituent elements are in low weight percentage, using a multilayer or sandwich arrangement advantageously ensures a proper pre-mixing of these constituent elements with the magnesium which may be in the form of magnesium turnings. The morphology of constituent elements may be in powder, ingot shot or wire form. Considering the different possibilities, the multilayer or sandwich arrangement provides the best uniformity while stirring and pouring and subsequently in the final cast.

Step (b) may be performed at a temperature of about 700 °C to about 850 °C, about 725 °C to about 850 °C, about 750 °C to about 850 °C, about 775 °C to about 850 °C, about 800 °C to about 850 °C, about 825 °C to about 850 °C, about 700 °C to about 825 °C, about 700 °C to about 800 °C, about 700 °C to about 775 °C, about 700 °C to about 750 °C, about 700 °C to about 725 °C, or about 700 °C, about 725 °C, about 750 °C, about 775 °C, about 800 °C, about 825 °C, about 850 °C, or any value or range therein.

The stirring in step (c) may be performed at about 400 rpm to about 500 rpm, about 425 rpm to about 450 rpm, about 450 rpm to about 500 rpm, about 475 rpm to about 500 rpm, about 400 rpm to about 475 rpm, about 400 rpm to about 450 rpm, about 400 rpm to about 425 rpm, or about 400 rpm, about 425 rpm, about 450 rpm, about 475 rpm, about 500 rpm, or any value or range therein.

The rate of the chosen stirring speed advantageously allows for uniform dispersion of the secondary phase particles in the melt. The optimized stirring speeds avoids agglomeration in the melt and the constituent elements are thoroughly mixed in the molten or semi-solid form. In the disclosed method, the alloy components are introduced in a sandwiched or multilayer form. Hence, optimized stirring advantageously improves the wettability of the first alloy component with the second alloy component.

The jets of inert gas in step (d) may be jets of nitrogen or argon. The number of jets used may be 2, 3 4, 5, or 6 jets. The diameter of each jet nozzle may be about 1mm to about 2mm and the gas flow rate may be about 20 L/min to about 30 L/min. The number of gas jets and gas flow rate may be adjusted so as to disintegrate the melt into millimeter size droplets. Flow rates and the number of jets affects the disintegration of the molten metal while it is bottom poured into the mold. Optimizing these parameters assists in

Claims

1. A method for producing an alloy comprising:
   (a) placing alloy components in a crucible, wherein the alloy components are placed in the crucible in a multilayer arrangement;
   (b) melting the alloy components at 700 °C to 850 °C;
   (c) stirring the melt of step (b) at 400 rpm to 500 rpm;
   (d) atomizing the melt of step (c) into millimeter size droplets using jets of inert gas; and
   (e) cooling and depositing the atomized alloy melt to obtain an ingot

   wherein step (a) comprises controlling the volume of the alloy components to 70% to 75% the volume of the crucible.

2. The method of claim 1, wherein the alloy is of Formula (I):

   Mg-Zn-X -- Formula (I)

   wherein:

   X represents –Ca-Mn or –Dy-Sr;

   Mg is magnesium, Zn is zinc, Dy is dysprosium, Sr is strontium, Ca is calcium and Mn is manganese;

   wherein said alloy comprises, based on total weight:

   0.1 wt% to 3.0 wt% Zn;
   0.1 wt% to 0.7 wt% Dy;
   0.1 wt% to 0.9 wt% Sr;
   0.1 wt% to 1.5 wt% Ca;
   0.1 wt% to 0.9 wt% Mn; and
   balance of Mg and impurities.

3. The method of claim 1 or 2, wherein the multilayer arrangement of step (a) comprises an A-B-A arrangement, wherein A consists of a first alloy component and B consists of a second alloy component, wherein the first and second alloy components may each consist of a single alloy material or a blended alloy mixture of two or more alloy materials.

4. The method of any one of claims 1 to 3, wherein the multilayer arrangement of step (a) comprises an A-B-A-B-A arrangement, wherein A consists of a first alloy component and B consists of a second alloy component, wherein the first and second alloy components may each consist of a single alloy material or a blended alloy mixture of two or more alloy materials.

5. The method of claim 3 or 4, wherein A consists of magnesium and B consists of a blended alloy mixture of zinc and X.

6. The method of any one of claims 1 to 4, wherein each layer of the multilayer arrangement is of substantially equal volume.

7. The method of any one of claims 1 to 6, wherein step (d) comprises using 2 to 4 jets of inert gas.

8. The method of any one of claims 1 to 7, wherein the inert gas in step (d) is argon.

9. The method of any one of claims 1 to 8, wherein the diameter of each jet in step (d) is 1 mm to 2 mm.

10. The method of any one of claims 1 to 9, wherein the gas flow rate in step (d) is 20 to 30 litres per minute.

11. The method of any one of claims 1 to 10, further comprising step (f) subjecting the ingot to hot extrusion at 250 °C to 400 °C.

12. The method of claim 11, wherein the extrusion ratio range is 25:1 to 12:1.