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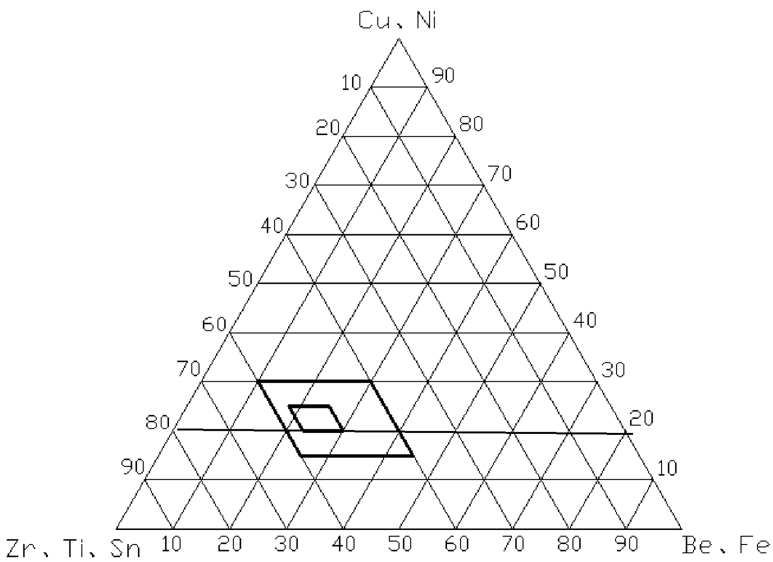
(54) **A Zr-based amorphous alloy and a preparing method thereof**

(57) In one aspect, a Zr-based amorphous alloy comprises Zr, Ti, Cu, Ni, Fe, Be, and Sn. In another aspect, a Zr-based amorphous alloy comprises about 30-75 atomic percent of ($Zr_xTi_ySn_z$), about 10-35 atomic percent of ($Cu_mNi_n$), about 0.1-15 atomic percent of Fe, and about 0.1-35 atomic percent of Be. Reference numerals x, y and z are atomic fractions, and x+y+z equals to 1, wherein x is about 0.6-0.85 , and z is in the range of about 0.01x - 0.1x. Reference numerals m and n are atomic fractions, and m+n equals to 1, and wherein m is about 0.5-0.65. In yet another aspect, a method for preparing a Zr-based amorphous alloy comprises melting a raw material comprising Zr, Ti, Cu, Ni, Fe, Be, and Sn to form an alloy mixture; and molding the alloy mixture to form the amorphous alloy.

**FIG. 1**

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## Description

**[0001]** The present application claims priority to Chinese Patent Application No. 200710187786.2, filed November 30, 2007, the entirety of which is hereby incorporated by reference.

## FIELD OF THE DISCLOSURE

**[0002]** The present disclosure relates to a Zr-based amorphous alloy and a preparing method thereof.

## BACKGROUND OF THE DISCLOSURE

**[0003]** Amorphous metallic alloys are disordered in the long range but ordered in the short range. They have desirable physical and chemical properties, such as high strength, high hardness, high wearing resistance, high corrosion resistance, relatively wide elastic range, high electric resistance, good superconductivity, and low magnetic loss. Amorphous metallic alloys have huge potential when used as structural materials. They are widely used in many fields such as mechanics, IT electronics, the military industry and so on.

**[0004]** However, some characteristics of the amorphous metallic alloys limit their applications. For example, it is difficult to manufacture large size amorphous alloys. To obtain the disordered structure in the long range, atoms' spontaneous movement in the freezing process shall be restrained. The higher the cooling speed is, the lower the possibility is for the atoms to form orderly arrayed crystalline materials via spontaneous movement. But as product size increases, the internal cooling speed within the product is declining. Thus, the internal amorphous degree is low in the long range and it is difficult to form large size amorphous structures.

**[0005]** Also, it is difficult to effectively improve the plasticity characteristics of the amorphous materials. Due to their particular structure, while under stress, the amorphous alloy materials do not have the internal deformation mechanism as crystalline materials do in order to resist deformation. So when the stress reaches a certain degree, the amorphous alloy material may break suddenly, which may lead to catastrophic accidents. Thus, the applications of the amorphous alloy materials as structural materials are limited.

**[0006]** Zhao et al. discloses a Zr-Ti-Cu-Ni-Be-Fe bulk amorphous alloy and its preparing method (Forming And Performance of The Zr-Ti-Cu-Ni-Be-Fe Bulk Amorphous Alloy And Amorphous-Based Nano-Composite, Zhao De Qian, Zhang Yong, Pan Ming Xiang, Meng Li Qin , Wang Wei Hua, Acta Metallurgica Sinica, March, 2000). The method comprises adding 2-10 atomic percent of Fe to form a nano crystalline composite material in order to change the magnetic susceptibility of the material. As a result of the addition of Fe in increasing amount, sharp diffraction peaks begin to appear in the XRD diagram, indicating crystallization. It shows that the addition of relatively large amount of iron is effective in affecting the amorphous alloy forming ability. Zhao et al. however does not address the issues of large size amorphous alloy manufacturing and the plasticity of the amorphous alloy materials.

## SUMMARY OF THE DISCLOSURE

**[0007]** In one aspect, a Zr-based amorphous alloy comprises Zr, Ti, Cu, Ni, Fe, Be, and Sn.

**[0008]** In another aspect, a Zr-based amorphous alloy comprises about 30-75 atomic percent of ($Zr_xTi_ySn_z$), about 10-35 atomic percent of ($Cu_mNi_n$), about 0.1-15 atomic percent of Fe, and about 0.1-35 atomic percent of Be. Reference numerals x, y and z are atomic fractions, and x+y+z equals to 1, wherein x is about 0.6-0.85, and z is in the range of about 0.01x - O.lx. Reference numerals m and n are atomic fractions, and m+n equals to 1, and wherein m is about 0.5-0.65.

**[0009]** In yet another aspect, a method for preparing a Zr-based amorphous alloy comprises melting a raw material comprising Zr, Ti, Cu, Ni, Fe, Be, and Sn to form an alloy mixture; and molding the alloy mixture to form the amorphous alloy.

## DESCRIPTION OF THE DRAWINGS

**[0010]** Fig. 1 is the quasi-three component phase diagram (Zr, Ti, Sn)-(Cu, Ni)-(Be, Fe) of the amorphous alloy.

**[0011]** Fig. 2 is the stress-strain diagram of the amorphous alloy prepared in Example 1 and Control 1.

**[0012]** Fig. 3 is the XRD diagram of the amorphous alloy prepared in the Examples 1-5 and Control 1.

## DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

**[0013]** According to one embodiment of the present disclosure, a Zr-based amorphous alloy is provided. The Zr-based amorphous alloy comprises about 30-75 atomic percent of ($Zr_xTi_ySn_z$), about 0-15 atomic percent of ETM, about 10-35 atomic percent of ($Cu_mNi_n$), about 0.1-15 atomic percent of Fe, about 0-15 atomic percent of LTM, and about 0.1-35 atomic percent of Be. More preferably, the Zr-based amorphous alloy comprises about 40-60 atomic percent of $(Zr_xTi_ySn_z)$, about 0-10 atomic percent of ETM, about 15-25 atomic percent of $(Cu_mNi_n)$, about 0.5-5 atomic percent of Fe, about 0-10 atomic percent of LTM, and about 15-25 atomic percent of Be. Reference numerals x, y and z are atomic fractions, and x+y+z equals to 1. Preferably, x is about 0.6-0.85, and z is in the range of about 0.01x - 0.1x. Reference numerals m and n are atomic fractions, and m+n equals to 1. Preferably, m is about 0.5-0.65.

**[0014]** ETM is one or more elements selected from Group IIIB, Group IVB, Group VB and Group VIB of the Element Periodic Table, excluding Zr and Ti. Preferably, ETM is one or two elements selected from Sc, Y, La, Ce, Pr, Nd, Hf, V, Nb, Ta, Cr, Mo, W. LTM is one or more elements selected from Group IB, Group VIIB and Group VIII of the Element Periodic Table, excluding Cu, Ni, and Fe. Preferably, LTM is one or two elements selected from Mn, Tc, Re, Ru, Os, Co, Rh, Ir, Pd, Pt, Ag, Au, Zn, Cd, Hg. Preferably, ETM and LTM includes 1-3 elements.

**[0015]** Referring to Fig. 1, the quasi-three component phase diagram of the amorphous alloy composition is shown. The large parallelogram area is the amorphous alloy forming area, the boundary of which is determined by the composition range of the amorphous alloy according to one embodiment of the present disclosure. The small parallelogram area is the preferred amorphous alloy forming area, the boundary of which is determined by the preferred composition range of the amorphous alloy according to one embodiment of the present disclosure. The three vertexes of the quasi-three component phase diagram respectively represent the elements in the amorphous alloy. The alloy in Fig. 1 does not include ETM and LTM. The numbers on each axis represent the atomic percentages of the elements in the alloy.

**[0016]** According to another embodiment of the present disclosure, a method for preparing a Zr-based amorphous alloy is provided. The method comprises vacuum melting an amorphous alloy material and cooling the amorphous alloy material to form an amorphous alloy, both under inert gas.

**[0017]** The material for preparing the Zr-based amorphous alloy comprises Zr, Ti, Cu, Ni, Fe, and Be. The material for preparing the Zr-based amorphous alloy can also comprise Sn, and optionally ETM and LTM.

**[0018]** The amount of each element added should be adjusted such that the elements in the raw material have the following formula: $(Zr_xTi_ySn_z)_a : ETM_b : (Cu_mNi_n)_c : Fe_d : LTM_e : Bef$, wherein a, b, c, d, e and f, x, y and z, m and n, ETM, and LTM are as defined above.

**[0019]** In a preparing method for a Zr-based amorphous alloy, any suitable melting method can be used. For example, the melted raw materials should be mixed first, and then cooled to form ingots. In this step, the raw materials can be melted in an electric arc melting equipment or an induction melting equipment. The melting temperature and time differ to some extent according to the heating process selected. Usually, the melting temperature can be about 1,000-2,700°C, preferably about 1,500-2,000°C. The melting time is about 5-20 minutes. The vacuum level is not higher than about 200 Pa, preferably about 0.01-5 Pa.

**[0020]** As a pre-process before molding, the ingots were crushed as if the molding process need. The ingots then can be re-melted and molding.. Electric arc melting, induction melting, and resistance melting are commonly used in the re-melting process. The re-melting temperature can be about 1,000-2,300°C, preferably about 1,000-1,500°C. The vacuum level is not higher than about 200 Pa, preferably about 0.01-5 Pa. Any suitable molding method can be used to form the amorphous alloy. For example, melt-spinning, copper mold casting, suction casting, die casting, jetting molding, or water quenching can be used. The cooling speed of the molding process can be about $10\text{-}10^4$ K/s. Since the critical dimensions differ among different components, different molding methods can be selected. The inert gas can be one or more elements selected from the $SF_6$ gas and Group Zero elements of the Element Periodic Table.

**[0021]** Example 1

**[0022]** A preparation method of a Zr-based amorphous alloy is illustrated in this example.

**[0023]** Raw materials Zr, Ti, Sn, Cu, Ni, Fe, Be (about 25 grams) were added to an electric arc melting equipment (Shen Yang Scientific Instrument Manufacturing Company Limited). The formulars of the raw materials were as follows: $(Zr_{0.74}Ti_{0.25}Sn_{0.01})_{55.34}(Cu_{0.56}Ni_{0.44})_{20.65}Fe_{1.96}Be_{22.05}$. The equipment was vacuumized to about 5 Pa. The raw material was melted at about 2,000 °C under Ar protection for about 6 minutes. The molten master alloy was mixed sufficiently, and then cooled into an ingot. The ingot was re-melted at about 1,500 °C using electric arc melting, and then cooled in a copper mold casting process with a cooling speed of about $10^2$ k/s to obtain the Zr-based amorphous alloy sample C1.

**[0024]** Example 2

**[0025]** Another preparation method of a Zr-based amorphous alloy is illustrated in this example.

**[0026]** Raw materials Zr, Ti, Sn, Cu, Ni, Fe, Be (about 200 kg) were added to an induction melting equipment (Zhongbei Technology). The formulars of the raw materials were as follows: $(Zr_{0.74}Ti_{0.25}Sn_{0.01})_{55.34}(Cu_{0.56}Ni_{0.44})_{20.65}Fe_{1.96}Be_{22.05}$. The equipment was vacuumized to about 5 Pa. The raw materials were melted at about 1,800 °C under Ar protection for about 10 minutes. The molten master alloy was mixed sufficiently, and then cooled into an ingot. The ingot was re-melted at about 1,200 °C using resistance heating, and then cooled in a die-casting process with a cooling speed of about $10^4$ k/s to obtain the Zr-based amorphous alloy sample C2.

**[0027]** Example 3

**[0028]** Yet another preparation method of a Zr-based amorphous alloy is illustrated in this example.

**[0029]** Raw materials Zr, Ti, Sn, Cu, Ni, Fe, Be (about 20 g) were added to a quartz tube (Zhongbei Technology). The formulars of the raw materials were as follows: $(Zr_{0.80}Ti_{0.17}Sn_{0.03})_{40}Y^5Nb_5(Cu_{0.64}Ni_{0.36})_{25}Fe_5Be_{20}$. The tube was vacuumized to about 200 Pa. The raw materials were melted at about 2,000 °C by induction heating under Ar protection for about 5 minutes. The molten master alloy was mixed sufficiently, and then cooled into an ingot. The ingot was re-melted at about 1,500 °C by induction heating, and then cooled in a water quenching process with a cooling speed of about $10^3$ k/s to obtain the Zr-based amorphous alloy sample C3.

**[0030]** Example 4

**[0031]** Still another preparation method of a Zr-based amorphous alloy is illustrated in this example.

**[0032]** Raw materials Zr, Ti, Sn, Cu, Ni, Fe, Be (about 200 kg) were added into an induction melting equipment. The formulas of the raw materials were as follows: $(Zr_{0.65}Ti_{0.29}Sn_{0.06})_{50}(Cu_{0.5}Ni_{0.5})_{20}Co_{10}Fe_3Be_{17}$. The equipment was vacuumized to about 5 Pa. The raw materials were induction melted at about 1,800 °C under Ar protection for about 10 minutes. The molten master alloy was mixed sufficiently, and then cooled it into an ingot. The ingot was re-melted at about 1,000 °C by resistance heating, and then was melt-spinned with a cooling speed of about $10^4$ k/s to obtain the Zr-based amorphous alloy sample C4.

**[0033]** Example 5

**[0034]** Yet still another preparation method of a Zr-based amorphous alloy is illustrated in this example.

**[0035]** Raw materials Zr, Ti, Sn, Cu, Ni, Fe, Be (about 20 g) were added into a quartz tube (Middle North Technology). The formulas of the raw materials were as follows: $(Zr_{0.75}Ti_{0.24}Sn_{0.01})_{60}W_3(Cu_{0.55}Ni_{0.45})_{15}Pd_2Zn_1Fe_4Be_{15}$. The tube was vacuumized to about $2\times10^{-2}$ Pa. The raw materials were induction melted at about 2,000 °C under Ar protection for about 5 minutes. The molten master alloy was mixed sufficiently, and then cooled into an ingot. The ingot was re-melted at about 1,500 °C by induction heating, and then cooled in a water quenching process with a cooling speed of about $10^4$ k/s to obtain the Zr-based amorphous alloy sample C5.

**[0036]** Control 1

**[0037]** The control illustrates an amorphous material prepared according to the present art.

**[0038]** Raw materials Zr, Ti, Cu, Ni, Be, Fe (about 25 grams) were added into an electric arc melting equipment (Shen Yang Technical Instruments Manufacture Company Limited). The formulas of the raw materials were as follows: $Zr_{41}Ti_{14}Cu_{11}Ni_{9.5}Fe_2Be_{22.5}$. The equipment was vacuumized to about 5 Pa. The starting materials were melted at about 2,000 °C under Ar protection for about 6 minutes. The molten master alloy was mixed sufficiently, and then cooled into an ingot. The ingot was re-melted at about 1,500 °C by electric arc melting, and then was copper mold cast with a cooling speed of about $10^2$ k/s to obtain the Zr-based amorphous alloy sample D1.

**[0039]** Experimental:

**[0040]** Testing methods

**[0041]** (1) Compression test

**[0042]** The samples were tested on a XinSansi CMT5000 series testing machine with a measuring range of 30KN and a loading speed of about 0.5 mm/minute. The stress-strain conditions of the sample C1 and D1 were tested. The test results are showed in Fig 2.

**[0043]** (2) Hardness test

**[0044]** The samples were tested on a Micro Hardness Text Hv1000 Vickers Hardness Testing Machine. The weight of the pressure head was about 200 g, and the loading time was about 10 seconds. Datas of three test points were obtained for each sample to calculate the arithmetic average value. The results are showed in Table 1.

**[0045]** (3) XRD analysis

**[0046]** XRD analyzes the physical phase of an alloy material in order to estimate whether the alloy is amorphous. The samples were made into powder for test on a Model D-MAX2200PC X-ray Powder Diffractometer. Using a Cu K$\alpha$ radiation. The incidence wave length $\lambda$ was about 1.54060 Å. The accelerating voltage was about 40 kV. The current was about 20 mA. Step scan was used with a step size of about 0.04 degree. The test results are showed in Fig 3.

**[0047]** (4) The test of critical dimensions

**[0048]** A wedged sample formed in the copper mold casting process was cut from the top by a thickness of about 1 mm. The cross section after cutting was analyzed by XRD. The structure type was determined. If the structure type was an amorphous alloy, then the cutting process was continued until the structure was no longer an amorphous alloy. The total cutting thickness was recorded. The critical dimension was the total cutting thickness minus 1 mm. The results are showed in Table 1.

**[0049]**

Table 1

| Serial No. | C1 | C2 | C3 | C4 | C5 | D1 |
|---|---|---|---|---|---|---|
| Critical Dimension (mm) | >14 | >14 | 14 | 12 | 12 | 8 |
| Average Hardness (Hv) | 553 | 553 | 547 | 539 | 548 | 537 |

**[0050]** From the results showed in Table 1, the Zr-based amorphous alloys provided according to embodiments of the present disclosure have critical dimensions larger than about 1 centimeter. Meanwhile, they have relatively higher hardness. As shown in Fig. 3, there are no sharp diffraction peaks in the XRD diagrams of Sample C1, C2, C3, C4, C5 and D1, which indicates the alloys have a high degree of amorphization. As shown in Fig. 2, the Zr-based amorphous alloy C1 provided according to one embodiment of the present disclosure and the Zr-based amorphous alloy D1 provided according to the prior art assume substantially overlapping curves in the low stress area when identical stresses were applied. However, as the stresses increased, D1 could only sustain a relatively low strain, and would break easily. Meanwhile, the curve representing the C1 alloy was bending, which indicates that the strain capacity of the C1 alloy is much better than D1, that is, the Zr-based amorphous alloy according to embodiments of the present disclosure has better plasticity.

**[0051]** Many modifications and other embodiments of the present disclosure will come to mind to one skilled in the art to which the present disclosure pertains having the benefit of the teachings presented in the foregoing description; and it will be apparent to those skilled in the art that variations and modifications of the present disclosure can be made without departing from the scope or spirit of the present disclosure. Therefore, it is to be understood that the invention is not to be limited to the specific embodiments disclosed and that modifications and other embodiments are intended to be included within the scope of the appended claims. Although specific terms are employed herein, they are used in a generic and descriptive sense only and not for purposes of limitation.

## Claims

1. A Zr-based amorphous alloy, comprising:
Zr, Ti, Cu, Ni, Fe, Be, and Sn.

2. The amorphous alloy according to claim 1, further comprising one or both of ETM and LTM, wherein ETM comprises at least one element selected from Group IIIB, Group IVB, Group VB and Group VIB of the Element Periodic Table, provided that ETM is not Zr or Ti, preferably ETM is one or two elements selected from the Group consisting of Sc, Y, La, Ce, Pr, Nd, Hf, V, Nb, Ta, Cr, Mo, and W, wherein LTM comprises at least one element selected from Group IB, Group IIB, Group VIIB, Group VIII of the Element Periodic Table, provided that LTM is not Cu, Ni or Fe, preferably LTM is one or two elements selected from the Group consisting of Mn, Tc, Re, Ru, Os, Co, Rh, Ir, Pd, Pt, Ag, Au, Zn, Cd, and Hg, more preferably ETM and LTM together comprises 1-3 elements.

3. The amorphous alloy according to claim 1 or 2, which comprises about 30-75 atomic percent, preferably about 40-60 atomic percent of ($Zr_xTi_ySn_z$), about 0-15 atomic percent, preferably about 0-10 atomic percent of ETM, about 10-35 atomic percent, preferably about 15-25 atomic percent of ($Cu_mNi_n$), about 0.1-15 atomic percent, preferably about 0.5-5 atomic percent of Fe, about 0-15 atomic percent, preferably about 0-10 atomic percent of LTM, and about 0.1-35 atomic percent, preferably about 15-25 atomic percent of Be,
wherein x, y and z are atomic fractions, and x+y+z equals to 1;
wherein x is about 0.6-0.85 , and z is in the range of about 0.01x - 0.1x;
wherein m and n are atomic fractions, and m+n equals to 1; and
wherein m is about 0.5-0.65.

4. The amorphous alloy according to any one of claims 1 to 3, the critical dimension of which is large than about 1 mm.

5. A Zr-based amorphous alloy, comprising about 30-75 atomic percent of ($Zr_xTi_ySn_z$), about 10-35 atomic percent of ($Cu_mNi_n$), about 0.1-15 atomic percent of Fe, and about 0.1-35 atomic percent of Be,
wherein x, y and z are atomic fractions, and x+y+z equals to 1,
wherein x is about 0.6-0.85 , and z is in the range of about 0.01x - 0.1x;
wherein m and n are atomic fractions, and m+n equals to 1; and
wherein m is about 0.5-0.65.

6. A method for preparing a Zr-based amorphous alloy comprising: melting a raw material comprising Zr, Ti, Cu, Ni, Fe, Be, and Sn to form an alloy mixture; and molding the alloy mixture to form the amorphous alloy.

7. The method according to claim 6, wherein the raw material further comprises one or both of ETM and LTM, wherein ETM comprises at least one element selected from Group IIIB, Group IVB, Group VB and Group VIB of the Element Periodic Table, provided that ETM is not Zr or Ti, preferably ETM is one or two elements selected from the Group consisting of Sc, Y, La, Ce, Pr, Nd, Hf, V, Nb, Ta, Cr, Mo, and W, wherein LTM comprises at least one element

selected from Group IB, Group IIB, Group VIIB, Group VIII of the Element Periodic Table, provided that LTM is not Cu, Ni or Fe, preferably LTM is one or two elements selected from the Group consisting of Mn, Tc, Re, Ru, Os, Co, Rh, Ir, Pd, Pt, Ag, Au, Zn, Cd, and Hg, more preferably ETM and LTM together comprises 1-3 elements.

**8.** The method according to claim 6 or 7, wherein the elements in the raw material have the following formular: $(Zr_xTi_ySn_z)_a : ETM_b : (Cu_mNi_n)_c : Fe_d : LTM_e : Be_f$,
wherein a, b, c, d, e and f are atomic percentages;
wherein a is about 30-75%, preferably about 40-60% , b is about 0-15%, preferably about 0-10% , c is about 10-35%, preferably about 15-25% , d is about 0.1-15%, preferably about 0.5-5% ,e is about 0-15%, preferably about 0-10% , and f is about 0.1-35%, preferably about 15-25%,
wherein x, y and z are atomic fractions, and x+y+z equals to 1,
wherein x is about 0.6-0.85 , and z is in the range of about 0.01x - 0.1x;
wherein m and n are atomic fractions, and m+n equals to 1; and
wherein m is about 0.5-0.65.

**9.** The method according to any one of claims 6 to 8, wherein the melting step comprises:

melting the raw material to form a molten mixture;
cooling the molten mixture to form at least one ingot; and
re-melting the at least one ingot to form the alloy mixture.

**10.** The method according to any one of claims 6 to 9, wherein the raw material is melted under a vacuum of less than about 5 Pa.

**11.** The method according to any one claims 6 to 10, wherein the raw material is melted at a temperature of about 1,000 - 2,700 °C.

**12.** The method according to any one of claims 6 to 11, wherein the molding is a cold molding process.

**13.** The method according to claim any one of claims 6 to 12, wherein the cooling speed of the cooling molding process is about $10\text{-}10^4$ K/s.

**14.** The method according to any one of claims 6 to 13, wherein the molding is a process selected from a Group consisting of melt-spinning, copper mold casting, suction casting, die casting, jetting molding, and water quenching.

**15.** The method according to any one of claims 6 to 14, wherein the raw material is melted in the presence of an inert gas, preferably in the presence of one or more gases selected from the Group consisting of $SF_6$ and Group Zero gases.

FIG. 1

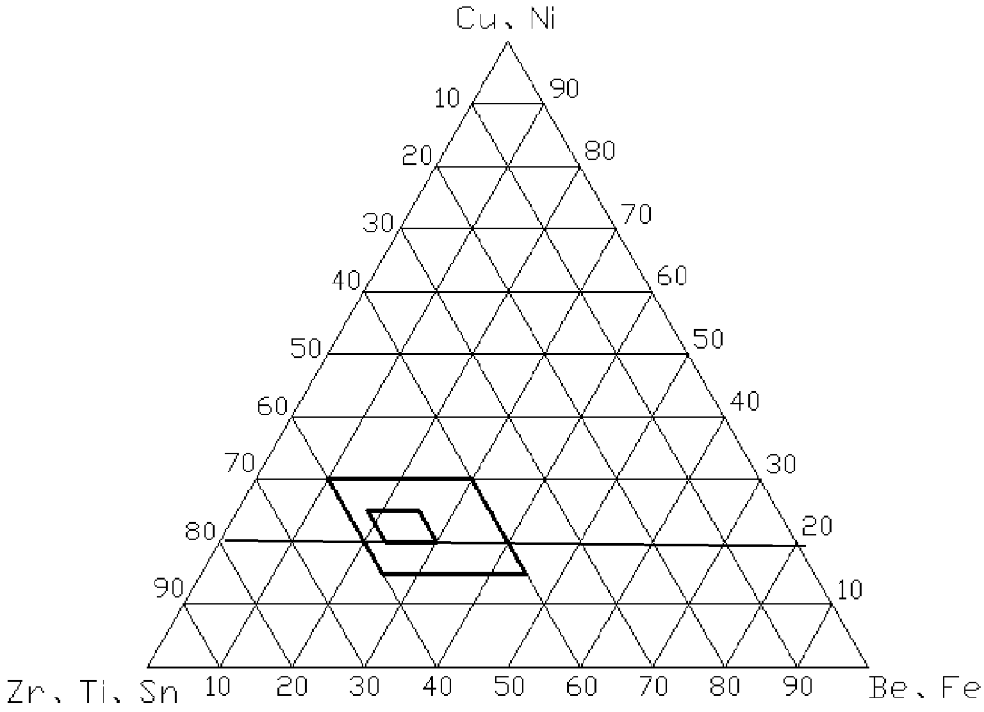

Cu、Ni
10
20
30
40
50
60
70
80
90
90
80
70
60
50
40
30
20
10
Zr、Ti、Sn
10 20 30 40 50 60 70 80 90
Be、Fe

Fig. 2

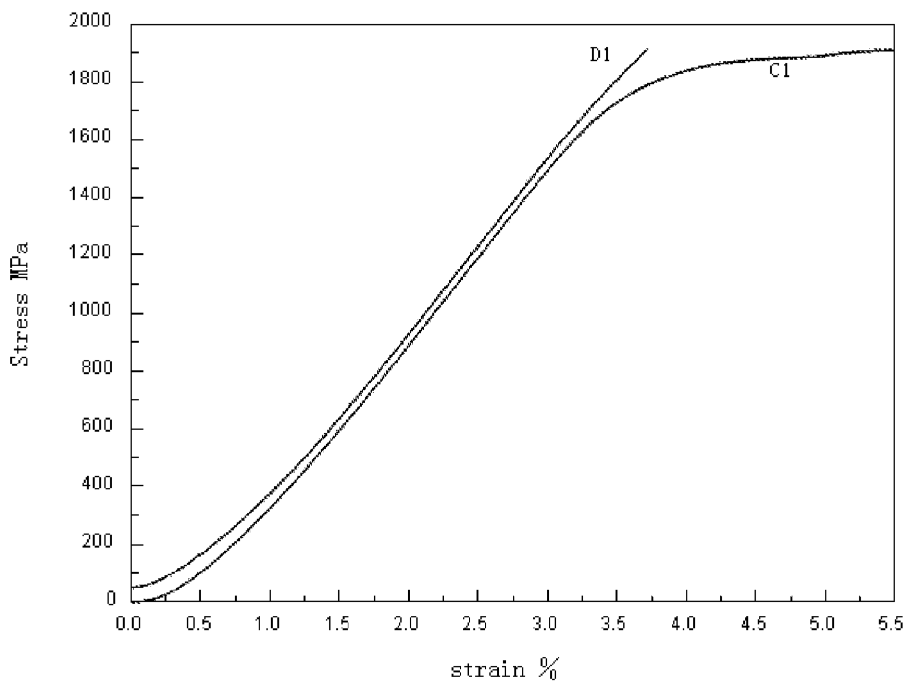
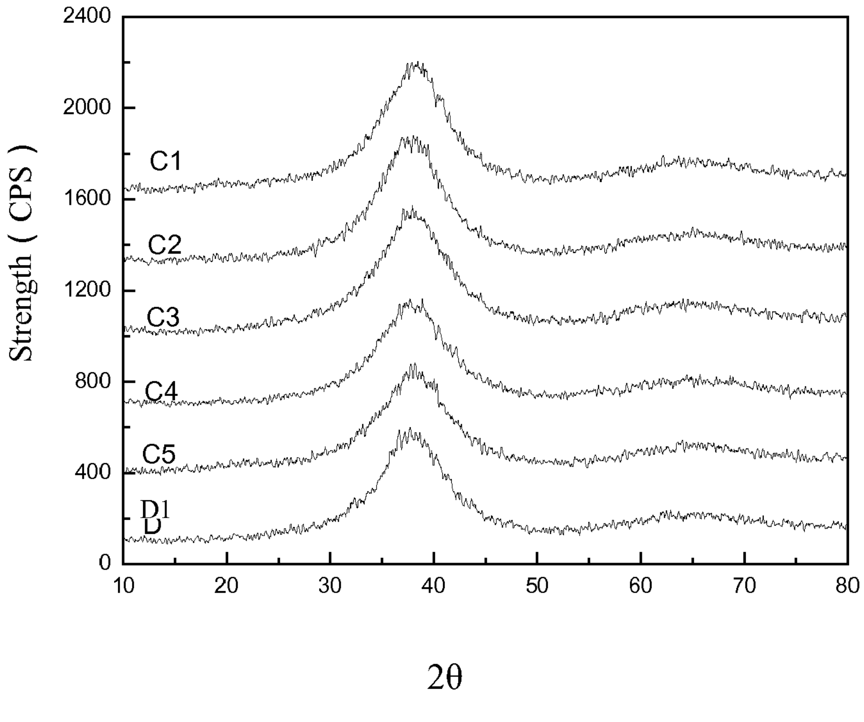

2000
1800
1600
1400
1200
1000
800
600
400
200
0
Stress MPa
D1
C1
0.0 0.5 1.0 1.5 2.0 2.5 3.0 3.5 4.0 4.5 5.0 5.5
strain %

**Fig. 3**


2400
2000
1600
1200
800
400
0
Strength ( CPS )
C1
C2
C3
C4
C5
D1
D
10
20
30
40
50
60
70
80
2θ

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# EUROPEAN SEARCH REPORT

Application Number
EP 08 17 0293

## DOCUMENTS CONSIDERED TO BE RELEVANT

| Category | Citation of document with indication, where appropriate, of relevant passages | Relevant to claim | CLASSIFICATION OF THE APPLICATION (IPC) |
|---|---|---|---|
| D,A | ZHAO, DEQIAN; WANG, WEIHUA; ZHUANG, YANXIN; PAN MINGXIANG; JI, YINGFEI; MA, XUEMING: "FORMATION AND PERFORMANCE OF NEW ZR-TI-CU-NI-BE-FE BULD AMORPHOUS ALLOY"<br>SCIENCE IN CHINA (SERIES A), [Online]<br>vol. 43, no. 3, 1 March 2000 (2000-03-01), pages 307-311, XP002512309<br>ISSN: 1862-2763<br>Retrieved from the Internet:<br>URL:http://www.springerlink.com/content/62188vn764568505/> [retrieved on 2009-01-27]<br>* the whole document * | 1-15 | INV.<br>C22C1/00<br>C22C16/00 |
| A | SUN,JIAN-FEI;SHEN,JUN;GAO,YUI-LAI: "Effect of Sn addition on thermal stability of (Zr52.5Ti5Al10Ni14.6Cu17.9)(100-x)Snx alloys"<br>TRANS. NONFERROUS MET. SOC. CHINA,<br>vol. 13, May 2003 (2003-05), pages 64-67, XP008101301<br>* the whole document * | | TECHNICAL FIELDS SEARCHED (IPC)<br>C22C |
| A | JOHNSON W L: "Fundamental aspects of bulk metallic glass formation in multicomponent alloy"<br>MATERIALS SCIENCE FORUM, AEDERMANNSFDORF, CH,<br>vol. 225-227, 1 January 1996 (1996-01-01), pages 35-50, XP008100967<br>ISSN: 0255-5476<br>* abstract; table 1 *<br>* page 37, line 26 - line 32 * | | |

The present search report has been drawn up for all claims

| Place of search | Date of completion of the search | Examiner |
|---|---|---|
| The Hague | 5 February 2009 | Ugarte, Eva |

2

CATEGORY OF CITED DOCUMENTS

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## REFERENCES CITED IN THE DESCRIPTION

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### Patent documents cited in the description


- CN 200710187786 **[0001]**


### Non-patent literature cited in the description


- **ZHAO DE QIAN ; ZHANG YONG ; PAN MING XIANG ; MENG LI QIN ; WANG WEI HUA.** Forming And Performance of The Zr-Ti-Cu-Ni-Be-Fe Bulk Amorphous Alloy And Amorphous-Based Nano-Composite. *Acta Metallurgica Sinica,* March 2000 **[0006]**