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(54) **HIGH-STRENGTH HIGH-TOUGHNESS AMORPHOUS ZIRCONIUM ALLOY**

(57) An amorphous Zr alloy has a composition expressed as  $Zr-Al_a-Ni_b-Cu_c-M_d$ . M is one or more elements selected from Ti, Nb and Pd. The a, b, c, and d are amounts in atomic %, and satisfy the following formulas.  $5 \leq a \leq 50$ ;  $30b + c \leq 50$ ;  $b/c \leq 1/3$ ; and  $0 < d \leq 7$ . The remainder are Zr and inevitable impurities. The alloy contains a non-crystalline phase of 90% or higher by volume. Also, the amorphous alloy indicates an excellent glass-forming ability with a supercooled liquid range over 100°C (indicated by a difference between the crystallization temperature and the glass transition temperature) and which has a thickness of 1mm or thicker. Further, it has excellent strength and toughness indicated by the following mechanical characteristics: tensile strength of 1800 MPa or higher; flexural strength of 2500 MPa or higher; Charpy impact value of 100 kJ/m<sup>2</sup> or higher; and fracture toughness value of 50 MPa\*m<sup>1/2</sup> or higher.

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**Description**

## FIELD OF THE INVENTION

5 **[0001]** The present invention relates to amorphous Zr alloys which have a high glass-forming ability and excellent strength and toughness.

## RELATED ART

10 **[0002]** Amorphous metal materials having various forms, such as thin ribbons, filaments, particles and the like, can be obtained by rapidly cooling molten alloys. A thin-ribbon-shaped amorphous alloy is easily manufactured by means of a single roll method, a twin-roller method, an in-rotating water melt spinning method and the like, in which a large cooling speed can be obtained. Conventionally, various amorphous alloys have been provided using alloys of Fe, Ni, Co, Pd, Cu, Zr or Ti; those amorphous alloys show properties unique to amorphous alloys such as high corrosion resist-  
 15 **[0003]** However, shapes of the amorphous alloys manufactured by means of previously mentioned methods are limited to thin ribbons or thin wires; it is difficult to process the amorphous alloys of those shapes into a form of final products. Therefore, the uses of such amorphous alloys are limited in industry.

20 **[0004]** On the other hand, it is known that when amorphous alloys are heated, some of alloys undergo transition to a phase of supercooled liquid before crystallization and indicate a decline in viscosity. For example, when heated at a speed of 40°C per minute, an amorphous Zr alloy is observed to remain in the supercooled liquid phase for a range of temperature of the maximum of 120°C before crystallization starts (see Mater. Trans., JIM, Vol. 32, (1991), 1005).

25 **[0005]** In the supercooled liquid phase, the low viscosity of the amorphous alloy allows one to form it into a given shape by closed squeeze casting process and the like; for example, gears can be formed of an amorphous alloy (see Nikkan Kogyo Shinbun, November 12, 1992). Hence, amorphous alloys having a wide range of the supercooled liquid phase can be said to provide excellent workability. Among such amorphous alloys having a wide range of supercooled liquid phase, an amorphous Zr-Al-Ni-Cu alloy has a range of temperature of 100°C as the supercooled liquid phase,  
 30 therefore, is considered to be an amorphous alloy with excellent applicability, such as high corrosion resistance (see Japanese Examined Patent Application Publication H07-122120).

**[0006]** The glass-forming ability and a method for manufacturing of those amorphous alloys have been further improved. As a result, Japanese Laid-Open Patent Application Publication H08-74010 discloses development of an amorphous Zr alloy having a 100° C range for the supercooled liquid phase and a thickness exceeding 5mm. Also, various manufacturing methods to improve mechanical characteristics of the amorphous alloys have been tried (Japanese Laid-Open Patent Application Publications: 2000-24771, 2000-26943, 2000-26944); however, these amorphous Zr alloys do not provide sufficient mechanical characteristics as structural materials.

## DETAILS OF THE INVENTION

40 (Problems to be Solved)

**[0007]** The amorphous Zr alloy described previously has a high glass-forming ability and relatively good strength characteristics due to the range of the supercooled liquid phase above 100°C. Nonetheless, attempts to improve its mechanical characteristics have been made only in the manufacturing method; attempts to improve the composition of alloys has not been made.

(Solution of the Problems)

50 **[0008]** Intending to provide an amorphous Zr alloy material having improved strength and toughness without impairing a temperature range for the supercooled liquid phase and a size enabling application to industrial use, inventors of the present invention studied the above issues. They discovered the an amorphous Zr alloy having high strength and toughness as well as excellent glass-forming ability can be obtained by melting an alloy in which a given amount of M element (one or two or more elements selected from a group consisting of Ti, Nb and Pd) is added to a Zr-Al-Ni-Cu-M alloy of a given composition, followed by rapid cooling for solidification.

55 **[0009]** In other words, the present invention intends to provide an amorphous Zr alloy which contains non-crystalline phase of 90% or higher by volume wherein the alloy has a composition expressed as Zr-Al<sub>3</sub>-Ni<sub>b</sub>-Cu<sub>c</sub>-M<sub>d</sub> (in this expression terms are defined as follows:

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M: one or two or more elements selected from a group consisting of Ti, Nb and Pd;

a, b, c, and d: atomic % wherein:

5  $5 \leq a \leq 10;$

$$30 \leq b+c \leq 50;$$

10  $b/c \leq 1/3;$

$$0 < d \leq 7;$$

remainder: Zr and inevitable impurities).

15 **[0010]** Further, a "range of the supercooled liquid phase" is defined as a difference between a glass transition temperature, obtained by differential scanning thermogravimetry at a speed of heating of 40°C per minute, and a crystallization temperature. The "range of the supercooled liquid phase" indicates resistance to crystallization, that is, stability of glass-forming ability. The alloy of the present invention has a range of the supercooled liquid phase over 100°C.

### 20 PREFERRED EMBODIMENTS OF THE PRESENT INVENTION

**[0011]** The following describes the most preferable embodiments of the present invention.

**[0012]** In an amorphous Zr alloy of the present invention, Ni and Cu are main elements forming the non-crystalline phase; a sum of the amounts of Ni and Cu contained is more than 30 atomic % and less than 50 atomic %. When the  
25 sum is less than 30 atomic % or more than 50 atomic %, the single roll method with a high cooling speed can provide the non-crystalline phase while the casting method with a low cooling speed cannot. Further, a ratio of the amount of Ni to the amount of Cu contained, i.e., b/c ratio, is defined to be less than 1/3. This ratio provides dense random packing of the atomic structure of the non-crystalline phase such that the glass-forming ability is maximized.

**[0013]** Also, Al is an element to drastically increase the glass-forming ability of an amorphous Zr alloy of the present  
30 invention. The amount of Al contained is more than 5 atomic % and less than 10 atomic %. When the amount contained is less than 5 atomic % or more than 10 atomic %, the glass-forming ability decreases.

**[0014]** M is one or two or more elements selected from a group consisting of Ti, Nb and Pd; additionally, it accelerates the dense random packing of the atomic structure while effectively strengthening the bond strength between atoms. As a result, higher strength and toughness are given to an amorphous Zr alloy having the high glass-forming  
35 ability. The amount of M contained is more than 0 atomic % and less than 7 atomic %; more preferably, the amount of Ti and Nb is less than 4 atomic % while Pd is less than 7 atomic %. When the amount of each element contained exceeds the defined atomic %, the bond strength between atoms becomes too strong such that a compound phase with Zr or Al will be formed. The compound phase causes structural discontinuity in the interface with the noncrystalline phase such that the structure is weakened; therefore, desired strength or toughness cannot be obtained.

**[0015]** The amorphous Zr alloy of the present invention can be cooled for solidification by various methods, such as a single roll method, a twin-roller method, an in-rotating water melt spinning method, and an atomizing method to provide various forms, such as thin ribbons, filaments, and particles. Also, the alloy of the present invention has a significantly improved glass-forming ability; therefore, it can be formed into a rod or a plate of a given shape by injecting the molten alloy into a mold. For example, using a known metal mold casting process, a bulk of the alloy can be obtained  
45 by injecting casting of the melt into metal mold, which is melted in a quartz tube in an Ar atmosphere, the injecting pressure was fixed to be 0.5kg/cm<sup>2</sup>. Furthermore, the amorphous Zr alloy of the present invention has an optimized alloy composition, compared to a conventional amorphous Zr alloy; hence, an excellent glass-forming ability and high strength and toughness can be obtained.

50 (Examples 1 through 14, Comparisons 1 through 8)

**[0016]** The following describes examples of the present invention.

**[0017]** Rod-shaped samples with a diameter of 5mm and a length of 50mm were prepared using materials having alloy compositions shown in Table 1 by a metal mold casting method. Then, glass transition temperatures (T<sub>g</sub>) and crystallization starting temperatures (T<sub>x</sub>) were measured using a differential scanning calorimeter (DSC); based on the  
55 measurements, a range of the supercooled liquid phase (T<sub>x</sub> - T<sub>g</sub>) was calculated. A ratio of a non-crystalline phase contained in a rod-shaped sample by volume (v<sub>f</sub>) was evaluated by comparing the amount of heat generation when the rod-shaped sample crystallized against the amount of heat generation when a completely non-crystallized single rolled

sheet crystallized using DSC. In addition, each rod-shaped sample was tested by means of a tensile test, a three-point bending test and the Charpy impact test to measure tension fracture strength ( $\sigma_f$ ), flexural strength ( $\sigma_{B.f}$ ), i.e., "bending resistance strength", Charpy impact value (E) and fracture toughness (K<sub>Ic</sub>).

5

Table 1

		Tx-Tg (K)	Vf (%)	$\sigma_f$ (MPa)	$\sigma_{B.f}$ (MPa)	E (kJ/m <sup>2</sup> )	K <sub>Ic</sub> (MPa*m <sup>1/2</sup> )	
10	Example 1	Zr <sub>63</sub> Al <sub>5</sub> Ni <sub>5</sub> Cu <sub>25</sub> Ti <sub>2</sub>	104	98	1930	2840	125	54
	Example 2	Zr <sub>48.5</sub> Al <sub>7.5</sub> Ni <sub>10</sub> Cu <sub>30</sub> Ti <sub>4</sub>	110	95	2020	3010	136	63
	Example 3	Zr <sub>41</sub> Al <sub>5</sub> Ni <sub>5</sub> Cu <sub>45</sub> Ti <sub>4</sub>	108	94	1980	2990	131	60
	Example 4	Zr <sub>55.5</sub> Al <sub>7.5</sub> Ni <sub>5</sub> Cu <sub>30</sub> Nb <sub>2</sub>	112	97	1890	2700	128	57
15	Example 5	Zr <sub>46</sub> Al <sub>10</sub> Ni <sub>10</sub> Cu <sub>30</sub> Nb <sub>4</sub>	125	100	2050	3100	141	66
	Example 6	Zr <sub>46</sub> Al <sub>5</sub> Ni <sub>10</sub> Cu <sub>35</sub> Nb <sub>4</sub>	101	94	1970	2920	128	59
	Example 7	Zr <sub>55.5</sub> Al <sub>7.5</sub> Ni <sub>5</sub> Cu <sub>30</sub> Pd <sub>2</sub>	109	100	2100	3350	150	69
20	Example 8	Zr <sub>56</sub> Al <sub>10</sub> Ni <sub>5</sub> Cu <sub>25</sub> Pd <sub>4</sub>	121	100	2080	3300	144	68
	Example 9	Zr <sub>44</sub> Al <sub>10</sub> Ni <sub>10</sub> Cu <sub>30</sub> Pd <sub>6</sub>	108	100	2210	3510	154	71
	Example 10	Zr <sub>48</sub> Al <sub>5</sub> Ni <sub>5</sub> Cu <sub>35</sub> Pd <sub>7</sub>	106	100	2130	3200	139	65
	Example 11	Zr <sub>51</sub> Al <sub>5</sub> Ni <sub>10</sub> Cu <sub>30</sub> Ti <sub>2</sub> Pd <sub>2</sub>	115	100	2000	2990	123	54
25	Example 12	Zr <sub>51</sub> Al <sub>5</sub> Ni <sub>5</sub> Cu <sub>35</sub> Ti <sub>2</sub> Nb <sub>2</sub>	118	98	2080	3150	137	63
	Example 13	Zr <sub>43.5</sub> Al <sub>7.5</sub> Ni <sub>10</sub> Cu <sub>35</sub> Nb <sub>2</sub> Pd <sub>2</sub>	113	96	2150	3220	139	63
	Example 14	Zr <sub>60</sub> Al <sub>5</sub> Ni <sub>5</sub> Cu <sub>25</sub> Ti <sub>2</sub> Nb <sub>1</sub> Pd <sub>2</sub>	112	100	1890	2840	120	51
30	Comparison 1	Zr <sub>55</sub> Al <sub>10</sub> Ni <sub>5</sub> Cu <sub>30</sub>	104	100	1620	1710	71	44
	Comparison 2	Zr <sub>42</sub> Al <sub>5</sub> Ni <sub>5</sub> Cu <sub>40</sub> Ti <sub>8</sub>	88	70	1400	1210	40	22
	Comparison 3	Zr <sub>42</sub> Al <sub>5</sub> Ni <sub>5</sub> Cu <sub>40</sub> Nb <sub>8</sub>	69	51	1260	1170	35	20
	Comparison 4	Zr <sub>42</sub> Al <sub>5</sub> Ni <sub>5</sub> Cu <sub>40</sub> Pd <sub>8</sub>	98	78	1650	1680	73	45
35	Comparison 5	Zr <sub>54</sub> Al <sub>2</sub> Ni <sub>10</sub> Cu <sub>30</sub> Pd <sub>4</sub>	70	55	1180	990	32	18
	Comparison 6	Zr <sub>43.5</sub> Al <sub>12.5</sub> Ni <sub>10</sub> Cu <sub>30</sub> Ti <sub>4</sub>	43	30	670	690	19	11
	Comparison 7	Zr <sub>41</sub> Al <sub>10</sub> Ni <sub>13</sub> Cu <sub>30</sub> Pd <sub>6</sub>	118	100	1720	1750	88	48
40	Comparison 8	Zr <sub>42</sub> Al <sub>5</sub> Ni <sub>20</sub> Cu <sub>30</sub> Ti <sub>3</sub>	65	48	980	1050	36	21

**[0018]** As is clearly shown in Table 1, die-cast amorphous alloy materials of Examples 1 through 14 show: a range of the supercooled liquid phase of over 100°C; a ratio of the non-crystalline phase by volume of 90% or higher, providing a large glass-forming ability; tensile strength of 1800 MPa or higher; flexural strength of 2500 MPa or higher; Charpy impact values of 100 kJ/m<sup>2</sup> or higher; fracture toughness values of 50 MPa\*m<sup>1/2</sup> or higher, providing excellent strength and toughness.

**[0019]** On the other hand, the alloy of Comparison 1 shows an excellent glass-forming ability in which a cast material with a diameter of 5mm is completely non-crystallized; however, a lack of the M element causes deteriorated mechanical characteristics. Also, the cast materials of Comparisons 2, 3 and 4 contain the M element for the amount exceeding the predetermined 7%; as a result, a range of the supercooled liquid phase and a ratio of the non-crystalline phase by volume are less than 100°C and 90%, respectively, indicating no improvement in mechanical characteristics. Comparisons 5 and 6 do not satisfy the predetermined amount of Al contained, more than 5% or less than 10%; hence, the supercooled liquid range and the glass-forming ability are 100°C and 90%, respectively, and the mechanical characteristics are extremely poor. Further, Comparisons 7 and 8 show no improvement in the mechanical characteristics since the ratio of Ni to Cu, b/c, exceeds the value predetermined in the present invention, 1/3.

Application of the Present Invention

**[0020]** As described above, an amorphous Zr alloy of the present invention indicates a supercooled liquid range over 100°C, as well as excellent strength and toughness shown by: tensile strength of 1800 MPa or higher; flexural strength of 2500 MPa or higher; Charpy impact values of 100 kJ/m<sup>2</sup> or higher; fracture toughness values of 50 MPa\*m<sup>1/2</sup> or higher. Therefore, the present invention is able to provide a useful amorphous Zr alloy which has a high glass-forming ability and excellent strength and toughness.

**Claims**

10

1. An amorphous Zr alloy which has a composition expressed as Zr-Al<sub>a</sub>-Ni<sub>b</sub>-Cu<sub>c</sub>-M<sub>d</sub> (in this expression terms are defined as follows:

15 M: one or more elements selected from a group consisting of Ti, Nb and Pd;  
a, b, c, and d: atomic % wherein:

$$5 \leq a \leq 10$$

20

$$30 \leq b+c \leq 50;$$

$$b/c \leq 1/3;$$

$$0 < d \leq 7;$$

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remainder: Zr and inevitable impurities)

wherein said amorphous Zr alloy contains a non-crystalline phase of 90% or higher by volume.

30

2. An amorphous Zr alloy according to Claim 1 which indicates an excellent glass-forming ability with a supercooled liquid range over 100°C (indicated by a difference between the crystallization temperature and the glass transition temperature) and which has a thickness of 1mm or thicker.

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3. An amorphous Zr alloy according to Claim 1 or 2 which has excellent strength and toughness indicated by the following mechanical characteristics:

tensile strength of 1800 MPa or higher;

flexural strength of 2500 MPa or higher;

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Charpy impact value of 100 kJ/m<sup>2</sup> or higher; and

fracture toughness value of 50 MPa\*m<sup>1/2</sup> or higher.

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INTERNATIONAL SEARCH REPORT

International application No.  
PCT/JP99/05872

<p>A. CLASSIFICATION OF SUBJECT MATTER Int.Cl.<sup>7</sup> C22C 16/00</p> <p>According to International Patent Classification (IPC) or to both national classification and IPC</p>																																			
<p>B. FIELDS SEARCHED</p> <p>Minimum documentation searched (classification system followed by classification symbols) Int.Cl.<sup>7</sup> C22C 1/00 - 45/10</p> <p>Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Jitsuyo Shinan Koho 1926-1996 Jitsuyo Shinan Toroku Koho 1996-2000 Kokai Jitsuyo Shinan Koho 1971-2000 Toroku Jitsuyo Shinan Koho 1994-2000</p> <p>Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)</p>																																			
<p>C. DOCUMENTS CONSIDERED TO BE RELEVANT</p> <table border="1"> <thead> <tr> <th>Category*</th> <th>Citation of document, with indication, where appropriate, of the relevant passages</th> <th>Relevant to claim No.</th> </tr> </thead> <tbody> <tr> <td>A</td> <td>JP, 07-062502, A (Ken Masumoto), 07 March, 1995 (07.03.95), page 5; Table 1 (Family: none)</td> <td>1-3</td> </tr> <tr> <td>A</td> <td>JP, 07-188877, A (Ken Masumoto), 25 July, 1995 (25.07.95), page 4; Table 1 (Family: none)</td> <td>1-3</td> </tr> <tr> <td>A</td> <td>JP, 08-199318, A (Res. Dev Corp. of Japan.), 06 August, 1996 (06.08.96), page 5; table 1 &amp; US, 5803996, A</td> <td>1-2</td> </tr> <tr> <td>A</td> <td>JP, 10-186176, A (A. Inoue), 25 July, 1995 (25.07.95), page 4; table 1 &amp; EP, 000851253, A &amp; CN, 001186252, A</td> <td>1-3</td> </tr> </tbody> </table> <p><input type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/> See patent family annex.</p> <table border="1"> <tr> <td>* Special categories of cited documents:</td> <td>"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</td> </tr> <tr> <td>"A" document defining the general state of the art which is not considered to be of particular relevance</td> <td>"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</td> </tr> <tr> <td>"E" earlier document but published on or after the international filing date</td> <td>"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</td> </tr> <tr> <td>"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)</td> <td>"&amp;" document member of the same patent family</td> </tr> <tr> <td>"O" document referring to an oral disclosure, use, exhibition or other means</td> <td></td> </tr> <tr> <td>"P" document published prior to the international filing date but later than the priority date claimed</td> <td></td> </tr> </table> <table border="1"> <tr> <td>Date of the actual completion of the international search 07 January, 2000 (07.01.00)</td> <td>Date of mailing of the international search report 25 January, 2000 (25.01.00)</td> </tr> <tr> <td>Name and mailing address of the ISA/ Japanese Patent Office</td> <td>Authorized officer</td> </tr> <tr> <td></td> <td>Telephone No.</td> </tr> </table>			Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.	A	JP, 07-062502, A (Ken Masumoto), 07 March, 1995 (07.03.95), page 5; Table 1 (Family: none)	1-3	A	JP, 07-188877, A (Ken Masumoto), 25 July, 1995 (25.07.95), page 4; Table 1 (Family: none)	1-3	A	JP, 08-199318, A (Res. Dev Corp. of Japan.), 06 August, 1996 (06.08.96), page 5; table 1 & US, 5803996, A	1-2	A	JP, 10-186176, A (A. Inoue), 25 July, 1995 (25.07.95), page 4; table 1 & EP, 000851253, A & CN, 001186252, A	1-3	* 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	"E" earlier document but published on or after the international filing date	"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	"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)	"&" document member of the same patent family	"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 07 January, 2000 (07.01.00)	Date of mailing of the international search report 25 January, 2000 (25.01.00)	Name and mailing address of the ISA/ Japanese Patent Office	Authorized officer		Telephone No.
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