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(71) Applicants:
• **Shenzhen BYD Auto R&D Company Limited**
Shenzhen, Guangdong 518118 (CN)
• **BYD Company Limited**
Shenzhen, Guangdong 518118 (CN)

(72) Inventors:
• **LI, Yunchun**
Shenzhen
Guangdong 518118 (CN)
• **ZHANG, Faliang**
Shenzhen
Guangdong 518118 (CN)

(74) Representative: **Gulde Hengelhaupt Ziebig &
Schneider**
Patentanwälte - Rechtsanwälte
Wallstraße 58/59
D-10179 Berlin (DE)

(54) **AN AMORPHOUS ALLOY DIE CASTING AND THE THERMAL TREATMENT PROCESS THEREOF**

(57) A heat treatment process for an amorphous alloy die cast comprises: the amorphous alloy die cast is subjected to an aging treatment at a temperature of 0.5-0.6 T_g, for a time of 10 minutes to 24 hours. The amorphous alloy die cast comprises Zr, and is represented by a for-

mula of (Zr_{1-x}Ti_x)_a(Cu_{1-y}Ni_y)_bAl_cM_d, in which M is selected from the group consisting of: Be, Y, Sc, La, and combinations thereof, 38≤a≤65, 0≤x≤0.45, 0≤y≤0.75, 20≤b≤40, 0≤c≤15, 0≤d≤30, and the sum of a, b, c, and d in atomic percentages equals to 100.

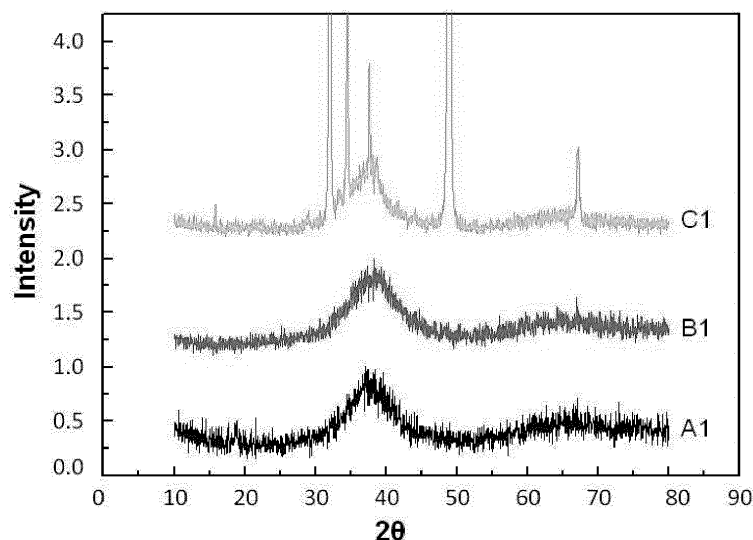


Fig. 1

Description

[0001] The present disclosure relates to methods of manufacturing amorphous alloys, more particularly to an amorphous alloy die cast and a heat treatment process of the same.

BACKGROUND

[0002] Extensive research and numerous experiments demonstrated that crystal boundaries, dislocations, stacking faults, or other crystal defects do not exist in amorphous alloys. Hence, amorphous alloys possess a plurality of advantageous material properties that crystal metals do not have, such as better corrosion resistance, higher frictional resistance, and improved magnetic and electric properties. Amorphous alloys are widely used in electronic, mechanical, chemical, and national defense industries.

[0003] At present, bulk amorphous alloy, also known as metallic glass, is usually formed by rapid cooling of melted metal alloy to a temperature below the glass transition temperature. It is believed that rapid cooling may prevent the formation and growth of crystal nucleus. Thus the melted alloy may solidify directly to form amorphous alloy which has a long range disordered structure. Bulk amorphous alloys usually are millimeter-sized. Nowadays, bulk amorphous alloys are mainly prepared in research laboratories. Amorphous alloys may be prepared by several processes including melting and suction-casting process in an electrical arc furnace, solvent packaging process, water quenching process, or other processes. However, in these processes, preparation of bulk amorphous alloys to achieve desired material properties may require stringent processing conditions, such as highly purified raw materials, high degree of vacuum, very rapid cooling, etc. These processes may not be applicable in the manufacturing industry because of their high costs and low efficiencies.

[0004] Therefore, large corporations and research institutes are both seeking for an amorphous alloy preparation process suitable for high volume manufacturing under normal processing conditions. Die casting is one of the most popular methods for preparing amorphous alloys. However, material properties are usually unstable for amorphous alloys prepared by present die castings processing method under current available conditions. Thus, the applications of amorphous alloys obtained by die casting are very limited.

[0005] Chinese Patent Application Publication No. CN101550521A discloses a rare-earth-based bulk amorphous alloy and its composite material. The composite material is obtained based on the bulk amorphous alloy through a heat treatment process. The heat treatment process includes an isothermal annealing of the rare-earth-based bulk amorphous alloy in a furnace at a temperature within the supercooled liquid region (325-650°C). The process is performed in a 10^{-3} Pa vacuum environment. The composite material prepared thereof has improved thermal stability, higher electrical resistance, good soft magnetic property, and excellent processing capability in the supercooled liquid region. However, this heat treatment process requires relatively high annealing temperature. The temperature required must reside in the supercooled liquid region and is higher than the glass transition temperature T_g . Hence, the annealing process may cause portion of the amorphous alloy become crystallized.

SUMMARY

[0006] The present disclosure aims to solve at least one of the foregoing problems, including the unstable properties of amorphous alloy obtained by die-casting techniques and complexity associated with known processes of bulk amorphous alloy preparation.

[0007] One embodiment of the present disclosure provides a novel heat treatment process of an amorphous alloy die cast. The heat treatment process includes an aging treatment performed to the amorphous alloy die cast at a temperature of 0.5 T_g to 0.6 T_g for a time period of 10 minutes to 24 hours.

[0008] In one embodiment, the amorphous alloy die cast is prepared by a low-speed die casting process in a vacuum environment. The process is performed under a pressure of 50 Pascal (Pa) to 200 Pa, with a die casting speed of 3 meter per second (m/s) to 5 m/s. The amorphous alloy die cast has a thickness of 0.5 millimeter (mm) to 2 mm.

[0009] In some embodiments, the aging process is performed in a positive pressure of 0.1 MPa to 0.5 MPa.

[0010] In some embodiments, the amorphous alloy die cast has a thickness of 1.0 mm to 1.5 mm. The aging treatment is performed at a temperature of 0.53 T_g to 0.57 T_g , for a time period of 30 minutes to 60 minutes.

[0011] In another embodiment of the present disclosure, a Zirconium (element Zr) based amorphous alloy die cast is provided. The Zirconium based amorphous alloy die cast is prepared by the heat treatment processes described above. The Zirconium based amorphous alloy die cast is composed of $(Zr_{1-x}Ti_x)_a(Cu_{1-y}Ni_y)_bAl_cM_d$, wherein M is selected from the group consisting of: Be, Y, Sc, La, and combinations thereof; and $38 \leq a \leq 65$, $0 \leq x \leq 0.45$, $0 \leq y \leq 0.75$, $20 \leq b \leq 40$, $0 \leq c \leq 15$, $0 \leq d \leq 30$; and the sum of a, b, c, and d in atomic percentages equals to 100.

[0012] In various embodiments, the amorphous alloy die cast obtained by the disclosed heat treatment process exhibits higher bending resistance and decreased property instability.

[0013] While the amorphous alloys and methods thereof will be described in connection with various preferred illustrative embodiments, it will be understood that it is not intended to limit the amorphous alloy die casts and methods thereof to those embodiments. On the contrary, it is intended to cover all alternatives, modifications, and equivalents as may be included within the spirit and scope of the disclosed subject matter as defined by the appended claims.

BRIEF DESCRIPTION OF THE DRAWINGS

[0014] 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 shows the X-ray Diffraction (XRD) patterns of samples A1, B1, and C1 according to an embodiment of the present disclosure; and

Fig. 2 shows the Differential Scanning Calorimetry (DSC) patterns of samples A1, B1, and C1 according to an embodiment of the present disclosure.

DETAILED DESCRIPTION OF THE EMBODIMENTS

[0015] Traditional amorphous alloy die cast is usually not subjected to heat treatment. During the high-pressure, high-speed casting process of traditional metal alloys such as Aluminum alloys, Zinc alloys, or Magnesium alloys, gas in the die cast mold can be unavoidably trapped inside the die cast and form subsurface porosities. If the die cast is subsequently subjected to a heat treatment process, gas bubbles may be formed at the surface, causing deformation of the die cast. Hence, both the properties and the appearance of the die cast are negatively affected.

[0016] In contrast to traditional Aluminum, Zinc, Magnesium or their combinational alloys, amorphous alloy has a low temperature supercooled liquid region. The disclosed subject matter provides a novel process method that utilizes this supercooled liquid region to significantly reduce the gas trapped in the amorphous alloy comparing to that in the traditional metal alloys. Specifically, the disclosed subject matter provides a die casting process that is performed under a vacuum pressure of 50 Pa to 200 Pa, and at a low die casting speed of 3 m/s to 5 m/s. In addition, risk of die cast bubbling during heat treatment may be effectively eliminated if the post die cast heat treatment is performed under atmospheric pressure or positive pressure, i.e., 0.1 Pa to 0.5 MPa, in the range of middle to high pressure.

[0017] One embodiment of the present disclosure discloses a novel heat treatment process of an amorphous alloy die cast. The heat treatment process comprises two steps.

[0018] The first step comprises die casting and molding the amorphous alloy die cast at a pressure of 50 Pa to 200 Pa and at a die casting speed of 3m/s to 5m/s. The resulted amorphous alloy die cast has a thickness ranging from 0.5 mm to 2 mm, with most of the die casts having thicknesses ranging from 1.0 mm to 1.5 mm.

[0019] The second step comprises performing an aging treatment on the amorphous alloy die cast, at a temperature of 0.5 Tg to 0.6 Tg, for a time period of 10 minutes to 24 hours. Tg refers to the glass transition temperature measured in Kelvin. A particular Tg of a certain amorphous alloy is obtained by DSC testing. DSC testing is a currently known technique. The aging treatment is performed at atmospheric pressure or positive pressure. In some embodiments, a positive pressure of 0.1 MPa to 0.5 MPa is preferred in order to prohibit gas from diffusing to the surface of the die cast. In some embodiments, the preferred aging temperature is 0.53 Tg to 0.57 Tg and the preferred aging time period is 30 minutes to 60 minutes for a amorphous alloy die cast with a thickness of 1.0 mm to 1.5 mm. Corresponding to different thicknesses of the die cast, the preferred aging treatment temperature may be increased or decreased; and the preferred heat treatment time period may be shortened or extended. However, the aging treatment should be kept within 0.5Tg to 0.6Tg range.

[0020] In various embodiments of the present disclosure, the amorphous alloy die cast that is subjected to the above disclosed heat treatment process neither crystallizes, nor has gas bubbles at the surface. The die cast exhibits improved material properties and enhanced stability. These improvements may be attributed to the following reasons.

[0021] First, during the amorphous alloy die cast preparation process, the die cast is cooled off after molding. Cooling rates at different parts of the die cast are different. The different cooling rates may cause some weak areas or stress concentration regions. In the present disclosure, the low aging treatment temperature ranging from 0.5 Tg to 0.6 Tg enables the relaxation and releasing of the concentrated stresses. Hence, the process disclosed in the present disclosure prevents the amorphous alloy die cast from premature fracturing before the material's yield point is reached. As a result, the material's performance and stability of the die cast are improved.

[0022] Second, the amorphous alloy die cast is formed at a vacuum pressure of 50 Pa to 200 Pa and at a low casting speed of 3 m/s to 5m/s. Because the amorphous alloy has a high viscosity, the amount of gases trapped within the amorphous alloy die cast is less than that in the traditional alloy die casts. During subsequent aging treatment performed under middle to high pressure (about 0.1 MPa to 0.5 MPa), the positive pressure prohibits the trapped gas from diffusing to the surface of the amorphous alloy die cast.

[0023] Third, when amorphous alloy is rapidly cooled, the microstructure of the amorphous alloy is in a highly disordered and unstable state. While the low temperature aging treatment may not provide sufficient energy to overcome the energy barrier required for crystallization, it can overcome the metastable energy barrier and enable the transformation of the material structure from a high-energy long-range disordered state to a short-range ordered state. Here, the low temperature aging refers to aging treatment performed below the glass transition temperature. The current disclosure discloses that such a temperature range is from 0.5T_g to 0.6 T_g.

[0024] After the low temperature aging process, the alloy become, for example, pentagonal or dodecagonal quasicrystals, both have short-range ordered structures. Although the short-range ordered structure cannot grow to become crystal, (the crystallization process requires re-melting into a disordered state), it can enhance the stability of the material properties. Referring to Figure 2, after the aging treatment, the die cast exhibits an increased area under the crystallization peak. The increased area under the crystallization peak indicates more energy is released during the crystallization and in turn, indicates a more stable crystal structure and a more stable material property.

[0025] Reference will be made in detail to embodiments of the present disclosure. The embodiments described herein with reference to drawings are explanatory, illustrative, and used to generally understand the present disclosure. The embodiments shall not be construed to limit the present disclosure. The same or similar elements and the elements having same or similar functions are denoted by like reference numerals throughout the descriptions.

[0026] In the two embodiments disclosed, aging treatments were performed on two typical Zr-based amorphous alloys composed of Zr₅₅Al₁₅Cu₂₅Ni₅ and Zr₄₁Ti₁₄Cu₁₅Ni₁₀Be₂₀, respectively. The two amorphous alloys have excellent glass forming ability, excellent mechanical properties and broad supercooled liquid region. Therefore, these two typical Zr-based alloys are selected to explain the effects of the aging treatment on the amorphous alloys.

[0027] In the first embodiment, high purity (purity is greater than 99.0wt%) Zr, Al, Cu, and Ni with a weight ratio corresponding to the composition of Zr₅₅Al₁₅Cu₂₅Ni₅ were melted in an electrical arc furnace. Subsequently, a copper mould was used for die casting in the presence of a protective Argon gas. The die casting was performed in a condition of: a pressure of 150 Pa and a casting speed of 3m/s. Fifteen amorphous alloy die casts were prepared for experimental purposes, each having a size of 80 mmx6 mmx1.5 mm. The fifteen amorphous alloy die casts were labeled as A1 to A15, and having a composition of Zr₅₅Al₁₅Cu₂₅Ni₅. The glass transition temperature T_g was determined to be 704K for this type of alloy by performing a DSC test. The fifteen die casts were divided into three groups.

[0028] The first group includes A1 to A5, all of which were not subjected to any aging treatments.

[0029] The second group includes A6 to A10, each of which was subjected to an aging treatment in a pressure of 0.2 MPa, at a temperature of 0.53T_g (373K), for a time period of 1 hour. The resulted die casts were labeled as B1 to B5.

[0030] The third group includes A11 to A15, each of which was subjected to an aging treatment in a pressure of 0.2 MPa, at a temperature of 0.81T_g (573K), for a time period of 1 hour. The resulted die casts were labeled as C1 to C5.

Property Tests

1) Bending resistance test

[0031] Pursuing to standard bending resistance test disclosed in GB/T14452-93 and using a CMT5105 universal material testing machine, the three-point bending fracturing tests were performed on each of the die casts groups A1-A5, B1-B5, and C1-C5. The resulted strength values were recorded. The average and variance of the strength values were calculated. All data are shown in Table 1.

2) XRD (X-Ray Diffraction) Analysis

[0032] In order to determine whether the alloy is amorphous, X-ray powder diffraction analyses were performed on die cast samples A1, B1, and C1. A D-MAX2200PC X-ray powder diffraction instrument was used, and the XRD analyses were performed under the following conditions: X-ray radiation was generated by a copper target; the incident wavelength λ is 1.54060Å; the accelerating voltage is 40 KV; the current is 20 mA; and the scan step is 0.04°. The XRD results are shown in Fig. 1. It can be seen that A1 and B1 have amorphous structures and C1 has a crystal structure (the sharp diffraction peaks of C1 indicate a crystal structure).

3) DSC Test

[0033] DSC tests were performed on A1, B1, and C1 with a STA409 Thermogravimetric and Differential Thermal Analyzer. An 99% pure Al₂O₃ crucible was selected. The results are shown in Fig. 2. It can be seen that B1, which was subjected to an aging treatment at a temperature of 0.53T_g, exhibits an increased area under the crystal peaks. The increased area means a more stable material property.

Table 1

Group 1	Bending Strength (MPa)	Group 2	Bending Strength (MPa)	Group 3	Bending Strength (MPa)
A1	1978.15	B1	2695.73	C1	965.02
A2	1645.26	B2	2681.6	C2	644.58
A3	1768.73	B3	2282.61	C3	1248.12
A4	1471.5	B4	2362.84	C4	683.6
A5	2280.92	B5	2482.1	C5	621.37
Average	1828.912	Average	2500.976	Average	832.538
Variance	333.7656	Variance	150.1512	Variance	219.2256

[0034] In the second embodiment, high purity (purity is greater than 99.0wt%) Zr, Ti, Cu, Ni and Be with a weight ratio corresponding to the composition of $Zr_{41}Ti_{14}Cu_{15}Ni_{10}Be_{20}$ were melted in an electrical arc furnace. Subsequently, a copper mould was used for die casting in the presence of a protective Argon gas. The die casting was performed under a pressure of 120 Pa and with a casting speed of 4m/s. Fifteen amorphous alloy die casts were prepared for experimental purposes, each having a size of 80 mm×18 mm×1 mm. The fifteen amorphous alloy die casts were labeled as D1 to D15, and having a composition of $Zr_{41}Ti_{14}Cu_{15}Ni_{10}Be_{20}$. The glass transition temperature T_g was determined to be 662K for this type of alloy by performing a DSC test. The fifteen die casts were divided into three groups.

[0035] The first group includes D1 to D5, all of which were not subjected to any aging treatments.

[0036] The second group includes D6 to D10, each of which was subjected to an aging treatment in an atmospheric pressure of 0.1 MPa, at a temperature of 0.57 T_g (377K), for a time period of 0.5 hour. The resulted die casts were labeled as E1 to E5.

[0037] The third group includes D11 to D15, each of which was subjected to an aging treatment under a pressure of 0.1 MPa, at a temperature of 0.47 T_g (311K), for a time period of 0.5 hour. The resulted die casts were labeled as F1 to F5.

Property Test

[0038] Bending resistance strength test was performed on the 3 groups of die casts.

[0039] Pursuing to standard bending resistance test disclosed in GB/T14452-93 and using a CMT5105 universal material testing machine, the three-point bending fracturing tests were performed on each of the die casts groups D1-D5, E1-E5, and F1-F5. The resulted strength values were recorded. The average and variance of the strength values were calculated. All data are shown in Table 2.

Table 2

Group 1	Bending Strength (MPa)	Group 2	Bending Strength (MPa)	Group 3	Bending Strength (MPa)
D1	2077.9	E1	2321.8	F1	2184.69
D2	1937.27	E2	2423.4	F2	2023.29
D3	1606.07	E3	2845.43	F3	1721.34
D4	1715.41	E4	2343.16	F4	1763.76
D5	1660.24	E5	2275.54	F5	2107.59
Average	1799.378	Average	2441.866	Average	1960.134
Variance	338.1664	Variance	161.4256	Variance	300.6715

Conclusion of the experiments

[0040] Referring to Table 1, it is shown that die casts B1-B5, which were subjected to an aging treatment at a temperature of 0.53 T_g , have better bending resistance and stability in comparison with die casts A1-A5, which were not subjected to aging treatments, and C1-C5, which subjected to an aging treatment at a temperature of 0.81 T_g . Referring to Table 2, die casts E1-E5 have improved bending resistance and stability, in comparison with die casts D1-D5, which were not subjected to any aging treatments, and die casts F1-F5, which were subjected to aging treatments under a temperature

of 0.47Tg.

[0041] In this specification, the terms "one embodiment," "some embodiments," "exemplary embodiment," "specific exemplary embodiment," or "some exemplary embodiments" mean that the described specific characteristics, structures, materials or features based on the underlining embodiments exist in at least one of the embodiments or exemplary embodiments. However, in this specification, an exemplary description associated with the above terms does not necessarily mean the same embodiment. In addition, the described specific characteristics, structures, materials or features may be properly combined in one or more embodiments or exemplary embodiments.

[0042] 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 may be made in the embodiments without departing from spirit and principles of the present disclosure.

Claims

1. A heat treatment process for an amorphous alloy die cast comprising subjecting the amorphous alloy die cast to an aging treatment at a temperature of 0.5 Tg to 0.6 Tg, and for a time period of 10 minutes to 24 hours; wherein Tg is a glass transition temperature of the alloy.
2. The heat treatment process of claim 1, wherein the amorphous alloy die cast is formed by a die casting process in a condition of: a pressure of 50 Pa to 200 Pa and a die casting speed of 3m/s to 5m/s; and wherein the amorphous alloy die cast has a thickness of 0.5 mm to 2 mm.
3. The heat treatment process of claim 1, wherein the aging treatment is performed under a positive pressure of 0.1 MPa to 0.5 MPa.
4. The heat treatment process of any one of claims 1-3, wherein the temperature is 0.53 Tg to 0.57 Tg, the time period is 30 minutes to 60 minutes, and amorphous alloy die cast has a thickness of 1 mm to 1.5 mm.
5. The heat treatment process of any one of claims 1-3, wherein the amorphous alloy die cast comprises Zr, and is represented by a formula of $(Zr_{1-x}Ti_x)_a(Cu_{1-y}Ni_y)_bAl_cM_d$, wherein
 M is selected from the group consisting of: Be, Y, Sc, La, and combinations thereof,
 "x" is in the range of from 0 to 0.35 in atomic percentage,
 "y" is in the range of from 0 to 0.75 in atomic percentage,
 "a" is in the range of from 38 to 65,
 "b" is in the range of from 20 to 40,
 "c" is in the range of from 0 to 15,
 "d" is in the range of from 0 to 30, and
 the sum of a, b, c, and d in atomic percentage equals to 100.
6. An amorphous alloy die cast, wherein the amorphous alloy die cast comprises Zr and is treated by the heat treatment process described in any one of claims 1-5.
7. The amorphous alloy die cast of claim 6, wherein the amorphous alloy die cast is represented by a formula of $(Zr_{1-x}Ti_x)_a(Cu_{1-y}Ni_y)_bAl_cM_d$, in which
 M is selected from the group consisting of: Be, Y, Sc, La, and combinations thereof,
 "x" is in the range of from 0 to 0.45,
 "y" is in the range of from 0 to 0.75,
 "a" is in the range of from 38 to 65,
 "b" is in the range of from 20 to 40,
 "c" is in the range of from 0 to 15,
 "d" is in the range of from 0 to 30, and
 the sum of a, b, c, and d in atomic percentage equals to 100.
8. The amorphous alloy die cast of claim 7, wherein the amorphous alloy die cast is represented by a formula of $Zr_{55}Al_{15}Cu_{25}Ni_5$ or $Zr_{41}Ti_{14}Cu_{15}Ni_{10}Be_{20}$.

9. The amorphous alloy die cast of claim 6, wherein the amorphous alloy die cast has a thickness of 0.5 mm to 2 mm.

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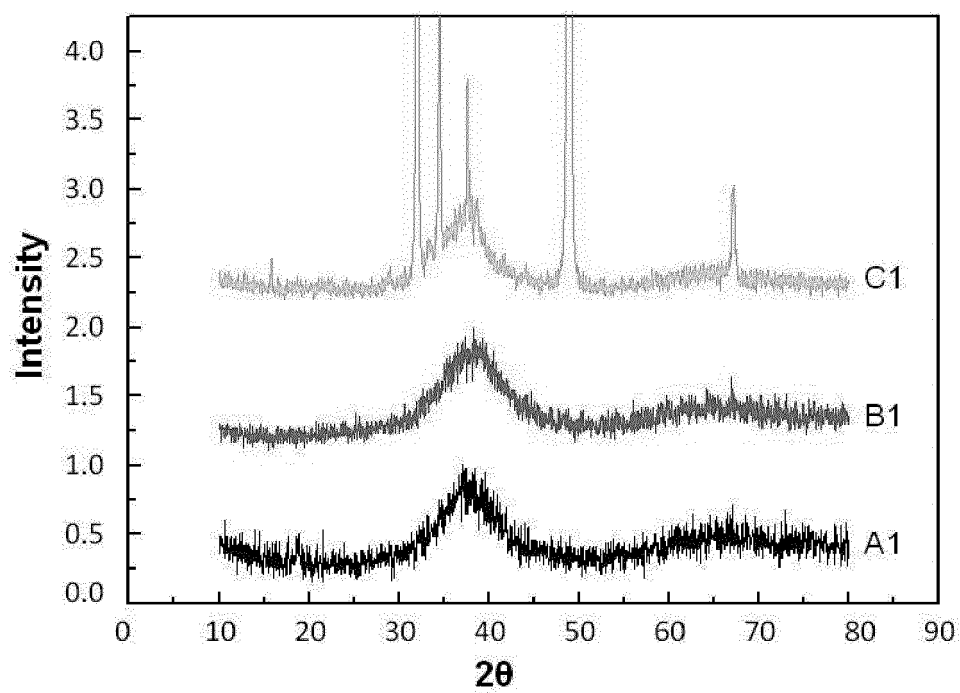


Fig. 1

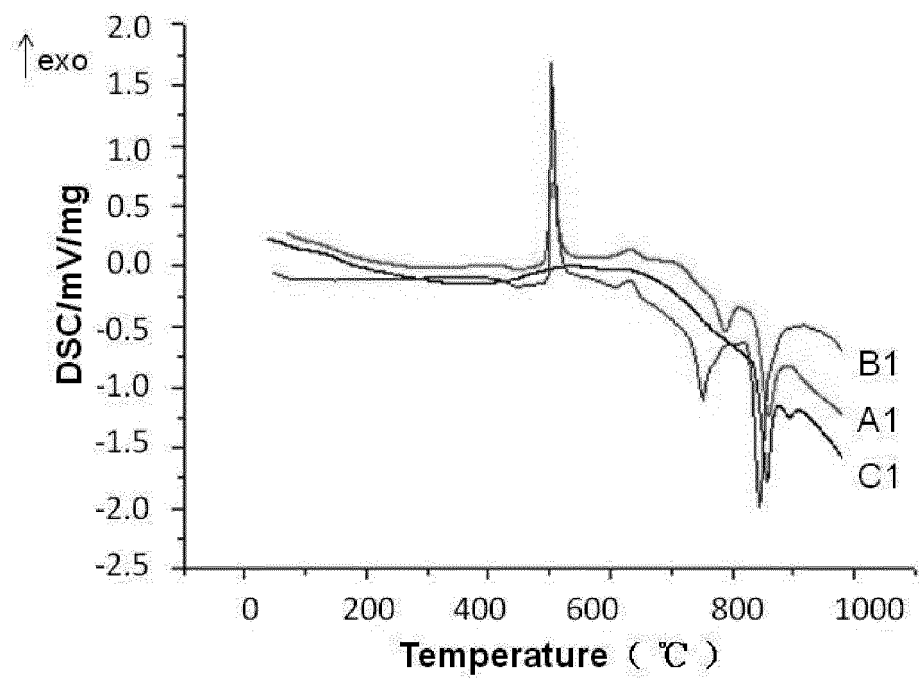


Fig. 2

INTERNATIONAL SEARCH REPORT

International application No.

PCT/CN2011/077762

A. CLASSIFICATION OF SUBJECT MATTER

See the 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: C22C45/-, C22F1/-, B22D18/-

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: metallic glass, die casting, thermal insulation, amorphous, non crystalline, glassy, cast+, alloy, heat treatment, ag+, heat+, keep+, insulation

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	Huang, Shengtao et al. Study on the Amorphous Phase Separation of Co-Ni-Fe-Based Metallic Glass by Artificial Ageing. SCIENCE IN CHINA, June 1986, issue 6 page 612, paragraph 5, lines 1-2, and page 609	1, 3-4, 6, 9
Y	page 612, paragraph 5, lines 1-2, and page 609	5, 7-8
Y	CN101570837A (BYD COMPANY LIMITED) 04 November 2009 (04.11.2009) claim 1	5, 7
Y	WANG, Gang et al. Tension Fracture Behavior of $Zr_{41.25}Ti_{13.75}Ni_{10}Cu_{12.5}Be_{22.5}$ Bulk Metallic Glass. ACTA METALLURGICA SINICA, March 2005, volume 41, issue 3, page 291	8
A	BA, Qixian et al. Influence of Heat treatment on Magnetic Aftereffect of Fe-Based Amorphous Alloys. JOURNAL OF NORTHEASTERN UNIVERSITY (NATURAL SCIENCE), August 1995, volume 16, issue 4, pages 406-409	1-9
A	CN101550521A (INSTITUTE OF PHYSICS, CHINESE ACADEMY OF SCIENCES) 07 October 2009 (07.10.2009) the whole document	1-9
A	US5876519A (INOUE A et al.) 02 March 1999 (02.03.1999) the whole document	1-9

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

* Special categories of cited documents:	"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
"A" document defining the general state of the art which is not considered to be of particular relevance	"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
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"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	

Date of the actual completion of the international search

21 October 2011 (21.10.2011)

Date of mailing of the international search report

03 November 2011 (03.11.2011)

Name and mailing address of the ISA/CN:

State Intellectual Property Office of the P.R.China
No. 6, Xitucheng Road, Jimenqiao, Haidian District, Beijing
100088, China
Fax No: (86-10) 62019451

Authorized officer

CHEN Dazhou

Telephone No. (86-10) 62084752

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/CN2011/077762

Patent Documents referred in the Report	Publication Date	Patent Family	Publication Date
CN101570837A	04.11.2009	None	
CN101550521A	07.10.2009	None	
US5876519A	02.03.1999	DE19711490A1	30.10.1997
		JP9256122A	30.09.1997

Form PCT/ISA /210 (patent family annex) (July 2009)

INTERNATIONAL SEARCH REPORT

International application No.

PCT/CN2011/077762

A. (Continuation second sheet). CLASSIFICATION OF SUBJECT MATTER

C22C45/00 (2006.01) i

C22F1/00 (2006.01) i

B22D18/00 (2006.01) i

REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

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- GB 1445293 T [0031] [0039]