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(54) Title: ZIRCONIUM-BASED AMORPHOUS ALLOY, PREPARING METHOD AND RECYCLING METHOD THEREOF

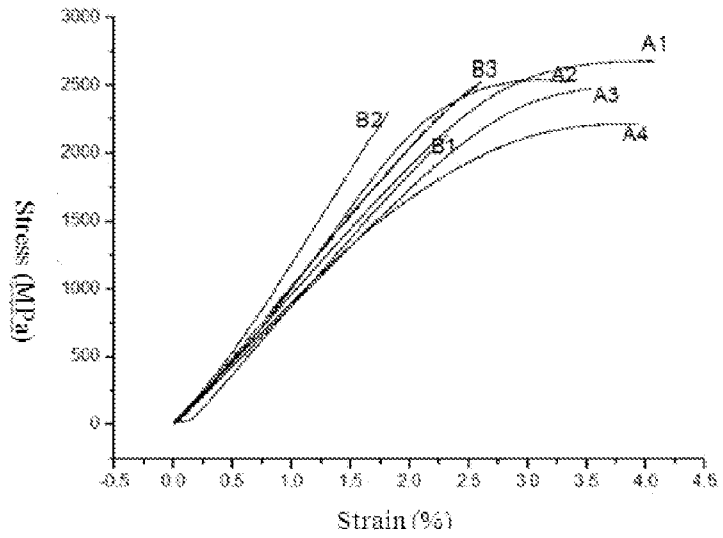

Fig. 1

(57) Abstract: A zirconium (Zr)-based amorphous alloy and a preparing method thereof are provided. The Zr-based amorphous alloy is represented by the general formula of $(Zr_aM_bN_c)_{100-x}Q_x$, in which M is at least one transition metal except Zr; N is Be or Al; Q is selected from the group consisting of CaO, MgO, Y_2O_3, Nd_2O_3 and combinations thereof; a, b and c are atomic percents of corresponding elements; and $45 \le a \le 75$, $20 \le b \le 40$, $1 \le c \le 25$, $a+b+c=100$, and $1 \le x \le 15$. A method for recycling a Zr-based amorphous alloy is also provided.

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Zr-BASED AMORPHOUS ALLOY AND METHODS OF PREPARING AND RECYCLING THE SAME

CROSS-REFERENCE TO RELATED APPLICATIONS

This application claims priority to, and benefit of the following applications:

1) Chinese Patent Application No. 200910221643.8 filed with State Intellectual Property Office, P. R. C. on November 11, 2009; and

2) Chinese Patent Application No. 200910254397.6 filed with State Intellectual Property Office, P. R. C. on December 28, 2009.

The entire contents of the above patent applications are incorporated herein by reference.

FIELD

The present disclosure relates to Zr-based amorphous alloys, and methods for preparing and recycling the same.

BACKGROUND

With the structure of long-range disorder but short-range order, amorphous alloys have excellent physical, chemical and mechanical properties, such as high strength, high hardness, high wear resistance, high corrosion resistance, high plasticity, high resistance, good superconductivity, and low magnetic loss, thus having been applied in a wide range of fields, such as mechanics, medical equipments, electrics, military industries, etc.

However, the conventional method for preparing the amorphous alloy requires raw materials with high purity and conditions with high vacuum degree. For example, low content of impurities, such as oxygen, can greatly reduce the glass formability of the amorphous alloy. Therefore, the demanding preparing conditions may significantly increase the manufacturing cost, which seriously hampers the large-scale application of the amorphous alloys.

Moreover, some inherent defects of the amorphous alloys may also hamper their large-scale applications. For example, under load, amorphous alloys may not deform to resist the load, and finally may be suddenly broken when the stress reaches the fracture strength, which hampers the wide applications of the amorphous alloys.

Chinese patent No. 1578846A discloses a bulk amorphous alloy. The bulk amorphous alloy comprises a bulk amorphous alloy base containing various metals, and additional metals, and is represented by the formula of $(M_{1a}M_{2b}\cdots M_{3c})_{100-x}Q_x$, where Q is the additional metal, which may be selected from the group consisting of La, Y, Ca, Al and Be. The addition of the oxophilic metals, such as La, Y, Ca, Al and Be, to the bulk amorphous alloy may effectively inhibit the adverse effects of the impurities, thus reducing the requirements for the preparing conditions, and

further reducing the manufacturing cost. However, the toughness of the amorphous alloy may not be improved yet.

In practical production, the performance of the bulk amorphous alloy is sensitive to the purity of the raw materials, impurities, the environment, etc. Especially, during the casting step or other steps, few impurities, such as oxygen, may be introduced unavoidably, which may reduce the performance of the amorphous alloy during recycling the amorphous alloy waste. Once the performance of the amorphous alloy can not meet the requirements of the customers, it will be discarded. Therefore, the manufacturing cost of the amorphous alloy is very high, which hampers its large-scale applications. Conventional methods for recycling the amorphous alloy waste mainly include the method of adding damaged elements in the bulk amorphous alloy base and the method of adding oxophilic elements. The method of adding damaged elements in the bulk amorphous alloy base may be realized by detecting the composition of the amorphous alloy waste before adding the damaged elements. When the original elements in the amorphous alloy are not greatly damaged, the amorphous alloy waste can be re-melted. However, during the re-melting step, oxygen or other impurities may be acted as the active center, which may reduce the glass formability and the comprehensive performance of the amorphous alloy. The method of adding oxophilic elements may remove oxygen in the amorphous alloy waste and improve the performance of the amorphous alloy to a certain extent. However, the mechanical properties of the amorphous alloy may be reduced. Worse still, with the increasing of the recycling times, the deterioration of the mechanical properties may be accumulated. After many times of recyclying, the performance of the amorphous alloy, especially toughness, may be so significantly reduced that the performance requirements for forming products may not be satisfied.

SUMMARY

In viewing thereof, the present disclosure is directed to solve at least one of the problems existing in the prior art. Accordingly, a Zr-based amorphous alloy may need to be provided with enhanced toughness. Further, methods of preparing the Zr-based amorphous alloy and recycling the Zr-based amorphous alloy waste are also need to be provided for overcoming the dramatic mechanical property deterioration, such as toughness, in conventional methods.

According to an aspect of the present disclosure, a Zr-based amorphous alloy represented by a general formula of $(Zr_aM_bN_c)_{100-x}Q_x$ is provided, in which M may be at least one transition metal except Zr; N is Be or Al; Q is selected from the group consisting of CaO, MgO, Y_2O_3, Nd_2O_3, and combinations thereof; a, b, and c are atomic percents of corresponding elements; and $45\leq a\leq 75$, $20\leq b\leq 40$, $1\leq c\leq 25$, $a+b+c=100$, and $1\leq x\leq 15$.

According to another aspect of the present disclosure, a method for preparing a Zr-based amorphous alloy is provided. The method may comprise the step of: mixing raw materials

comprising Zr, M, N and Q according to a molar ratio for $Zr_aM_bN_c$: Q: Zr of about (100-x): (x+y): y to form a mixture; melting the mixture to form a molten mixture; and filtering, casting and cooling the molten mixture to form the Zr-based amorphous alloy. The Zr-based amorphous alloy may be represented by the general formula of $(Zr_aM_bN_c)_{100-x}Q_x$, in which M is at least one transition metal except Zr; N is Be or Al; Q is selected from the group consisting of CaO, MgO, Y_2O_3, Nd_2O_3, and combinations thereof; a, b, and c are atomic percents of corresponding elements; and $45\leq a\leq 75$, $20\leq b\leq 40$, $1\leq c\leq 25$, $a+b+c=100$, $1\leq x\leq 15$, and $0.1\leq y\leq 5$.

It has been found by the inventors that, the Zr-base amorphous alloy generally comprises ZrO_2. During the transition of ZrO_2 from high temperature tetragonal phase to low temperature rhombohedral phase, the volume of ZrO_2 may expand by about 5% to about 7%. During the rapid cooling step of the glass formation process, the external phase of the amorphous alloy may be solidified, while the internal phase may be cooled rather slowly. Thus, during the transition process of the internal phase, there is no sufficient space for expansion, which may result in an expansion stress, so that the amorphous alloy may be fragile. It has been unexpectedly found by the inventors that, by the method for preparing the Zr-based amorphous alloy according to an embodiment of the present disclosure, the metal oxide (i.e. at least one compound selected from the group consisting of CaO, MgO, Y_2O_3, and Nd_2O_3) may be introduced in the Zr-based amorphous alloy, thus significantly improving the toughness of the Zr-based amorphous alloy. On the other hand, excess Zr and excess metal oxide (i.e. at least one compound selected from the group consisting of CaO, MgO, Y_2O_3, and Nd_2O_3) are added to the raw materials, and the excess metal oxide may react with ZrO_2 formed during preparing the Zr-based amorphous alloy, to form a refractory composite oxide, which may be removed by the subsequent filtering step. At the same time, the excess Zr may compensate the Zr element lost during the reaction of the metal oxide and ZrO_2. Thus, the amount of ZrO_2 in the Zr-based amorphous alloy may be reduced, thus avoiding the expansion stress formed during the phase transition of ZrO_2 in the cooling step. Therefore, the Zr-based amorphous alloy prepared by the method according to an embodiment of the present disclosure may have better toughness.

According to a further aspect of the present disclosure, a method for recycling a Zr-based amorphous alloy waste is provided. The method may comprise the steps of: mixing a Zr-based amorphous alloy waste with an additive to form a mixture; melting the mixture under vacuum to form a molten mixture; and filtering, casting and cooling the molten mixture under an inert gas to form a Zr-based amorphous alloy. The additive is a mixture of Zr and a metal oxide, and the metal oxide is selected from the group consisting of CaO, MgO, Y_2O_3, Nd_2O_3, and combinations thereof.

It has been found by the inventors that, element Zr has a high binding energy with element oxygen in the Zr-based amorphous alloy waste, so that there is little free oxygen in the Zr-based amorphous alloy waste. Thus, it is quite difficult to remove the oxygen in the Zr-based amorphous

alloy waste by adding rare earth elements or other oxophilic elements into the Zr-based amorphous alloy waste. By a plurality of experiments, it has been found by the inventors that the excess Zr and excess metal oxide (i.e. at least one compound selected from the group consisting of CaO, MgO, Y_2O_3, and Nd_2O_3) are added to the Zr-based amorphous alloy waste, and the excess metal oxide may react with ZrO_2 formed during recycling the Zr-based amorphous alloy, to form a refractory composite oxide, such as $Y_2(ZrO_3)_3$ with a free energy of about -3887153 J/mol, which may be removed by the subsequent filtering step. Therefore, the amount of ZrO_2 in the recycled Zr-based amorphous alloy may be significantly reduced. At the same time, the excess Zr may compensate the Zr element lost during the reaction of the metal oxide and ZrO_2, thus adding the damaged element Zr. Moreover, by a plurality of experiments, CaO, MgO, Y_2O_3 and Nd_2O_3 may all prevent the low temperature phase transition and the volume expansion of ZrO_2, thus preventing the Zr-based amorphous alloy from being fragile. Therefore, after multiple recovery, the Zr-based amorphous alloy may still have stable mechanical properties.

According to the embodiments of the present disclosure, the Zr-based amorphous alloy may have a bending strength of about 2780 MPa, a maximum plastic strain of about 4.5%, and an impact toughness of about 110 KJ/m^2, thus having better toughness.

Additional aspects and advantages of the embodiments of present disclosure will be given in part in the following descriptions, become apparent in part from the following descriptions, or be learned from the practice of the embodiments of the present disclosure.

BRIEF DISCRIPTION OF THE DRAWINGS

These and other aspects and advantages of the present disclosure will become apparent and more readily appreciated from the following descriptions taken in conjunction with the drawings in which:

Fig. 1 is a stress-strain diagram of the Zr-based amorphous alloys according to Embodiments 1-4 and Comparative Embodiments 1-2 of the present disclosure;

Fig. 2 is an XRD pattern of the Zr-based amorphous alloys according to Embodiments 1-2 of the present disclosure; and

Fig. 3 is a structure diagram of a pouring cup for recycling a Zr-based amorphous alloy waste according to an embodiment of the present disclosure.

DETAILED DISCRIPTION OF THE EMBODIMENTS

Reference will be made in detail to embodiments of the present disclosure. The embodiments described herein are explanatory, illustrative, and used to generally understand the present disclosure. The embodiments shall not be construed to limit the present disclosure.

According to an aspect of the present disclosure, a Zr-based amorphous alloy represented by

a general formula of $(Zr_aM_bN_c)_{100-x}Q_x$ is provided, in which M may be at least one transition metal except Zr; N is Be or Al; Q is selected from the group consisting of CaO, MgO, Y_2O_3, Nd_2O_3, and combinations thereof; a, b, and c are atomic percents of corresponding elements; and $45\leq a\leq 75$, $20\leq b\leq 40$, $1\leq c\leq 25$, $a+b+c=100$, and $1\leq x\leq 15$. In an alternative embodiment, $50\leq a\leq 70$, $25\leq b\leq 35$, $3\leq c\leq 23$, and $2\leq x\leq 5$, so that the Zr-based amorphous alloy may have better toughness.

In an alternative embodiment, M is two or more metals selected from the group consisting of: Ti, Ni and Cu. Therefore, the Zr-based amorphous alloy may have better toughness and glass formability. In a further alternative embodiment, M may be the combination of Ni and Cu with an atom ratio of about 1: 10 to about 1: 3.5 , or the combination of Ni, Cu and Ti with an atom ratio for Ni: Cu:Ti of about 1: (1-2): (1.2-2.5).

According to another aspect of the present disclosure, a method for preparing a Zr-based amorphous alloy is provided. The method may comprise the step of: mixing raw materials comprising Zr, M, N and Q according to a molar ratio for $Zr_aM_bN_c$: Q: Zr of about (100-x): (x+y): y to form a mixture; melting the mixture to form a molten mixture; filtering, casting and cooling the molten mixture to form the Zr-based amorphous alloy. The Zr-based amorphous alloy may be represented by the general formula of $(Zr_aM_bN_c)_{100-x}Q_x$, in which M is at least one transition metal except Zr; N is Be or Al; Q is selected from the group consisting of CaO, MgO, Y_2O_3, Nd_2O_3, and combinations thereof; a, b, and c are atomic percents of corresponding elements; and $45\leq a\leq 75$, $20\leq b\leq 40$, $1\leq c\leq 25$, $a+b+c=100$, $1\leq x\leq 15$, and $0.1\leq y\leq 5$.

According to an embodiment of the present disclosure, the molar ratio of $Zr_aM_bN_c$: Q: Zr may be about (100-x): (x+y): y. On the one hand, Q (i.e. at least one compound selected from the group consisting of CaO, MgO, Y_2O_3, and Nd_2O_3) with a molar percent of x/(100+2y) may be added to the raw materials, thus introducing Q in the Zr-based amorphous alloy. On the other hand, Q with a molar percent of y/(100+2y) (i.e. relatively excess Q) may react with ZrO_2 formed during preparing the Zr-based amorphous alloy, to form a refractory composite oxide, which may be removed by the subsequent filtering step. At the same time, Zr with a molar percent of y/(100+2y) may compensate the Zr element lost during the reaction of Q and ZrO_2. In this embodiment, y may be determined by the mole of ZrO_2 formed during preparing a Zr-based amorphous alloy represented by the formula of $Zr_aM_bN_c$, in which M is at least one transition metal; N is Be or Al; and a, b, and c are atomic percents, in which $45\leq a\leq 75$, $20\leq b\leq 40$, $1\leq c\leq 25$, and $a+b+c=100$. The mole of ZrO_2 formed during preparing the Zr-based amorphous alloy can be obtained by testing the oxygen content of the Zr-based amorphous alloy. In an embodiment, the oxygen content may be tested by an IRO-II oxygen content analyzer. In an embodiment, when the raw materials comprises Zr, M, N and Q according to a molar ratio for $Zr_aM_bN_c$: Q: Zr of about (100-x): (x+y): y, and $1\leq x\leq 15$, $0.1\leq y\leq 5$; alternatively $0.2\leq y\leq 2$.

In an alternative embodiment, $50\leq a\leq 70$, $25\leq b\leq 35$, $3\leq c\leq 23$, and $2\leq x\leq 5$, so that the Zr-based

amorphous alloy may have improved toughness.

In an alternative embodiment, M is two or more metals selected from the group consisting of: Ti, Ni and Cu. Therefore, the Zr-based amorphous alloy may have better toughness and glass formability. In a further alternative embodiment, M may be the combination of Ni and Cu with an atom ratio of about 1: 10 to about 1: 3.5, or the combination of Ni, Cu and Ti with an atom ratio for Ni: Cu:Ti of about 1: (1-2): (1.2-2.5).

According to an embodiment of the present disclosure, the raw materials may be melted to form a molten mixture. The melting step may be performed in a melting furnace having a melting chamber. There are no special limits on the melting step. In an alternative embodiment, the melting chamber may be vacuumized to a vacuum degree of about 0.1 Pa to about 10 Pa at a temperature of about 100℃ above the melting temperature of the Zr-based amorphous alloy, followed by filling an inert gas in the melting chamber until the vacuum degree reaches about 30 kPa to about 50 kPa. In an further alternative embodiment, the melting chamber may be vacuumized to a vacuum degree of about 0.5 Pa to about 5 Pa at a temperature of about 100℃ to about 300℃ above the melting temperature of the Zr-based amorphous alloy, followed by filling an inert gas in the melting chamber until the vacuum degree reaches about 35 kPa to about 45 kPa. The inert gas may be selected from helium, nitrogen, argon, krypton, xenon, radon, and combinations thereof, preferably helium and/or argon. As used herein, the term "vacuum degree" mentioned above refers to absolute pressure.

In an embodiment, after the melting step, the molten mixture may be allowed standing for about 1 min to about 5 min, followed by filtering and casting the molten mixture. The standing step on the one hand may cool the molten mixture to a suitable casting temperature, on the other hand may facilitate the molten slag to suspend onto the surface of the molten mixture, thus ensuring the molten slag be filtered out sufficiently.

According to an embodiment of the present disclosure, the molten mixture may be filtered through a high temperature resistant mesh. In an embodiment, the high temperature resistant mesh may have a diameter of about 0.5 mm to about 5 mm, alternatively about 0.8 mm to about 2 mm. The high temperature resistant mesh may be a filtering mesh made of any material which may sustain the temperature of about 750℃ to about 1500℃. In an embodiment of the present disclosure, the high temperature resistant mesh may be selected from the group consisting of steel wire mesh, ceramic mesh, Mo wire mesh, and fiber mesh.

According to an embodiment of the present disclosure, the molten mixture may be cast in a conventional mould. There are no special limits on the casting conditions. In an embodiment of the present disclosure, the casting may be performed at a temperature of about 30℃ to about 80℃ above the melting temperature of the Zr-based amorphous alloy, under protection of an inert gas. The inert gas may be selected from helium, nitrogen, argon, krypton, xenon, radon, and

combinations thereof, preferably helium and/or argon.

According to an embodiment of the present disclosure, the cooling step may be performed under an inert gas. In an embodiment of the present disclsoure, the inert gas may be selected from helium, nitrogen, argon, krypton, xenon, radon, and combinations thereof, preferably helium and/or argon.

According to a further aspect of the present disclosure, a method for recycling a Zr-based amorphous alloy waste is provided. The method may comprise the steps of: mixing a Zr-based amorphous alloy waste with an additive to form a mixture; melting the mixture under vacuum to form a molten mixture; filtering, casting and cooling the molten mixture under an inert gas to form a Zr-based amorphous alloy. The additive is a mixture of Zr and a metal oxide, and the metal oxide is selected from the group consisting of CaO, MgO, Y_2O_3, Nd_2O_3, and combinations thereof.

There are no special limits on the amount of Zr and the metal oxide. In an embodiment, the amount of Zr and the metal oxide may be determined by the oxygen content of the Zr-based amorphous alloy waste. In an embodiment, relative to 100 parts by weight of the Zr-based amorphous alloy waste, the amount of Zr is about W_1 parts by weight, and the amount of the metal oxide is about W_2 parts by weight, in which $W_1=(0.5\text{-}12)\times A$, and $W_2=(0.5\text{-}7)\times A$, in which A is the weight percent of oxygen in the Zr-based amorphous alloy waste. In an alternative embodiment, $W_1=(5\text{-}7)\times A$, and $W_2=(3\text{-}4)\times A$. In a further alternative embodiment, the total amount of Zr and metal oxide is W_3 parts by weight relative to 100 parts by weight of the Zr-based amorphous alloy waste, in which $W_3=(8.5\text{-}11)\times A$. Generally, based on the weight of the Zr-based amorphous alloy waste, the oxygen content of the Zr-based amorphous alloy waste may be more than about 0.1 wt% (i.e. more than 1000 ppm), particularly about 0.1 wt% to about 0.5 wt%, that is to say, A may be about 0.1 to about 0.5. The oxygen content of the Zr-based amorphous alloy waste mentioned above may be tested by an IRO-II oxygen content analyzer.

According to an embodiment of the present disclosure, the Zr-based amorphous alloy waste may be mixed with the additive. The melting step may be known to those skilled in the art. In an embodiment, the melting may be performed at a vacuum degree of about 0.05 Pa to about 5 Pa, at a temperature of about 200℃ to about 500℃ above the melting temperature of the Zr-based amorphous alloy for about 2 min to about 10 min, alternatively at a vacuum degree of about 0.08 Pa to about 0.5 Pa at a temperature of about 250℃ to about 400℃ above the melting temperature of the Zr-based amorphous alloy for about 2 min to about 10 min, alternatively about 4 min to about 10 min, so that the Zr-based amorphous alloy may have better performance. As used herein, the term “vacuum degree” mentioned above refers to absolute pressure.

In an embodiment, after the melting step, the molten mixture may be allowed standing for about 1 min to about 10 min, followed by filtering and casting the molten mixture. The standing step on the one hand may cool the molten mixture to a suitable casting temperature, on the other

hand may facilitate the molten slag to suspend onto the surface of the molten mixture, thus ensuring the molten slag be filtered out sufficiently. In an embodiment, by testing the composition of the molten slag, the contents of Zr, metal elements in the metal oxides, and oxygen in the molten slag are all greater than those in the molten mixture, which may indicate that a composite oxide of ZrO and a metal oxide may be formed. The metal oxide may be at least one compound selected from the group consisting of CaO, MgO, Y_2O_3, and Nd_2O_3.

In an embodiment, the molten mixture may be filtered through a high temperature resistant mesh. In an embodiment, the high temperature resistant mesh may have a diameter of about 0.5 mm to about 10 mm, alternatively about 1 mm to about 6 mm. The high temperature resistant mesh may be a filtering mesh made of any material which may sustain the temperature of about 750℃ to about 1500℃. In an embodiment, the high temperature resistant mesh may be selected from the group consisting of steel wire mesh, ceramic mesh, Mo wire mesh, and fiber mesh.

In an embodiment, the filtering and casting steps may be performed by a pouring cup 1 as shown in Fig. 3. In Fig. 3, the pouring cup 1 is provided with a high temperature resistant mesh 2 at the outlet, to ensure the molten mixture passing into the mould not contain the molten slag or contain a trace amount of molten slag. In an embodiment, the casting step may be performed at a temperature of about 50℃ to about 150℃ above the melting temperature of the Zr-based amorphous alloy, alternatively about 80℃ to about 120℃ above the melting temperature of the Zr-based amorphous alloy.

In an embodiment, the cooling step may be performed under the protection of inert gas. In an embodiment, the inert gas may be selected from helium, nitrogen, argon, krypton, xenon, radon, and combinations thereof, preferably helium and/or argon.

The Zr-based amorphous alloy waste mentioned above may be any scrap or unqualified sample during preparing the Zr-based amorphous alloys or preparing the articles made from the Zr-based amorphous alloys. Particularly, the Zr-based amorphous alloy waste may be the scrap or the unqualified sample of the Zr-based amorphous alloy formed by die casting or casting. The Zr-based amorphous alloy may be any conventional one known to those skilled in the art. In an embodiment, the Zr-based amorphous alloy may be represented by the general formula of $Zr_aM_bN_cY_d$, in which M is at least one transition metal; N is Be or Al; and a, b, c and d are atomic percents of corresponding elements, in which $45\leq a\leq 65$, $20\leq b\leq 40$, $1\leq c\leq 25$, and $0\leq d\leq 5$, alternatively $50\leq a\leq 64$, $25\leq b\leq 35$, $3\leq c\leq 23$, $0\leq d\leq 1$. In a further alternative embodiment, d may be 0, that is to say, the Zr-based amorphous alloy may not include the Y element; and M may be Cu, Ni and/or at least one of other transition metal elements.

In an embodiment, the Zr-based amorphous alloy waste may be pretreated prior to the mixing step. The pretreatment step may be that known in the art, for example, the crushing treatment, the derusting treatment, the surface oxide removing treatment, and the degreasing treatment.

The present disclosure will be described in detail with reference to the following embodiments.

EMBODIMENT 1

A method of preparing a Zr-based amorphous alloy comprises the following steps.

a) Raw materials comprising Zr, Al, Cu, Ni, and Y_2O_3 according to a molar ratio for $Zr_{55}Al_{10}Cu_{30}Ni_5$: Y_2O_3: Zr of about 97: 4: 1 were mixed to form a mixture, in which Al, Cu and Ni were all high purity metals, Zr was zirconium sponge commercially available from Baoti Huashen Titanium Industry Co., Ltd., Jinzhou, P. R. C., and Y_2O_3 was a metal oxide. The mixture was added in the melting chamber with a nominal capacity of about 25 Kg in a ZG-03 medium frequency vacuum induction melting furnace commercially available from Sante Vacuum Metallurgy Technology Industry Co., Ltd., Jinzhou, P. R. C. The melting chamber was vacuumized to a vacuum degree of about 3 Pa, and then argon was filled in the melting chamber until the vacuum degree reached about 40 kPa. The mixture was completely melted at a power of about 25 kW to form a molten mixture.

b) The molten mixture was kept at a temperature of about 950℃ (about 100℃ above the melting temperature of the Zr-based amorphous alloy) for about 5 min, then was allowed standing at room temperature for about 3 min.

c) When the temperature of the molten mixture dropped to about 920℃(about 70℃ above the melting temperature of the Zr-based amorphous alloy), the molten mixture was filtered by a pouring cup having a Mo wire mesh with a diameter of about 0.8 mm, cast in a mould, then cooled to room temperature under argon to form a Zr-based amorphous alloy ingot A1. The Zr-based amorphous alloy ingot A1 was analyzed by an inductively coupled plasma spectrometer (ICP) to obtain a composition of $(Zr_{55}Al_{10}Cu_{30}Ni_5)_{97}(Y_2O_3)_3$.

COMPARATIVE EMBODIMENT 1

A method of preparing a Zr-based amorphous alloy comprises the following steps. The method was substantially similar to that in Embodiment 1, with the exception that raw materials was consisted of Zr, Al, Cu and Ni according to the composition of $Zr_{55}Al_{10}Cu_{30}Ni_5$. The Zr-based amorphous alloy ingot B1 was formed and analyzed by the same method as that in Embodiment 1 to obtain a composition of $Zr_{55}Al_{10}Cu_{30}Ni_5$.

EMBODIMENT 2

A method of preparing a Zr-based amorphous alloy comprises the following steps.

a) Raw materials comprising Zr, Ti, Cu, Ni, Be, and Y_2O_3 Zr according to a molar ratio for $Zr_{41}Ti_{14}Cu_{12.5}Ni_{10}Be_{22.5}$: Y_2O_3: Zr of about 98: 3.5: 1.5 were mixed to form a mixture, in which Al,

Cu, Ni and Be were all high purity metals, Zr was zirconium sponge commercially available from Baoti Huashen Titanium Industry Co., Ltd., Jinzhou, P. R. C., and Y_2O_3 was a metal oxide. The mixture was added in the melting chamber with a nominal capacity of about 25 Kg in a ZG-03 medium frequency vacuum induction melting furnace commercially available from Sante Vacuum Metallurgy Technology Industry Co., Ltd., Jinzhou, P. R. C. The melting chamber was vacuumized to a vacuum degree of about 5 Pa, and then argon was filled in the melting chamber until the vacuum degree reached about 40 kPa. The mixture was completely melted at a power of about 25 kW to form a molten mixture.vacuumized

b) The molten mixture was kept at a temperature of about 1050℃ (about 300℃ above the melting temperature of the Zr-based amorphous alloy) for about 5 min, then was allowed standing at room temperature for about 3 min.

c) When the temperature of the molten mixture dropped to about 830℃ (about 80℃ above the melting temperature of the Zr-based amorphous alloy), the molten mixture was filtered by a pouring cup having a steel wire mesh with a diameter of about 1 mm, cast in a mould, then cooled to room temperature under argon to form a Zr-based amorphous alloy ingot A2. The Zr-based amorphous alloy ingot A2 was analyzed by the same method as that in Embodiment 1 to obtain a composition of $(Zr_{41}Ti_{14}Cu_{12.5}Ni_{10}Be_{22.5})_{98}(Y_2O_3)_2$.

COMPARATIVE EMBODIMENT 2

A method of preparing a Zr-based amorphous alloy comprises the following steps. The method was substantially similar to that in Embodiment 2, with the exception that raw materials was consisted of Zr, Ti, Cu, Ni and Be according to the composition of $Zr_{41}Ti_{14}Cu_{12.5}Ni_{10}Be_{22.5}$. The Zr-based amorphous alloy ingot B2 was formed and analyzed by the same method as that in Embodiment 1 to obtain a composition of $Zr_{41}Ti_{14}Cu_{12.5}Ni_{10}Be_{22.5}$.

EMBODIMENT 3

A method of preparing a Zr-based amorphous alloy comprises the following steps.

a) Raw materials comprising Zr, Al, Cu, Ni, and MgO according to a molar ratio for $Zr_{63.5}Al_{3.6}Cu_{26}Ni_{6.9}$: MgO: Zr of about 96: 4.8: 0.8 were mixed to form a mixture, in which Al, Cu and Ni were all high purity metals, Zr was zirconium sponge commercially available from Baoti Huashen Titanium Industry Co., Ltd., Jinzhou, P. R. C., and Y_2O_3 was a metal oxide. The mixture was added in the melting chamber with a nominal capacity of about 25 Kg in a ZG-03 medium frequency vacuum induction melting furnace commercially available from Sante Vacuum Metallurgy Technology Industry Co., Ltd., Jinzhou, P. R. C. The melting chamber was vacuumized to a vacuum degree of about 1.5 Pa, and then argon was filled in the melting chamber

until the vacuum degree reached about 40 kPa. The mixture was completely melted at a power of about 25 kW to form a molten mixture.

b) The molten mixture was kept at a temperature of about 950℃ (about 100℃ above the melting temperature of the Zr-based amorphous alloy) for about 5 min, then was allowed standing at room temperature for about 3 min.

c) When the temperature of the molten mixture dropped to about 920℃ (about 70℃ above the melting temperature of the Zr-based amorphous alloy), the molten mixture was filtered by a pouring cup having a Mo wire mesh with a diameter of about 0.8 mm, cast in a mould, then cooled to room temperature under argon to form a Zr-based amorphous alloy ingot A3. The Zr-based amorphous alloy ingot A3 was analyzed by the same method as that in Embodiment 1 to obtain a composition of $(Zr_{63.5}Al_{3.6}Cu_{26}Ni_{6.9})_{96}(MgO)_4$.

COMPARATIVE EMBODIMENT 3

A method of preparing a Zr-based amorphous alloy comprises the following steps. The method was substantially similar to that in Embodiment 3, with the exception that raw materials was consisted of Zr, Al, Cu, Ni and Ca according to a molar ratio for $Zr_{63.5}Al_{3.6}Cu_{26}Ni_{6.9}$: Ca of about 96: 4. The Zr-based amorphous alloy ingot B3 was formed and analyzed by the same method as that in Embodiment 1 to obtain a composition of $(Zr_{63.5}Al_{3.6}Cu_{26}Ni_{6.9})_{96}Ca_4$.

EMBODIMENT 4

A method of preparing a Zr-based amorphous alloy comprises the following steps.

a) Raw materials comprising Zr, Ti, Cu, Ni, Be, MgO, and CaO according to a molar ratio for $Zr_{62.4}Ti_{11.2}Cu_{13.3}Ni_{9.8}Be_{3.3}$: $(MgO)_{50}(CaO)_{50}$: Zr of about 96: 6: 2 were mixed to form a mixture, in which Al, Cu and Ni were all high purity metals, Zr was zirconium sponge commercially available from Baoti Huashen Titanium Industry Co., Ltd., Jinzhou, P. R. C., and Y_2O_3 was a metal oxide. The mixture was added in the melting chamber with a nominal capacity of about 25 Kg in a ZG-03 medium frequency vacuum induction melting furnace commercially available from Sante Vacuum Metallurgy Technology Industry Co., Ltd., Jinzhou, P. R. C. The melting chamber was vacuumized to a vacuum degree of about 4 Pa, and then argon was filled in the melting chamber until the vacuum degree reached about 40 kPa. The mixture was completely melted at a power of about 25 kW to form a molten mixture.

b) The molten mixture was kept at a temperature of about 1050℃ (about 300℃ above the melting temperature of the Zr-based amorphous alloy) for about 5 min, then was allowed standing at room temperature for about 3 min.

c) When the temperature of the molten mixture dropped to about 830℃ (about 80℃ above the melting temperature of the Zr-based amorphous alloy), the molten mixture was filtered by a

pouring cup having a steel wire mesh with a diameter of about 1 mm, cast in a mould, then cooled to room temperature under argon to form a Zr-based amorphous alloy ingot A4. The Zr-based amorphous alloy ingot A4 was analyzed by the same method as that in Embodiment 1 to obtain a compositionvacuumized of $(Zr_{62.4}Ti_{11.2}Cu_{13.3}Ni_{9.8}Be_{3.3})_{96}((MgO)_{50}(CaO)_{50})_4$.

EMBODIMENT 5

A method of recycling a Zr-based amorphous alloy waste comprises the following steps.

a) A scrap of a Zr-based amorphous alloy represented by the formula of $Zr_{63.5}Al_{3.6}Cu_{26}Ni_{5.9}Y_1$ was jaw crushed into bulk wastes with an average size of about 3 cm to about 5 cm. About 5 Kg of bulk wastes were weighed, and subjected to the derusting treatment, the surface oxide removing treatment, and the degreasing treatment successively.

b) The bulk wastes were analyzed by an IRO-II type oxygen content analyzer to obtain an oxygen content of about 1085 ppm. That is to say, the oxygen content was about 0.1085 wt%, based on the weight of the bulk wastes, or A was about 0.1085. The bulk wastes were mixed with about 19.15 g (i.e. W_2=3.53A) of Y_2O_3 and about 30.87 g (i.e. W_1=5.69A) of Zr to form a mixture. The mixture was added in the melting chamber with a nominal capacity of about 25 Kg in a ZG-03 medium frequency vacuum induction melting furnace commercially available from Sante Vacuum Metallurgy Technology Industry Co., Ltd., Jinzhou, P. R. C. The melting chamber was vacuumized to a vacuum degree of about 0.08 Pa, and then argon was filled in the melting chamber until the vacuum degree reached about 40 kPa. The mixture was completely melted at a power of about 25 kW to form a molten mixture.

c) The molten mixture was kept at a temperature of about 1050°C (about 200°C above the melting temperature of the Zr-based amorphous alloy) for about 5 min, then was allowed standing at room temperature for about 3 min.

d) When the temperature of the molten mixture dropped to about 920°C (about 70°C above the melting temperature of the Zr-based amorphous alloy), the molten mixture was filtered by a pouring cup as shown in Fig. 3 having a Mo wire mesh with a diameter of about 0.8 mm, cast in a mould, then cooled to room temperature under argon to form a Zr-based amorphous alloy ingot S1.

COMPARATIVE EMBODIMENT 51

A method of recycling a Zr-based amorphous alloy waste comprises the following steps. The method was substantially similar to that in Embodiment 5, with the exception that the bulk wastes were not mixed with Y_2O_3 and Zr, but melted directly to form a Zr-based amorphous alloy ingot D51.

COMPARATIVE EMBODIMENT 52

A method of recycling a Zr-based amorphous alloy waste comprises the following steps. The method herein was substantially similar to that in Embodiment 5, with the exception that the bulk wastes were mixed with about 20 g of Y to form a mixture, and the mixture was melted to form a Zr-based amorphous alloy ingot D52.

COMPARATIVE EMBODIMENT 53

A method of recycling a Zr-based amorphous alloy waste comprises the following steps. The method was substantially similar to that in Embodiment 5, with the exception that the bulk wastes were mixed with about 20 g of Y_2O_3 to form a mixture, and the mixture was melted to form a Zr-based amorphous alloy ingot D53.

EMBODIMENT 6

A method of recycling a Zr-based amorphous alloy waste comprises the following steps.

a) A scrap of a Zr-based amorphous alloy represented by the formula of $Zr_{62.4}Ti_{11.2}Cu_{13.3}Ni_{9.8}Be_{3.3}$ was jaw crushed into bulk wastes with an average size of about 3 cm to about 5 cm. About 5 Kg of bulk wastes were weighed, and subjected to the derusting treatment, the surface oxide removing treatment, and the degreasing treatment successively.

b) The bulk wastes were analyzed by an IRO-II type oxygen content analyzer to obtain an oxygen content of about 2013 ppm. That is to say, the oxygen content was about 0.2013 wt%, based on the weight of the bulk wastes, or A was about 0.2013. The bulk wastes were mixed with about 37.12 g (i.e. W_2=3.53A) of Y_2O_3 and about 59.83 g (i.e. W_1=5.69A) of Zr to form a mixture. The mixture was added in the melting chamber with a nominal capacity of about 25 Kg in a ZG-03 medium frequency vacuum induction melting furnace commercially available from Sante Vacuum Metallurgy Technology Industry Co., Ltd., Jinzhou, P. R. C. The melting chamber was vacuumized, and then argon was filled in the melting chamber until the vacuum degree reached about 0.08 kPa. The mixture was completely melted at a power of about 25 kW to form a molten mixture.

c) The molten mixture was kept at a temperature of about 1050°C (about 300°C above the melting temperature of the Zr-based amorphous alloy) for about 5 min, then was allowed standing at room temperature for about 3 min.

d) When the temperature of the molten mixture dropped to about 830°C (about 80°C above the melting temperature of the Zr-based amorphous alloy), the molten mixture was filtered by a pouring cup as shown in Fig. 3 having a steel wire mesh with a diameter of about 1 mm, cast in a mould, then cooled to room temperature under argon to form a Zr-based amorphous alloy ingot S2.

COMPARATIVE EMBODIMENT 64

A method for recycling a Zr-based amorphous alloy waste comprises the following steps. The method was substantially similar to that in Embodiment 6, with the exception that the bulk wastes were not mixed with Y_2O_3 and Zr, but melted directly to form a Zr-based amorphous alloy ingot D64.

COMPARATIVE EMBODIMENT 65

A method for recycling a Zr-based amorphous alloy waste comprises the following steps. The method was substantially similar to that in Embodiment 6, with the exception that the bulk wastes were mixed with about 20 g of Y to form a mixture, and the mixture was melted to form a Zr-based amorphous alloy ingot D65.

COMPARATIVE EMBODIMENT 66

A method for recycling a Zr-based amorphous alloy waste comprises the following steps. The method was substantially similar to that in Embodiment 6, with the exception that the bulk wastes were mixed with about 20 g of Y_2O_3 to form a mixture, and the mixture was melted to form a Zr-based amorphous alloy ingot D66.

EMBODIMENT 7

A method for recycling a Zr-based amorphous alloy waste comprises the following steps.

a) About 5 Kg of bulk wastes according to Embodiment 6 with an oxygen content of about 2103 ppm (i.e. A=0.2103) were mixed with about 31.86 g (i.e. W_2=3.03A) of Y_2O_3 and about 72.45 g (i.e. W_1=6.89A) of Zr to form a mixture. The mixture was added in the melting chamber with a nominal capacity of about 25 Kg in a ZG-03 medium frequency vacuum induction melting furnace commercially available from Sante Vacuum Metallurgy Technology Industry Co., Ltd., Jinzhou, P. R. C. The melting chamber was vacuumized, and then argon was filled in the melting chamber until the vacuum degree reached about 0.08 kPa. The mixture was completely melted at a power of about 25 kW to form a molten mixture.

b) The molten mixture was kept at a temperature of about 1050°C (about 300°C above the melting temperature of the Zr-based amorphous alloy) for about 5 min, then was allowed standing at room temperature for about 3 min.

c) When the temperature of the molten mixture dropped to about 830°C (about 80°C above the melting temperature of the Zr-based amorphous alloy), the molten mixture was filtered by a pouring cup as shown in Fig. 3 having a steel wire mesh with a diameter of about 1 mm, cast in a mould, then cooled to room temperature under argon to form a Zr-based amorphous alloy ingot S3.

TEST

1) Bending Strength

Each of the Zr-based alloy ingots A1-4 and B1-3 was cast in an arc furnace to form a sheet with a size of about 3 mm × 6 mm × 15 mm. The bending strength of each sheet was tested by a CMT5105 microcomputer control electronic universal testing machine with a tonnage of about 1000 Kg commercially available from Shenzhen Sans Testing Machine Co., Ltd., P. R. C. according to the GB/T14452-93 method under the conditions of a span of about 50 mm and a loading speed of about 0.5 mm/min. The results were shown in Table 1. The stress-strain curve of each of the Zr-based alloy ingots A1-4 and B1-3 was obtained accordingly and shown in Fig. 1, and the maximum plastic strain of each of the Zr-based alloy ingots A1-4 and B1-3 was calculated accordingly and shown in Table 1.

The bending strength of the Zr-based alloy ingots S1-3, D51-53 and D64-66 were tested by the method described above respectively. The results were shown in Table 2.

2) Impact Toughness

Each of the Zr-based alloy ingots A1-4 and B1-3 was cast in an arc furnace to form a sheet with a size of about 3 mm × 6 mm × 15 mm. The impact toughness of each sheet was tested by a ZBC1251-2 pendulum impact tester commercially available from Shenzhen Sans Testing Machine Co., Ltd., P. R. C. The results were shown in Table 1.

The impact toughness of the Zr-based alloy ingots S1-3, D51-53 and D64-66 were tested by the method described above respectively. The results were shown in Table 2.

3) X-Ray Diffraction (XRD)

The Zr-based alloy ingots A1-4 and B1-3 were tested by D-MAX2200PC X-ray powder diffractometer under the conditions of: a copper target, an incident wavelength of about 1.54060 Å, an accelerating voltage of about 40 KV, a current of about 20 mA, and a scanning step of about 0.04° respectively. The diffraction patterns of the Zr-based alloy ingots A1-4 and B1-3 were shown in Fig. 2.

The Zr-based alloy ingots S1-3, D51-53 and D64-66 were tested by the method described above respectively. The results were shown in Fig. 2.

4) Oxygen Content

The Zr-based alloy ingots S1-3, D51-53 and D64-66 were tested by an IRO-II oxygen content analyzer commercially available from Beijing NCS Analytical Instruments Co., Ltd. respectively. The results were shown in Table 2.

Table 1

No.	Bending Strength (MPa)	Maximum Plastic Strain (%)	Impact Toughness (KJ/m^2)
A1	2780	4.1	110
A2	2676	3.3	98
A3	2533	3.6	88
A4	2574	3.9	91
B1	2133	2.3	66
B2	2311	1.8	71
B3	2405	2.6	80

Table 2

No.	Oxygen Content (PPM)	Bending Strength (MPa)	Impact Toughness (KJ/m^2)
S1	420	2648	66
D51	1180	2034	40
D52	800	1818	51
D53	520	2558	60
S2	1705	2910	61
D64	2103	2130	42
D65	1950	1890	39
D66	1745	2810	55
S3	1660	2880	59

As shown in Fig. 2 and Table 1, the Zr-based amorphous alloy prepared by the method according to the embodiments of the present disclosure may have high bending strength, high maximum plastic strain, high impact toughness and good glass formability, while the Zr-based alloy ingots S1-3, D51-53 and D64-66 have almost no crystalline phases.

As shown in Table 2, compared with the conventional Zr-based amorphous alloy, the Zr-based amorphous alloy recycled by the methods according to the embodiments of the present disclosure may have similar oxygen content and bending strength, and may even have enhanced

impact toughness. However, the Zr-based amorphous alloy recycled by the conventional method in the prior art may have increased oxygen content and significantly reduced mechanical properties. In addition, although the addition of oxophilic metal elements, such as Y, to the Zr-based amorphous alloy may not increase oxygen content, the mechanical properties of the Zr-based amorphous alloy may be significantly reduced.

Although explanatory embodiments have been shown and described, it would be appreciated by those skilled in the art that changes, alternatives, and modifications all falling into the scope of the claims and their equivalents can be made in the embodiments without departing from spirit and principles of the invention.

WHAT IS CLAIMED IS:

1. A Zr-based amorphous alloy represented by the general formula of: $(Zr_aM_bN_c)_{100-x}Q_x$, wherein:

M is at least one transition metal except Zr;

N is Be or Al;

Q is selected from the group consisting of CaO, MgO, Y_2O_3, Nd_2O_3, and combinations thereof;

a, b, and c are atomic percents of corresponding elements; and

$45\leq a\leq 75$, $20\leq b\leq 40$, $1\leq c\leq 25$, $a+b+c=100$, and $1\leq x\leq 15$.

2. The Zr-based amorphous alloy according to claim 1, wherein M is two or more metals selected from the group consisting of: Ti, Ni and Cu.

3. The Zr-based amorphous alloy according to claim 1, wherein $50\leq a\leq 70$, $25\leq b\leq 35$, $3\leq c\leq 23$, and $2\leq x\leq 5$.

4. A method of preparing a Zr-based amorphous alloy comprising the steps of:

mixing raw materials comprising Zr, M, N and Q according to a molar ratio for $Zr_aM_bN_c$: Q: Zr of about (100-x): (x+y): y to form a mixture;

melting the mixture to form a molten mixture; and

filtering, casting and cooling the molten mixture to form the Zr-based amorphous alloy represented by the general formula of $(Zr_aM_bN_c)_{100-x}Q_x$, wherein:

M is at least one transition metal except Zr;

N is Be or Al;

Q is selected from the group consisting of CaO, MgO, Y_2O_3, Nd_2O_3, and combinations thereof;

a, b, and c are atomic percents of corresponding elements; and

$45\leq a\leq 75$, $20\leq b\leq 40$, $1\leq c\leq 25$, $a+b+c=100$, $1\leq x\leq 15$, and $0.1\leq y\leq 5$.

5. The method according to claim 4, wherein M is two or more metals selected from the group consisting of: Ti, Ni and Cu.

6. The method according to claim 4, wherein $50\leq a\leq 70$, $25\leq b\leq 35$, $3\leq c\leq 23$, $2\leq x\leq 5$, and $0.2\leq y\leq 2$.

7. The method according to claim 4, wherein the melting step is performed in a melting furnace having a melting chamber; and the melting chamber is vacuumized to a vacuum degree of about 0.1 Pa to about 10 Pa at a temperature of about 100℃ above the melting temperature of the Zr-based amorphous alloy, followed by filling inert gas in the melting chamber until the vacuum degree therein reaches about 30 kPa to about 50 kPa.

8. The method according to claim 7, wherein the melting chamber is vacuumized to a vacuum degree of about 0.5 Pa to about 5 Pa at a temperature of about 100℃ to about 300℃ above the melting temperature of the Zr-based amorphous alloy, followed by filling an inert gas in the melting chamber until the vacuum degree reaches about 35 kPa to about 45 kPa.

9. The method according to claim 4, wherein the molten mixture is filtered through a high temperature resistant mesh with a mesh diameter of about 0.5 mm to about 5 mm.

10. The method according to claim 4, wherein the casting step is performed at a temperature of about 30℃ to about 80℃ above the melting temperature of the Zr-based amorphous alloy under protection of an inert gas.

11. A method of recycling a Zr-based amorphous alloy waste comprising the steps of:

mixing a Zr-based amorphous alloy waste with an additive to form a mixture;

melting the mixture under vacuum to form a molten mixture; and

filtering, casting and cooling the molten mixture respectively under protection of inert gas to form a Zr-based amorphous alloy; wherein the additive is a mixture of Zr and a metal oxide, and the metal oxide is selected from the group consisting of CaO, MgO, Y_2O_3, Nd_2O_3, and combinations thereof.

12. The method according to claim 11, wherein relative to 100 parts by weight of the Zr-based amorphous alloy waste, the amount of Zr is about W_1 parts by weight, and the amount of the metal oxide is about W_2 parts by weight, in which $W_1=(0.5\sim12)\times A$, and $W_2=(0.5\sim7)\times A$, in which A is the weight percent of oxygen in the Zr-based amorphous alloy waste.

13. The method according to claim 12, wherein $W_1=(5\text{-}7)\times A$, and $W_2=(3\text{-}4)\times A$.

14. The method according to claim 13, wherein the total amount of Zr and the metal oxide is W_3 parts by weight relative to 100 parts by weight of the Zr-based amorphous alloy waste, in which W_3 satisfies: $W_3=(8.5\sim11)\times A$.

15. The method according to any of claims 11-14, wherein the melting step is performed in conditions of: a vacuum degree of about 0.05 Pa to about 5 Pa, and a temperature of about 200℃ to about 500℃ above the melting temperature of the Zr-based amorphous alloy for about 2 min to about 10 min.

16. The method according to claim 15, wherein the melting step is performed in conditions of: a vacuum degree of about 0.08 Pa to about 0.5 Pa, and a temperature of about 250℃ to about 400℃ above the melting temperature of the Zr-based amorphous alloy for about 4 min to about 10 min.

17. The method according to claim 11, wherein the molten mixture is filtered through a high temperature resistant mesh with a mesh diameter of about 0.5 mm to about 10 mm.

18. The method according to claim 17, wherein the high temperature resistant mesh is selected from the group consisting of: steel wire mesh, ceramic mesh, Mo wire mesh and fiber

mesh.

19. The method according to any of claims 11-14, wherein the casting step is performed at a temperature of about 50℃ to about 150℃ above the melting temperature of the Zr-based amorphous alloy.

20. The method according to any of claims 11-14, wherein the inert gas is selected from helium, neon, argon, krypton, xenon, radon, and combinations thereof.

21. The method according to any of claims 11-14, wherein the Zr-based amorphous alloy is represented by the general formula of $Zr_aM_bN_cY_d$, in which

M is at least one transition metal;

N is Be or Al; and

a, b, c and d are atomic percents of corresponding elements, in which $45 \leq a \leq 65$, $20 \leq b \leq 40$, $1 \leq c \leq 25$, and $0 \leq d \leq 5$.

22. The method according to claim 11, wherein the molten mixture is allowed standing for about 1 min to about 10 min prior to the filtering step.

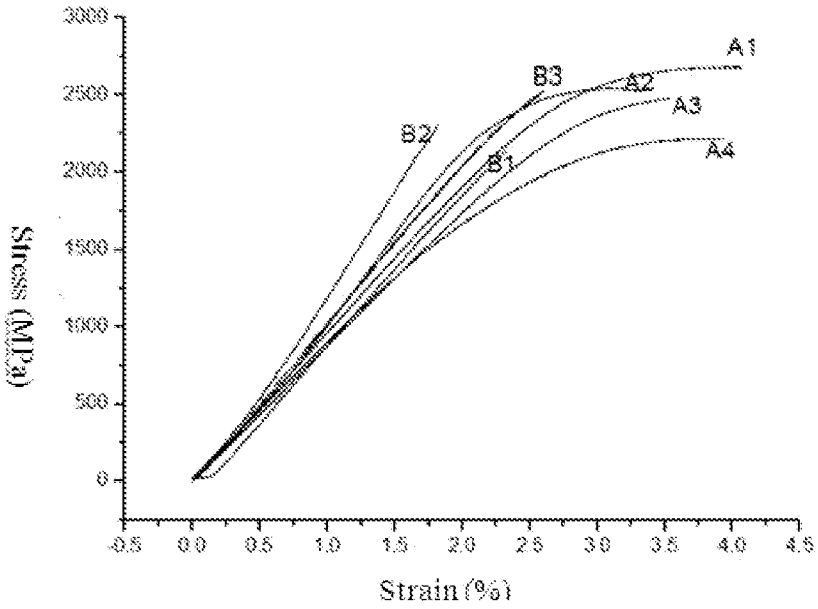

Fig. 1

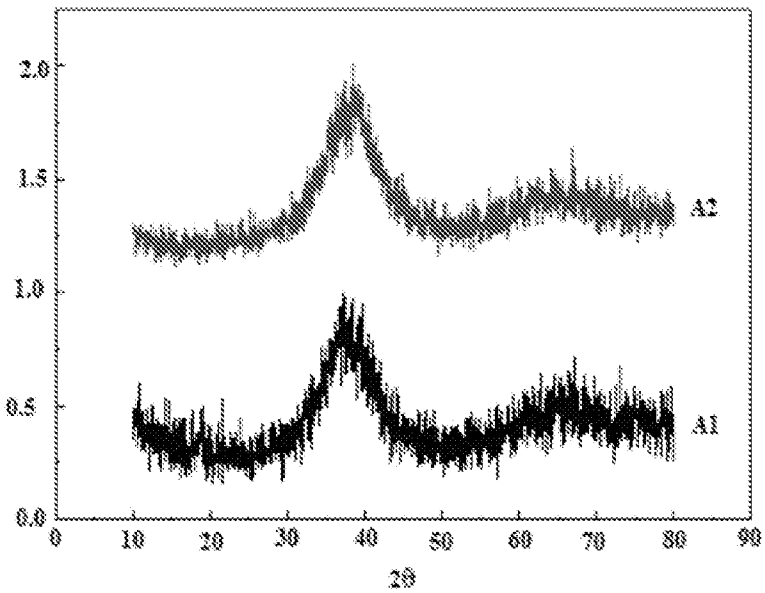

Fig. 2

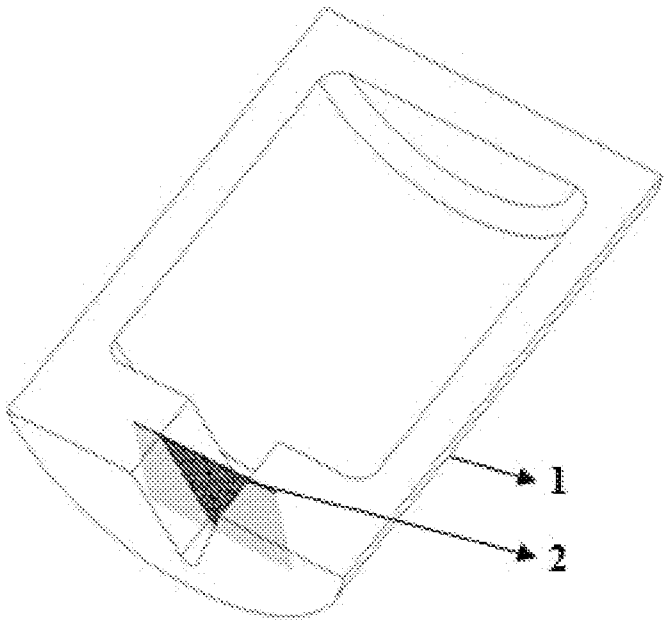

Fig. 3

INTERNATIONAL SEARCH REPORT

International application No.
PCT/CN2010/078525

A. CLASSIFICATION OF SUBJECT MATTER

See extra sheet

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: C22C1/-, C22C45/-

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

WPI, EPODOC, CN-PAT, CNKI: oxide?, Ca, calcium, Mg, magnesium, Y, yttrium, Nd, neodymium, CaO, MgO, Y_2O_3, Nd_2O_3, Zr, zirconium, amorphous, non cystal+, noncrystal+, metal, metallic, glass, recycl+, waste, reclaim+, circulat+

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	SUN Yajuan et al., EFFECT OF Gd ADDITION ON THE GLASS FORMING ABILITY AND MECHANICAL PROPERTIES IN A Zr-BASED BULK AMORPHOUS ALLOY, ACTA METALLURGICA SINICA, Vol.45, No.2, Feb.2009, pages 243-248	1-22
A	JP61-266545A (TDK CORP) 26 Nov.1986 (26.11.1986) whole document	1-22
A	JP60-131951A (TOHOKU METAL IND LTD) 13 Jul.1985 (13.07.1985) whole document	1-22
A	JP63-161142A (MITSUI PETROCHEM IND CO LTD) 04 Jul.1988 (04.07.1988) whole document	1-22
A	JP59-185052A (SEIKO DENSHI KOGYO KK) 20 Oct.1984 (20.10.1984) whole document	1-22
A	JP57-75253A (OTSUKA KAGAKU YAKUHIN KK) 11 May 1982 (11.05.1982) whole document	1-22

☒ Further documents are listed in the continuation of Box C. ☒ See patent family annex.

* 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
13 Jan.2011 (13.01.2011)	**24 Feb. 2011 (24.02.2011)**
Name and mailing address of the ISA/CN The State Intellectual Property Office, the P.R.China 6 Xitucheng Rd., Jimen Bridge, Haidian District, Beijing, China 100088 Facsimile No. 86-10-62019451	Authorized officer PANG Limin Telephone No. (86-10)62084751

Form PCT/ISA /210 (second sheet) (July 2009)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/CN2010/078525

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

Independent claim 1 involves a Zr-based amorphous alloy composed of Zr, M, N and Q with certain content respectively, in which M is least one transition metal except Zr, N is Be or Al, and Q is selected from CaO, MgO, Y_2O_3, Nd_2O_3 and combinations thereof. The claim is characterized in the combination of certain components with certain contents in the alloy.

Independent claim 11 involves a method for recycling a Zr-based amorphous alloy waste so as to form a new Zr-based amorphous alloy. The claim is characterized in the treating steps and additive used in the method which is the mixture of Zr and metal oxide selected from CaO, MgO, Y_2O_3, Nd_2O_3 and combinations thereof.

The two independent claims do not include the same or corresponding special technical feature, therefore they do not meet the requirements of unity of invention as defined in PCT Rules 13.1, 13.2 and 13.3.

1. ☒ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of additional fee.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on protest

☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.

☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.

☒ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/CN2010/078525

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP60-24346A (ALLIED CORP) 07 Feb.1985 (07.02.1985) whole document	1-22
A	WO2007/059062A2 (UNIV CALIFORNIA et al.) 24 May 2007 (24.05.2007) whole document	1-22
A	CN1616702A (UNIV LANZHOU SCI & ENG) 18 May 2005 (18.05.2005) whole document	1-22

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/CN2010/078525

Patent Documents referred in the Report	Publication Date	Patent Family	Publication Date
JP61-266545A	26.11.1986	NONE	
JP60-131951A	13.07.1985	JP62014212B	01.04.1987
		JP1405866C	27.10.1987
JP63-161142A	04.07.1988	JP2621151B2	18.06.1997
JP59-185052A	20.10.1984	NONE	
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		US7618500B2	17.11.2009
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CN1616702A	18.05.2005	CN1276117C	20.09.2006

INTERNATIONAL SEARCH REPORT

International application No.
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Continuation of: second sheet, A. CLASSIFICATION OF SUBJECT MATTER

C22C45/10 (2006.01)i

C22C45/00 (2006.01)i

C22C1/02 (2006.01)i