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(54) A METHOD OF PREPARING MAGNESIUM-ZINC-YTTRIUM QUASICRYSTAL AND BORON CARBIDE MIXED REINFORCED MAGNESIUM-BASED COMPOSITE MATERIAL

(57) The present invention relates to a method of preparing magnesium-zinc-yttrium quasicrystal and boron carbide mixed reinforced Mg-based composite materials. Based on the situations that the Mg-based composite materials have poor mechanical properties, in the present invention, magnesium-zinc-yttrium quasicrystal and boron carbide mixed reinforced Mg-based composite materials are prepared by adopting the magnesium alloy as the substrate, the endogenous magnesium-zinc-yttrium quasicrystal and boron carbide as the reinforced phase, via smelting in the vacuum medium frequency induction melting furnace, bottom blowing argon, mechanical stirring, squeeze casting and heat-treatment. The preparation method has advanced process and strict procedures, wherein the data is accurate and detailed and the prepared Mg-based composite materials have 315MPa tensile strength, 7% elongation, 108Hv hardness, making it an advanced preparation method of mixed reinforced Mg-based composite materials.

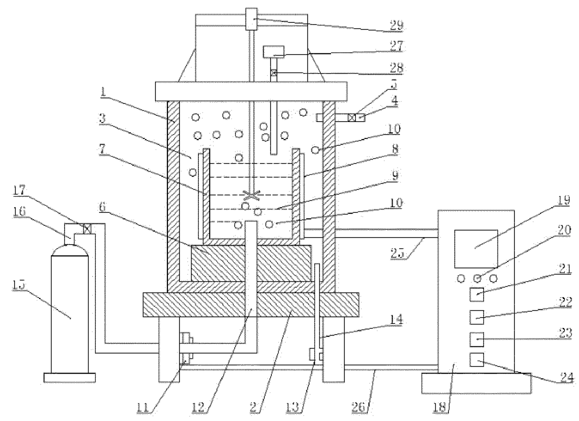

Fig.1

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Description

CROSS-REFERENCE TO RELATED APPLICATION

[0001] The application claims priority to Chinese Application No. 201810328616.X, filed on April 13, 2018, the contents of which are hereby incorporated herein by reference.

BACKGROUND

Field of Invention

[0002] The present invention relates to a method of preparing magnesium-zinc-yttrium quasicrystal and boron carbide mixed enforced Mg-based composite materials, which belong to the technical area of preparing and applying the non-ferrous metal materials.

Background of the Invention

[0003] The magnesium alloy materials have widely applied in the automobile and aerospace area for it they are characterized in low density, high specific strength, excellent shock resistance, strong electromagnetic shielding capability and easy processing. However, the application of magnesium alloy in the industrial area is restricted for its low hardness, low anti-tensile strength and poor corrosion resistance.

[0004] As the quascicrystal has high hardness, high elastic modules, low expansion coefficient and excellent corrosion resistance, it is extremely suitable to be used as the enhance phase of the magnesium alloy and can efficiently improve the mechanical property of the magnesium alloy. The boron carbide particles are of great application potential for they have low density, excellent chemical stability, abrasive resistance and can be evenly distributed in the magnesium substrate with a stable interface. However, mixed particles reinforced Mg-based composite materials are still in the research phase and the process technology needs to be improved.

SUMMARY

Invention Object

[0005] The present invention is done based on the situations introduced by the background art and aims at improving the mechanical property of the magnesium alloy by adopting the magnesium alloy as the substrate, the endogenous magnesium-zinc-yttrium quasicrystal and boron carbide as the reinforced phase, via smelting in the vacuum medium frequency induction melting furnace and then squeezing casting to prepare magnesium-zinc-yttrium quasicrystal and boron carbide mixed reinforced Mg-based composite materials.

Technical Solution

[0006] Chemical materials used in the present invention are: magnesium, zinc, magnesium yttrium interalloy, boron carbide, zinc oxide, talcum powder, water glass, deionized water, aluminum foil, absolute alcohol, argon, their amounts used in the composition are: (measured in gram, milliliter and centimeter^3):

magnesium	Mg	4127g±0.1g
Zinc	Zn	784g±0.1g
magnesium yttrium interalloy	$Mg_{89}Y_{11}$	571g±0.1g
boron carbide	B_4C	300g±0.1g
zinc oxide	ZnO	80g±1g
talcum powder	$Mg_3[Si_4O_{10}](OH)_2$	50g±1g
water glass	$Na_2SiO_3 \cdot 9H_2O$	25g±1g
deionized water	H_2O	1000mL±50mL
aluminum foil	Al	300mm×0.5mm×300mm
absolute alcohol	C_2H_5OH	3500mL±50mL
argon	Ar	800000cm^3±100 cm^3

the preparation method comprises:

(1) preparing the casting mold
the open-close type squeeze casting mold is manufactured by hot working dies steel with a rectangle cavity, wherein the size of the cavity is 200mm×160mm×90mm and the surface roughness of the cavity is Ra 0.08-0.16μm;
(2) preparing the coating agent
weighing out zinc oxide 80g±1g, talcum powder 50g±1g, water glass 25g±1g, measuring out deionized water 300mL±1mL, adding zinc oxide 80g±1g, talcum powder 50g±1g, water glass 25g±1g and deionized water 300mL±1mL into the mixinghollander and stirring them to obtain the coating agent presenting as viscous liquid, wherein the stirring speed is 50r/min, stirring time is 80min.
(3) pre-treating the boron carbide particles

①ball milling: weighing boron carbide 300g±0.1g, putting it into the ball mill tank of the ball mill and ball milling it to obtain fine powder with a particle size ≤9μm, wherein the ball milling speed is 80r/min, the ball milling time is 3h;
②ultrasonic dispersion washing: putting the fine powder after ball milling into a beaker and then adding absolute alcohol 500mL±1mL, mixing;
putting the beaker into an ultrasonic disperser and doing the ultrasonic dispersion washing to obtain the mixing liquid, wherein the ultrasonic frequency is 60kHz and the ultrasonic dispersion time is 80min;
③filtration: putting the mixing liquid into the cloth funnel of the filter bottle, filtering it with a microporous membrane, removing the supernatant, and keeping the filter cake;
④drying and oxidation treatment: putting the filter cake into the thermal treatment furnace, conducting the drying and high temperature oxidation treatment, obtaining the boron carbide fine powderafter drying, wherein the drying and oxidation temperature is 500°C and the drying and oxidation time is 2h;

(4)pre-treating the magnesium, zinc and magnesium yttrium interalloy and the open-close type squeeze casting mold

①mechanically cutting the magnesium, zinc and magnesium yttrium interalloy into patches, wherein the size of the patch is ≤30mm×30mm×10mm;
②washing the surface of the magnesium, zinc and magnesium yttrium interalloy with absolute alcohol and then putting it into the vacuum drying oven after washing, wherein the drying temperature is 100°C, the vacuum degree is 2 Pa and the drying period is 30min;
③wrapping the boron carbide with aluminum foil, putting it into the vacuum drying oven and drying, wherein the drying temperature is 100°C, the vacuum degree is 2 Pa and the drying period is 60min;
pre-heating the open-close type squeeze casting mold and coating the prepared coating agent on the inner surface of the mold cavity, wherein the thickness of the coating agent is 1mm; after the coating is completed, putting the open-close type squeeze casting mold into the heating furnace and preheating, wherein the pre-heating temperature is 150°C and the pre-heating time is 1h;

(5) smelting of the magnesium alloy
smelting of the magnesium alloy is conducted in the vacuum medium frequency induction melting furnace and completed by processes of medium frequency induction heating, vacuumizing, bottom blowing argon and mechanical stirring;

①opening the vacuum medium frequency induction melting furnace and clearing the internal part of the graphite melting crucible to make the internal part of the crucible clean;
②weighing magnesium block 4127g±0.1g, zinc block 784g±0.1g and magnesium yttrium interalloy block 571g±0.1g and putting them in the bottom of the crucible;
③closing the vacuum medium frequency induction melting furnace and getting it sealed;
turning on the vacuum pump and extracting the air within to allow the pressure within the furnace to reach 1Pa;
turning on the heater of the medium frequency induction melting furnace to start the heating, wherein the heating temperature is 610°C±1°C;
④turning on the argon bottom-blowing device to feed argon into the crucible, wherein the speed of the argon bottom-blowing is 200cm3/min; adjusting the pressure within the furnace to maintain the pressure within the furnace to be one bar pressure and it is regulated by the outlet valve;
⑤when the temperature of melt is 610°C±1°C, adding boron carbide fine powder with the vacuum feeding device; turning on the mechanical agitator, wherein the stirring speed is 20r/min and the stirring time is 10min;
⑥stopping the stirring and continuing the heating; when the temperature of melt reaches 730°C±1°C, turning

off the mechanical agitator and the argon bottom blowing pipe, standing for 10 min to prepare for the casting;

(6) squeeze casting

①opening the vacuum medium frequency induction melting furnace, removing the slag on the surface of the melt in the crucible, casting the alloy melt into the cavity of the squeeze casting mold; turning on the squeeze casting machine and squeezing the metal melt by the punch, wherein the squeeze pressure is 250MPa and the hold time is 20s;
the alloying reaction occurs during the solidification of Mg-Zn-Y quascicrystal and stable quascicrystal Mg_3Zn_6Y phase can be produced, wherein the reaction formula is

$$Mg+Zn+Mg_{89}Y_{11}+B_4C \xrightarrow[250MPa]{20s} \alpha\text{-}Mg+Mg_3Zn_6Y+B_4C$$

α-Mg : substrate magnesium phase
Mg_3Zn_6Y : magnesium zinc yttrium quasicrystalline phase

②ejecting the cast and cooling it to 25°C in the air to produce the magnesium-zinc-yttrium quasicrystal and boron carbide mixed reinforced Mg-based composite material blocks;

(7)thermal treatment of the cast

①putting the magnesium-zinc-yttrium quasicrystal and boron carbide mixed reinforced Mg-based composite material blocks into the vacuum heat treatment furnace for thermal treatment, wherein the temperature of the thermal treatment is 420°C, the vacuum degree is 2Pa, and the time of thermal treatment is 15h; and then putting the cast into warm water of 50°C fastly, quenching treatment, wherein the quenching time is 20s;
②putting the cast after quenching into the heat treatment furnace for aging treatment at 200°C for 8h; and then stopping the heating and cooling it to 25°C in the heat treatment furnace;

(8) cleaning, detecting, analyzing and characterizing
cleaning the surface of the cast to make it clean; detecting, analyzing and characterizing the microstructure and mechanical property;
analyzing the metallographic structure with an optical microscope;
conducting the tensile strength and hardness test with universal tensile testing machine and a hardness tester;
conducting the fracture morphology analysis with a scanning electron microscope;
conducting XRD analysis with X ray diffractometer;
conclusion: magnesium-zinc-yttrium quasicrystal and boron carbide mixed reinforced Mg-based composite materials are rectangle blocks, wherein the tensile strength thereof is 315MPa, the elongation is 7%, the hardness reaches 108Hv.

Beneficial effects

[0007] Compared with the background arts, the present invention has prominent advantages. Based on the situations that the Mg-based composite materials have poor mechanical properties, in the present invention, magnesium-zinc-yttrium quasicrystal and boron carbide mixed reinforced Mg-based composite materials are prepared by adopting the magnesium alloy as the substrate, the endogenous magnesium-zinc-yttrium quasicrystal and boron carbide as the reinforced phase, via smelting in the vacuum medium frequency induction melting furnace, protection of bottom blowing argon, mechanical stirring, squeeze casting and heat-treatment. The preparation method has advanced process and strict procedures, wherein the data is accurate and detailed, and the prepared Mg-based composite materials have 315MPa tensile strength, 7% elongation, 108Hv hardness, making it an advanced preparation method of mixed reinforced Mg-based composite materials.

BRIEF DESCRIPTION OF THE DRAWINGS

[0008]

Figure 1 is the smelting state diagram of the Mg-based composite materials;
Figure 2 is the metallographic structure diagram of Mg-based composite materials;
Figure 3 is the fracture topography of Mg-based composite materials;
Figure 4 is is X-ray diffraction intensity spectrum of Mg-based composite materials;

[0009] As shown in the figures, markers for the figures are listed as follow:

1. vacuum medium frequency induction melting furnace, 2. furnace base, 3. furnace chamber, 4. outlet pipe, 5. outlet valve, 6. worktable, 7. graphite melting crucible, 8. medium frequency induction heater, 9. alloy melt, 10. argon, 11. bottom blow motor, 12. bottom blow pipe, 13. vacuum pump, 14. vacuum pipe, 15. argon bottle, 16. argon pipe, 17. argon valve, 18. electric cabinet, 19. display screen, 20. indicator light, 21. power switch, 22. medium frequency induction heating controller, 23. bottom blow motor controller, 24. vacuum pump controller, 25. first cable, 26. second cable, 27. feed pipe, 28. feed valve, 29. mechanical agitator.

DETAILED DESCRIPTION OF THE EMBODIMENTS

[0010] Now the present invention will be further described in combination with the figures:
As shown in Figure 1, it shows the smelting state diagram of the Mg-based composite materials, wherein the location and connection relationship of each part should be correct and the ratio is conducted according to the amount and the process should be conducted according to the sequence.
[0011] The amount of the chemical materials used in the preparation of smelting is determined by the pre-configured scope, and they are measured in gram, milliliter and centimeter^3.
[0012] The smelting of Mg-based composite materials is conducted in the vacuum medium frequency induction melting furnace, and finished by the process of mediate frequency induction heating, bottom blowing argon and mechanical stirring.
[0013] The vacuum medium frequency induction melting furnace is a vertical one. The bottom of the vacuum medium frequency induction melting furnace 1 is a furnace base 2, and the inside of the vacuum medium frequency induction melting furnace 1 is a furnace chamber 3; a worktable 6 is configured in the bottom of the furnace chamber 3 and a graphite melting crucible 7 is put on the worktable 6. The outside of the graphite melting crucible 7 is surrounded by the medium frequency induction heater 8 and the inside of the graphite melting crucible 7 is the alloy melt 9; an outlet pipe 4 is configured on the top right of the vacuum medium frequency induction melting furnace 1 and it is controlled by the outlet valve 5; the argon bottle 15 is configured on the top left of the vacuum medium frequency induction melting furnace 1 and an argon pipe 16 and an argon valve 17 are configured on the argon bottle 15. The argon pipe 16 is connected to the bottom blow motor 11. The bottom blow motor 11 is connected to the bottom blow pipe 12. The bottom blow pipe 12 communicates to the graphite melting crucible 7 through the furnace base 2 and worktable 6 and bottom blows the alloy melt 9; a vacuum pump 13 is configured in the bottom right of the furnace base 2 and communicates to the furnace chamber 3 through a vacuum pipe 14; a feed pipe 27, a feed valve 28 and a mechanical agitator 29 are configured on the top of the vacuum medium frequency induction melting furnace 1 and the feed pipe 27 and the mechanical agitator 29 extends to the graphite melt crucible 7 through the furnace top base.
[0014] A electric cabinet 18 is configured on the right of the vacuum medium frequency induction melting furnace 1 and a display screen 19, an indicator light 20, a power switch 21, a medium frequency induction heating controller 22, a bottom blow motor controller 23 and a vacuum pump controller 24 are configured on the electric cabinet 18; the electric cabinet 18 is connected to the medium frequency induction heater 8 through a first cable 25; The electric cabinet 18 is connected to the bottom blow motor 11 and a vacuum pump 13 through the second cable 26; the furnace cavity 3 is filled with argon 10.
[0015] As shown in Figure 2, it shows the metallographic structure diagram of Mg-based composite materials, wherein there are no defects such as inclusion and air holes in the metallographic structure diagram and the quascicrystal phase Mg_3Zn_6Y and boron carbide particles can be evenly distributed in particles.
[0016] As shown in Figure 3, it shows the fracture topography of Mg-based composite materials, wherein massive small dimples exist in the fracture topography and it demonstrates that it has excellent plasticity.
[0017] As shown in Figure 4, it shows X-ray diffraction intensity spectrum of Mg-based composite materials. In the figure, the ordinate is diffraction intensity index and the abscissa is the diffraction angle 2θ. It can be seen that mainly α-Mg substrate magnesium phase, Mg_3Zn_6Y quascicrystal phase and B_4C reinforced phase exist in Mg-based composite materials.

Claims

1. A method of preparing a magnesium-zinc-yttrium quasicrystal and boron carbide mixed reinforced Mg-based composite materials, **characterized in that**, chemical materials used are: Magnesium, zinc, magnesium yittrium interalloy, boron carbide, zinc oxide, talcum powder, water glass, deionized water, aluminum foil, absolute alcohol, argon, their amounts are:

magnesium	Mg	4127g±0.1g
Zinc	Zn	784g±0.1g
magnesium yttrium interalloy	$Mg_{89}Y_{11}$	571g±0.1g
boron carbide	B_4C	300g±0.1g
zinc oxide	ZnO	80g±1g
talcum powder	$Mg_3[Si_4O_{10}](OH)_2$	50g±1g
water glass	$Na_2SiO_3{\cdot}9H_2O$	25g±1g
deionized water	H_2O	1000mL±50mL
aluminum foil	Al	300mm×0.5mm×300mm
absolute alcohol	C_2H_5OH	3500mL±50mL
argon	Ar	800000cm^3±100 cm^3

the preparation method comprises:

(1) preparing the casting mold
the open-close type squeeze casting mold is manufactured by hot working dies steel with a rectangle cavity, wherein the size of the cavity is 200mm×160mm×90mm and the surface roughness of the cavity is Ra 0.08-0.16μm;
(2) preparing the coating agent
weighing out zinc oxide 80g±1g, talcum powder 50g±1g, water glass 25g±1g, measuring out deionized water 300mL±1mL, adding zinc oxide 80g±1g, talcum powder 50g±1g, water glass 25g±1g and deionized water 300mL±1mL into the mixinghollander and stirring them to obtain the coating agent presenting as viscous liquid, wherein the stirring speed is 50r/min, stirring time is 80min;
(3) pre-treating the boron carbide particles

①ball milling: weighing boron carbide 300g±0.1g, putting it into the ball mill tank of the ball mill and ball milling it to obtain fine powder with a particle size ≤9μm, wherein the ball milling speed is 80r/min, the ball milling time is 3h;
②ultrasonic dispersion washing: putting the fine powder after ball milling into a beaker and then adding absolute alcohol 500mL±1mL, mixing;
putting the beaker into an ultrasonic disperser and doing the ultrasonic dispersion washing to obtain the mixing liquid, wherein the ultrasonic frequency is 60kHz and the ultrasonic dispersion time is 80min;
③filtration: putting the mixing liquid into the cloth funnel of the filter bottle, filtering it with a microporous membrane, removing the supernatant, and keeping the filter cake;
④drying and oxidation treatment: putting the filter cake into the thermal treatment furnace, conducting the drying and high temperature oxidation treatment, obtaining the boron carbide fine powderafter drying, wherein the drying and oxidation temperature is 500°C and the drying and oxidation time is 2h;

(4)pre-treating the magnesium, zinc and magnesium yttrium interalloy and the open-close type squeeze casting mold

①mechanically cutting the magnesium, zinc and magnesium yttrium interalloy into patches, wherein the size of the patch is ≤30mm×30mm×10mm;
②washing the surface of the magnesium, zinc and magnesium yttrium interalloy with absolute alcohol and then putting it into the vacuum drying oven after washing, wherein the drying temperature is 100°C, the vacuum degree is 2 Pa and the drying period is 30min;
③wrapping the boron carbide with aluminum foil, putting it into the vacuum drying oven and drying, wherein the drying temperature is 100°C, the vacuum degree is 2 Pa and the drying period is 60min;

pre-heating the open-close type squeeze casting mold and coating the prepared coating agent on the inner surface of the mold cavity, wherein the thickness of the coating agent is 1mm; after the coating is completed, putting the open-close type squeeze casting mold into the heating furnace and preheating, wherein the pre-heating temperature is 150°C and the pre-heating time is 1h;
(5) smelting of the magnesium alloy
smelting of the magnesium alloy is conducted in the vacuum medium frequency induction melting furnace and completed by processes of medium frequency induction heating, vacuumizing, bottom blowing argon and mechanical stirring;

①opening the vacuum medium frequency induction melting furnace and clearing the internal part of the graphite melting crucible to make the internal part of the crucible clean;
②weighing magnesium block 4127g±0.1g, zinc block 784g±0.1g and magnesium yttrium interalloy block 571g±0.1g and putting them in the bottom of the crucible;
③closing the vacuum medium frequency induction melting furnace and getting it sealed;
turning on the vacuum pump and extracting the air within to allow the pressure within the furnace to reach 1Pa; turning on the heater of the medium frequency induction melting furnace to start the heating, wherein the heating temperature is 610°C±1°C;
④turning on the argon bottom-blowing device to feed argon into the crucible, wherein the speed of the argon bottom-blowing is 200cm3/min; adjusting the pressure within the furnace to allow the pressure within the furnace to be one bar pressure and it is regulated by the outlet valve;
⑤when the temperature of melt is 610°C±1°C, adding boron carbide fine powder with the vacuum feeding device; turning on the mechanical agitator, wherein the stirring speed is 20r/min and the stirring time is 10min;
⑥stopping the stirring and continuing the heating; when the temperature of melt reaches 730°C±1°C, turning off the mechanical agitator and the argon bottom blowing pipe, standing for 10 min and prepare for the casting;

(6) squeeze casting

①opening the vacuum medium frequency induction melting furnace, removing the slag on the surface of the melt in the crucible, casting the alloy melt into the cavity of the squeeze casting mold; turning on the squeeze casting machine and squeezing the metal melt by the punch, wherein the squeeze pressure is 250MPa and the hold time is 20s;
the alloying reaction occurs during the solidification of Mg-Zn-Y quascicrystal and stable quascicrystal Mg_3Zn_6Y phase can be produced, wherein the reaction formula is

$$Mg+Zn+Mg_{89}Y_{11}+B_4C \xrightarrow[250MPa]{20s} \alpha\text{-}Mg+Mg_3Zn_6Y+B_4C$$

α-Mg : substrate magnesium phase
Mg_3Zn_6Y : magnesium-zinc-yttrium quasicrystalline phase

②ejecting the cast and cooling it to 25°C in the air to produce the magnesium-zinc-yttrium quasicrystal and boron carbide mixed reinforced Mg-based composite material blocks;

(7)thermal treatment of the cast

①putting the magnesium-zinc-yttrium quasicrystal and boron carbide mixed reinforced Mg-based composite material blocks into the vacuum heat treatment furnace for thermal treatment, wherein the temperature of the thermal treatment is 420°C, the vacuum degree is 2Pa, and the time of thermal treatment is 15h; and then putting the cast into warm water of 50°C fastly, quenching treatment, wherein the quenching time is 20s;
②putting the cast after quenching into the heat treatment furnace for aging treatment at 200°C for 8h; and then stopping the heating and cooling it to 25°C in the heat treatment furnace;

(8) cleaning, detecting, analyzing and characterizing
cleaning the surface of the cast to make it clean; detecting, analyzing and characterizing the microstructure and mechanical property;

analyzing the metallographic structure with an optical microscope; conducting the tensile strength and hardness test with universal tensile testing machine and a hardness tester;
conducting the fracture morphology analysis with a scanning electron microscope;
conducting XRD analysis with X ray diffractometer;
conclusion: magnesium-zinc-yttrium quasicrystal and boron carbide mixed reinforced Mg-based composite materials are rectangle blocks, wherein the tensile strength is 315MPa, the elongation is 7%, the hardness reaches 108Hv.

2. The method of preparing magnesium-zinc-yttrium quasicrystal and boron carbide mixed reinforced Mg-based composite materials according to claim 1, **characterized in that** the smelting of Mg-based composite materials are conducted in the vacuum medium frequency induction melting furnace and completed through the process of the medium frequency induction heating, bottom blowing argon and mechanical stirring;
the vacuum medium frequency induction melting furnace is a vertical one; The bottom of the vacuum medium frequency induction melting furnace (1) is nconfigured with a furnace base (2), and inside of the vacuum medium frequency induction melting furnace (1) is a furnace chamber (3); a worktable (6) is configured in the bottom of the furnace chamber (3) and a graphite melting crucible (7) is put on the worktable (6); The outside of the graphite melting crucible (7) is surrounded by the medium frequency induction heater (8) and the inside of the graphite melting crucible (7) is the alloy melt (9); an outlet pipe (4) is configured on the top right of the vacuum medium frequency induction melting furnace (1) and it is controlled by the outlet valve (5); the argon bottle (15) is configured on the top left of the vacuum medium frequency induction melting furnace (1) and an argon pipe (16) and an argon valve (17) are configured on the argon bottle (15). The argon pipe (16) is connected to the bottom blow motor (11). The bottom blow motor (11) is connected to the bottom blow pipe (12). The bottom blow pipe (12) communicates to the graphite melting crucible (7) through the furnace base(2) and worktable (6) and bottom blows the alloy melt (9); a vacuum pump (13) is configured in the bottom right of the furnace base (2) and communicates to the furnace chamber (3) through a vacuum pipe (14); a feed pipe (27), a feed valve (28) and a mechanical agitator (29) are configured on the top of the vacuum medium frequency induction melting furnace (1) and the feed pipe (27) and the mechanical agitator (29) extends to the graphite melt crucible (7) through the furnace top base;
a electric cabinet (18) is configured on the right of the vacuum medium frequency induction melting furnace (1) and a display screen (19), an indicator light (20), a power switch (21), a medium frequency induction heating controller (22), a bottom blow motor controller (23) and a vacuum pump controller (24) are configured on the electric cabinet (18); the electric cabinet (18) is connected to the medium frequency induction heater (8) through a first cable (25); The electric cabinet (18) is connected to the bottom blow motor (11) and a vacuum pump (13) through the second cable (26); the furnace cavity (3) is filled with argon (10).

Amended claims in accordance with Rule 137(2) EPC.

1. A method of preparing a magnesium-zinc-yttrium quasicrystal and boron carbide mixed reinforced Mg-based composite materials, **characterized in that**, chemical materials used are: Magnesium, zinc, magnesium yittrium interalloy, boron carbide, zinc oxide, talcum powder, water glass which is $Na_2SiO_3 \cdot 9H_2O$, deionized water, aluminum foil, absolute alcohol, argon, their amounts are:

magnesium	Mg	4127g±0.1g
Zinc	Zn	784g±0.1g
magnesium yttrium interalloy	$Mg_{89}Y_{11}$	571g±0.1g
boron carbide	B_4C	300g±0.1g
zinc oxide	ZnO	80g±1g
talcum powder	$Mg_3[Si_4O_{10}](OH)_2$	50g±1g
water glass	$Na_2SiO_3 \cdot 9H_2O$	25g±1g
deionized water	H_2O	1000mL±50mL
aluminum foil	Al	300mm×0.5mm×300mm
absolute alcohol	C_2H_5OH	3500mL±50mL
argon	Ar	800000cm^3±100 cm^3

the preparation method comprises:

(1) preparing the casting mold
the open-close type squeeze casting mold is manufactured by hot working dies steel with a rectangle cavity, wherein the size of the cavity is 200mm×160mm×90mm and the surface roughness of the cavity is Ra 0.08-0.16μm;
(2) preparing the coating agent
weighing out zinc oxide 80g±1g, talcum powder 50g±1g, water glass 25g±1g, measuring out deionized water 300mL±1mL, adding zinc oxide 80g±1g, talcum powder 50g±1g, water glass 25g±1g and deionized water 300mL±1mL into the mixinghollander and stirring them to obtain the coating agent presenting as viscous liquid, wherein the stirring speed is 50r/min, stirring time is 80min;
(3) pre-treating the boron carbide particles

①ball milling: weighing boron carbide 300g±0.1g, putting it into the ball mill tank of the ball mill and ball milling it to obtain fine powder with a particle size ≤9μm, wherein the ball milling speed is 80r/min, the ball milling time is 3h;
②ultrasonic dispersion washing: putting the fine powder after ball milling into a beaker and then adding absolute alcohol 500mL±1mL, mixing;
putting the beaker into an ultrasonic disperser and doing the ultrasonic dispersion washing to obtain the mixing liquid, wherein the ultrasonic frequency is 60kHz and the ultrasonic dispersion time is 80min;
③filtration: putting the mixing liquid into the cloth funnel of the filter bottle, filtering it with a microporous membrane, removing the supernatant, and keeping the filter cake;
④drying and oxidation treatment: putting the filter cake into the thermal treatment furnace, conducting the drying and high temperature oxidation treatment, obtaining the boron carbide fine powderafter drying, wherein the drying and oxidation temperature is 500°C and the drying and oxidation time is 2h;

(4)pre-treating the magnesium, zinc and magnesium yttrium interalloy and the open-close type squeeze casting mold

①mechanically cutting the magnesium, zinc and magnesium yttrium interalloy into patches, wherein the size of the patch is ≤30mm×30mm×10mm;
②washing the surface of the magnesium, zinc and magnesium yttrium interalloy with absolute alcohol and then putting it into the vacuum drying oven after washing, wherein the drying temperature is 100°C, the vacuum degree is 2 Pa and the drying period is 30min;
③wrapping the boron carbide with aluminum foil, putting it into the vacuum drying ovenand drying, wherein the drying temperature is 100°C, the vacuum degree is 2 Pa and the drying period is 60min;
pre-heating the open-close type squeeze casting mold and coating the prepared coating agent on the inner surface of the mold cavity, wherein the thickness of the coating agent is 1mm; after the coating is completed, putting the open-close type squeeze casting mold into the heating furnace and preheating, wherein the pre-heating temperature is 150°C and the pre-heating time is 1h;

(5) smelting of the magnesium alloy
smelting of the magnesium alloy is conducted in the vacuum medium frequency induction melting furnace and completed by processes of medium frequency induction heating, vacuumizing, bottom blowing argon and mechanical stirring;

①opening the vacuum medium frequency induction melting furnace and clearing the internal part of the graphite melting crucible to make the internal part of the crucible clean;
②weighing magnesium block 4127g±0.1g, zinc block 784g±0.1g and magnesium yttrium interalloy block 571g±0.1g and putting them in the bottom of the crucible;
③closing the vacuum medium frequency induction melting furnace and getting it sealed;
turning on the vacuum pump and extracting the air within to allow the pressure within the furnace to reach 1Pa;
turning on the heater of the medium frequency induction melting furnace to start the heating, wherein the heating temperature is 610°C±1°C;
④turning on the argon bottom-blowing device to feed argon into the crucible, wherein the speed of the argon bottom-blowing is 200cm^3/min; adjusting the pressure within the furnace to allow the pressure within the furnace to be one bar pressure and it is regulated by the outlet valve;
⑤when the temperature of melt is 610°C±1°C, adding boron carbide fine powder with the vacuum feeding device; turning on the mechanical agitator, wherein the stirring speed is 20r/min and the stirring time is 10min;
⑥stopping the stirring and continuing the heating; when the temperature of melt reaches 730°C±1°C,

turning off the mechanical agitator and the argon bottom blowing pipe, standing for 10 min and prepare for the casting;

(6) squeeze casting

①opening the vacuum medium frequency induction melting furnace, removing the slag on the surface of the melt in the crucible, casting the alloy melt into the cavity of the squeeze casting mold; turning on the squeeze casting machine and squeezing the metal melt by the punch, wherein the squeeze pressure is 250MPa and the hold time is 20s;
the alloying reaction occurs during the solidification of Mg-Zn-Y quascicrystal and stable quascicrystal Mg_3Zn_6Y phase can be produced, wherein the reaction formula is

$$Mg+Zn+Mg_{89}Y_{11}+B_4C \xrightarrow[250MPa]{20s} \alpha\text{-}Mg+Mg_3Zn_6Y+B_4C$$

α-Mg : substrate magnesium phase
Mg_3Zn_6Y : magnesium-zinc-yttrium quasicrystalline phase

②ejecting the cast and cooling it to 25°C in the air to produce the magnesium-zinc-yttrium quasicrystal and boron carbide mixed reinforced Mg-based composite material blocks;

(7)thermal treatment of the cast

①putting the magnesium-zinc-yttrium quasicrystal and boron carbide mixed reinforced Mg-based composite material blocks into the vacuum heat treatment furnace for thermal treatment, wherein the temperature of the thermal treatment is 420°C, the vacuum degree is 2Pa, and the time of thermal treatment is 15h; and then putting the cast into warm water of 50°C fastly, quenching treatment, wherein the quenching time is 20s;
②putting the cast after quenching into the heat treatment furnace for aging treatment at 200°C for 8h; and then stopping the heating and cooling it to 25°C in the heat treatment furnace;

(8) cleaning, detecting, analyzing and characterizing
cleaning the surface of the cast to make it clean; detecting, analyzing and characterizing the microstructure and mechanical property;
analyzing the metallographic structure with an optical microscope; conducting the tensile strength and hardness test with universal tensile testing machine and a hardness tester;
conducting the fracture morphology analysis with a scanning electron microscope;
conducting XRD analysis with X ray diffractometer;
conclusion: magnesium-zinc-yttrium quasicrystal and boron carbide mixed reinforced Mg-based composite materials are rectangle blocks, wherein the tensile strength is 315MPa, the elongation is 7%, the hardness reaches 108Hv.

2. The method of preparing magnesium-zinc-yttrium quasicrystal and boron carbide mixed reinforced Mg-based composite materials according to claim 1, **characterized in that** the smelting of Mg-based composite materials are conducted in the vacuum medium frequency induction melting furnace and completed through the process of the medium frequency induction heating, bottom blowing argon and mechanical stirring;
the vacuum medium frequency induction melting furnace is a vertical one; The bottom of the vacuum medium frequency induction melting furnace (1) is nconfigured with a furnace base (2), and inside of the vacuum medium frequency induction melting furnace (1) is a furnace chamber (3); a worktable (6) is configured in the bottom of the furnace chamber (3) and a graphite melting crucible (7) is put on the worktable (6); The outside of the graphite melting crucible (7) is surrounded by the medium frequency induction heater (8) and the inside of the graphite melting crucible (7) is the alloy melt (9); an outlet pipe (4) is configured on the top right of the vacuum medium frequency induction melting furnace (1) and it is controlled by the outlet valve (5); the argon bottle (15) is configured on the top left of the vacuum medium frequency induction melting furnace (1) and an argon pipe (16) and an argon valve (17) are configured on the argon bottle (15). The argon pipe (16) is connected to the bottom blow motor (11). The bottom blow motor (11) is connected to the bottom blow pipe (12). The bottom blow pipe (12) communicates to the graphite melting crucible (7) through the furnace base(2) and worktable (6) and bottom blows the alloy melt (9); a

vacuum pump (13) is configured in the bottom right of the furnace base (2) and communicates to the furnace chamber (3) through a vacuum pipe (14); a feed pipe (27), a feed valve (28) and a mechanical agitator (29) are configured on the top of the vacuum medium frequency induction melting furnace (1) and the feed pipe (27) and the mechanical agitator (29) extends to the graphite melt crucible (7) through the furnace top base;
a electric cabinet (18) is configured on the right of the vacuum medium frequency induction melting furnace (1) and a display screen (19), an indicator light (20), a power switch (21), a medium frequency induction heating controller (22), a bottom blow motor controller (23) and a vacuum pump controller (24) are configured on the electric cabinet (18); the electric cabinet (18) is connected to the medium frequency induction heater (8) through a first cable (25); The electric cabinet (18) is connected to the bottom blow motor (11) and a vacuum pump (13) through the second cable (26); the furnace cavity (3) is filled with argon (10).

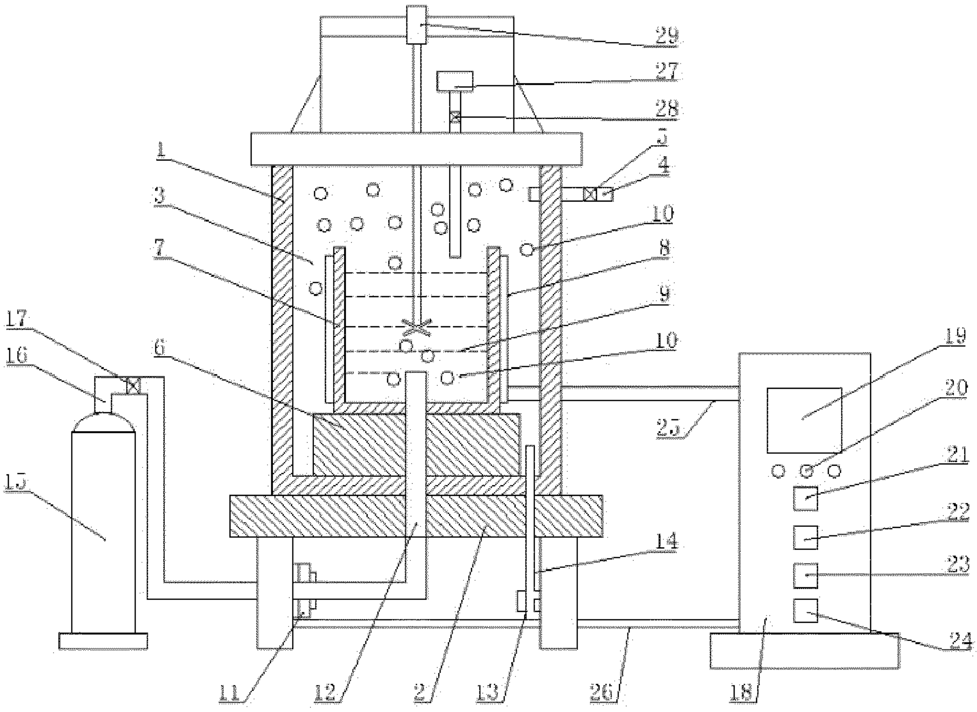
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Fig.1

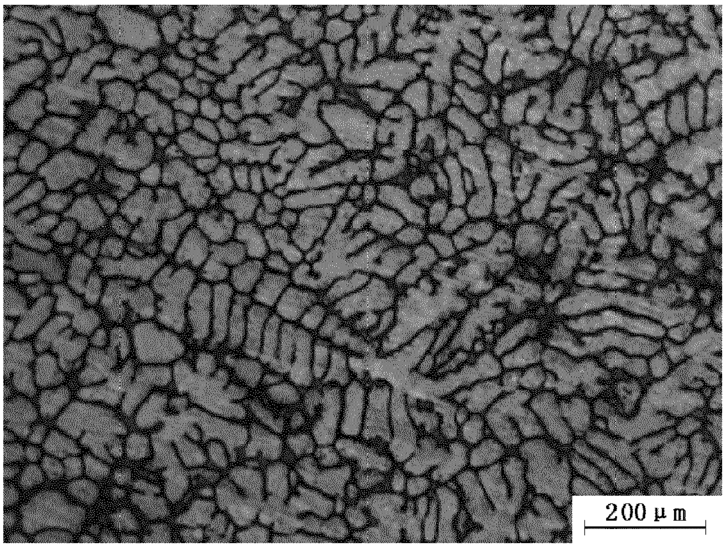
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Fig.2

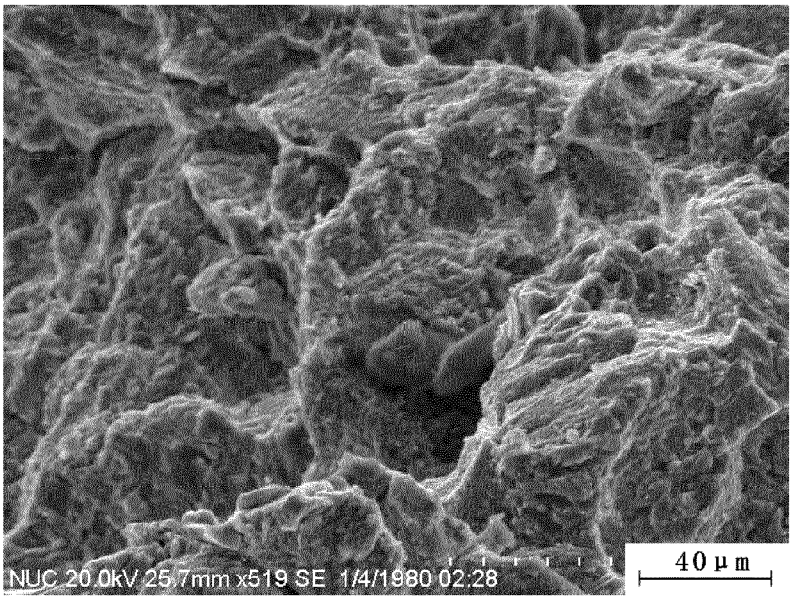
NUC 20.0kV 25.7mm x519 SE 1/4/1980 02:28
40μm

Fig.3

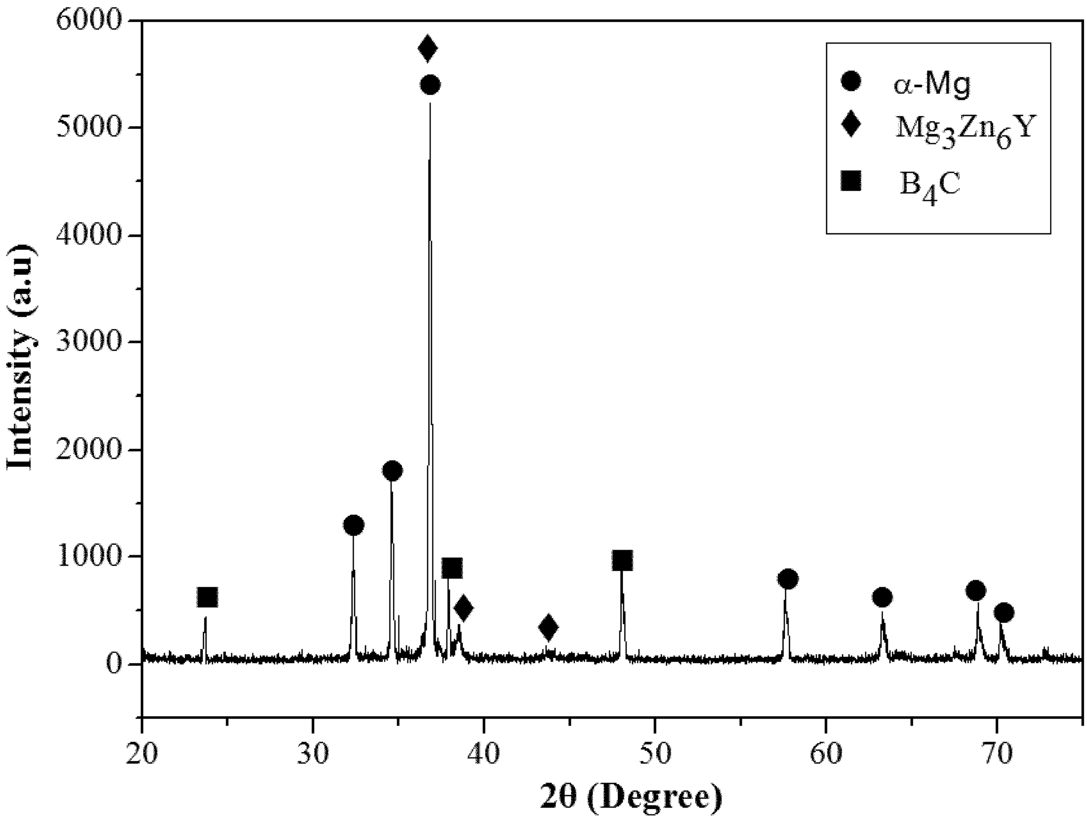
α-Mg
Mg3Zn6Y
B4C
Intensity (a.u)
2θ (Degree)
6000
5000
4000
3000
2000
1000
0
20
30
40
50
60
70

Fig.4

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EUROPEAN SEARCH REPORT

Application Number
EP 19 15 3314

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Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
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			TECHNICAL FIELDS SEARCHED (IPC)
			C22C

The present search report has been drawn up for all claims

1

Place of search	Date of completion of the search	Examiner
Munich	12 March 2019	Brown, Andrew

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12-03-2019

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