

US007591910B2

# (12) United States Patent

## Xu et al.

## (54) BULK AMORPHOUS REFRACTORY GLASSES BASED ON THE NI(-CU-)-TI(-ZR)-AL ALLOY SYSTEM

- (75) Inventors: Donghua Xu, Berkeley, CA (US); William L. Johnson, Pasadena, CA (US)
- (73) Assignee: California Institute of Technology, Pasadena, CA (US)
- (\*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 218 days.
- (21) Appl. No.: 10/535,317
- (22) PCT Filed: Dec. 4, 2003
- (86) PCT No.: PCT/US03/38683
  - § 371 (c)(1), (2), (4) Date: Feb. 3, 2006
- (87) PCT Pub. No.: WO2004/050930
  - PCT Pub. Date: Jun. 17, 2004

## (65) **Prior Publication Data**

US 2006/0137772 A1 Jun. 29, 2006

- (51) Int. Cl. *C22C 45/04* (2006.01) *C22C 19/03* (2006.01)
- (52) U.S. Cl. ..... 148/403; 420/449

## (56) **References Cited**

## U.S. PATENT DOCUMENTS

2,106,145	Α	4/1938	Floraday
2,124,538	Α	7/1938	Boyer
3,322,546	Α	5/1967	Tanzman et al.

## (10) Patent No.: US 7,591,910 B2

## (45) **Date of Patent:** Sep. 22, 2009

3,539,192 A	11/1970	Prasse
3,776,297 A	12/1973	Williford et al.
3,948,613 A	4/1976	Weill
3,970,445 A	7/1976	Gale et al.
3,986,867 A	10/1976	Masumoto et al.
3,986,892 A	10/1976	Eve et al.
4,024,902 A	5/1977	Baum
4,067,732 A	1/1978	Ray
4,124,472 A	11/1978	Riegert
4,125,737 A	11/1978	Andersson
4,163,071 A	7/1979	Weatherly et al.
4,260,416 A	4/1981	Kavesh et al.
4,268,567 A	5/1981	Harmony
4,330,027 A	5/1982	Narasimhan
4,374,900 A	2/1983	Hara et al.
4,381,943 A	5/1983	Dickson et al.
4,396,820 A	8/1983	Puschner

### (Continued)

### FOREIGN PATENT DOCUMENTS

CN 1354274 \* 6/2002

#### (Continued)

## OTHER PUBLICATIONS

T.G. Park, Development of new Ni-based amorphous alloys containing no metalloid that have large undercooled liquid regions, Scripta mater 43, (2000), p. 109-114.\*

#### (Continued)

Primary Examiner—George Wyszomierski Assistant Examiner—Mark L Shevin (74) Attorney, Agent, or Firm—Christie, Parker & Hale, LLP

## (57) ABSTRACT

Bulk amorphous alloys based on quaternary Ni—Zr—Ti— Al alloy system, and the extension of this quaternary system to higher order alloys by the addition of one or more alloying elements, methods of casting such alloys, and articles made of such alloys are provided.

## 15 Claims, 2 Drawing Sheets



Channel Number

## U.S. PATENT DOCUMENTS

4,409,296	Α	10/1983	Ward
4,482,612	Α	11/1984	Kuroki et al.
4,487,630	Α	12/1984	Crook et al.
4,488,882	Α	12/1984	Dausinger et al.
4,499,158	Α	2/1985	Onuma et al.
4,515,870	Α	5/1985	Bose et al.
4,523,625	Α	6/1985	Ast
4,526,618	Α	7/1985	Keshavan et al.
4,557,981	Α	12/1985	Bergmann
4,564,396	Α	1/1986	Johnson et al.
4,585,617	Α	4/1986	Tenhover et al.
4,612,059	Α	9/1986	Mori et al.
4,656,099	Α	4/1987	Sievers
4,668,310	А	5/1987	Kudo et al.
4,725,512	Α	2/1988	Scruggs
4,731,253	Α	3/1988	DuBois
4,741,974	Α	5/1988	Longo et al.
4,770,701	Α	9/1988	Henderson et al.
4,810,850	Α	3/1989	Tenkula et al.
4,960,643	Α	10/1990	Lemelson
5,127,969	Α	7/1992	Sekhar
5,189,252	Α	2/1993	Huffman et al.
5,288,344	Α	2/1994	Peker et al.
5,294,462	Α	3/1994	Kaiser et al.
5,368,659	Α	11/1994	Peker et al.
5,380,349	Α	1/1995	Taniguchi et al.
5,440,995	Α	8/1995	Levitt
5,482,577	Α	1/1996	Hashimoto et al.

5,567,251	Α	10/1996	Peker et al.
5,567,532	Α	10/1996	Peker et al.
5,735,975	Α	4/1998	Lin et al.
6,010,580	Α	1/2000	Dandliker et al.
6,183,889	B1	2/2001	Koshiba et al.
6,218,029	B1	4/2001	Rickerby
6,325,868	B1 *	12/2001	Kim et al 148/403
6,326,295	B1	12/2001	Figura
6,521,058	B1 *	2/2003	Inoue et al 148/403
2002/0003013	A1*	1/2002	Hays 148/561
2002/0036034	A1	3/2002	Xing et al.
2003/0140987	A1*	7/2003	Bae et al 148/403
2006/0231169	A1*	10/2006	Park et al 148/403
2006/0237105	A1*	10/2006	Yim et al 148/403

## FOREIGN PATENT DOCUMENTS

DE	010237992 A1	3/2003
GB	2005302	4/1979
JP	56-112449	9/1981
TW	458828 *	10/2001
WO	WO00/68469 A2	11/2000
WO	WO03/040422 A1	5/2003

## OTHER PUBLICATIONS

M.H. Lee et al. Quaternary and quinary Ni-based amorphous alloys in the 3Ni-Zr-Ti-X (X=Al,Si,P) and Ni-Zr-Ti-Si-Y (Y=Sn, Mo, Y) systems. Mat. Res. Soc. Symp. Proc., vol. 644, (2001) L.4.8.1-L4.8. 6.\*

\* cited by examiner

# Figure 1a



# Figure 1b



20

25

## **BULK AMORPHOUS REFRACTORY GLASSES BASED ON THE** NI(-CU-)-TI(-ZR)-AL ALLOY SYSTEM

## FIELD OF THE INVENTION

The present invention is directed to novel bulk solidifying amorphous alloy compositions, and more specifically to Nibase bulk solidifying amorphous alloy compositions.

## BACKGROUND OF THE INVENTION

Amorphous alloys (or glassy alloys or metallic glass alloys) have typically been prepared by rapid quenching a 15 molten material from above the melt temperature to ambient temperature. Generally, cooling rates of 1050 C./sec have been employed to achieve an amorphous structure in these materials. However, at such high cooling rates, the heat cannot be extracted from thick sections of such materials, and, as such, the thickness of articles made from amorphous alloys has been limited to tens of micrometers in at least in one dimension. This limiting dimension is generally referred to as the critical casting thickness and can be related by heat-flow calculations to the cooling rate (or critical cooling rate) required to form the amorphous phase.

This critical thickness (or critical cooling rate) can also be used as a measure of the processability of an amorphous alloy (or glass forming ability of an alloy). Until the early nineties, the processability of amorphous alloys was quite limited and amorphous alloys were readily available only in powder form or in very thin foils or strips with dimensions of less than 100 micrometers.

However, in the early nineties, a new class of amorphous alloys was developed that was based mostly on Zr and Ti alloy  $_{35}$ systems. It was observed that these families of alloys have much lower critical cooling rates of less than 10<sup>3</sup>° C./sec, and in some cases as low as 10° C./sec. Using these new alloys it was possible to form articles of amorphous alloys having critical casting thicknesses from about 1.0 mm to as large as about 20 mm. As such, these alloys are readily cast and shaped into three-dimensional objects using conventional methods such as metal mold casting, die casting, and injection casting, and are generally referred to as bulk-solidifying amorphous alloys (bulk amorphous alloys or bulk glass form-45 ing alloys). Examples of such bulk amorphous alloys have been found in the Zr-Ti-Ni-Cu-Be, Zr-Ti-Ni-Mg—Y—Ni—Cu, La—Ni—Cu—Al, Cu—Al, and Fe-based alloy families. These amorphous alloys exhibit high strength, a high elastic strain limit, high fracture toughness, 50 and other useful mechanical properties, which are attractive for many engineering applications.

Although a number of different bulk-solidifying amorphous alloy formulations have been disclosed in the past, it is still desirable to seek alloy compositions with higher tem- 55 perature stability, better corrosion resistance, higher processability, higher and modulus, higher specific strength and modulus, and lower raw material cost. Accordingly, a need exists to develop novel compositions of bulk solidifying amorphous alloys which will provide improvements in these 60 properties and characteristics.

## SUMMARY OF THE INVENTION

The present invention is directed to Ni-base bulk-solidify- 65 ing amorphous alloys, and particularly to alloys based on the Ni-Zr-Ti-Al quaternary system.

In one exemplary embodiment, the Ni-Zr-Ti-Al quaternary system is extended to higher alloys by adding one or more alloying elements.

In another embodiment, the invention is directed to methods of casting these alloys into three-dimensional bulk objects, while retaining a substantially amorphous atomic structure. In such an embodiment, the term three dimensional refers to an object having dimensions of least 0.5 mm in each dimension, and preferably 1.0 mm in each dimension. The term "substantially" as used herein in reference to the amor-10 phous metal alloy means that the metal alloys are at least fifty percent amorphous by volume. Preferably the metal alloy is at least ninety-five percent amorphous, and most preferably about one hundred percent amorphous by volume.

## BRIEF DESCRIPTION OF THE DRAWINGS

These and other features and advantages of the present invention will be better understood by reference to the following detailed description when considered in conjunction with the accompanying drawings wherein:

FIG. 1a is a graphical depiction of x-ray diffraction scans of an exemplary bulk amorphous alloy; and

FIG. 1b is a graphical depiction of differential scanning calorimetry (DSC) plots of an exemplary bulk amorphous alloy.

### DESCRIPTION OF THE INVENTION

The present invention is directed to bulk-solidifying amorphous alloys based on a Ni-Zr-Ti-Al quaternary system, and the extension of this ternary system to higher order alloys by the addition of one or more alloying elements. These alloys are referred to as Ni-based alloys herein.

Although a number of different Ni-Zr-Ti-Al combinations may be utilized in the Ni-based alloys of the current invention, a range of Ni content from about 27 to 58 atomic percentage, a range of Ti content from about 8 to 22 atomic percentage, a range of Zr content from about 13 to about 37 atomic percent, and a range of Al content from about 5 to about 17 atomic percent are preferably utilized.

To increase the ease of casting such alloys into larger bulk objects, and for increased processability, a formulation having a range of Ni content from about 37 to 49 atomic percentage, a range of Ti content from about 13 to 20 atomic percentage, a range of Zr content from about 25 to about 32 atomic percent, and a range of Al content from about 8 to about 12 atomic percent is preferred. Still more preferable is a Ni-based alloy having a range of Ni content from about 39 to 47 atomic percentage, a range of Ti content from about 15 to 18 atomic percentage, a range of Zr content from about 27 to about 30 atomic percent, and a range of Al content from about 9 to about 11 atomic percent.

Although only combinations of Ni, Ti, Zr and Al have been discussed thus far, it should be understood that other elements can be added to improve the ease of casting the Ni-based alloys of the invention into larger bulk objects or to increase the processability of the alloys. Additional alloying elements of potential interest are Cu, Co, Fe, and Mn, which can each be used as fractional replacements for Ni; Hf, Nb, Ta, V, Cr, Mo and W, which can be used as fractional replacements for Zr and Ti; and Si, Sn, Ge, B, and Sb, which can be used as fractional replacements for Al.

It should be understood that the addition of the above mentioned additive alloying elements may have a varying degree of effectiveness for improving the processability of the Ni-base alloys in the spectrum of compositional ranges

45

described above and below, and that this should not be taken as a limitation of the current invention.

Given the above discussion, in general, the Ni-base alloys of the current invention can be expressed by the following general formula (where a, b, c are in atomic percentages and 5 x, y, z are in fractions of whole):

 $(\mathrm{Ni}_{1\text{-}x}\mathrm{TM}_x)_a((\mathrm{Ti},\mathrm{Zr})_{1\text{-}y}\mathrm{ETM}_y)_b(\mathrm{Al}_{1\text{-}z}\mathrm{AM}_z)_c,$ 

where a is in the range of from 27 to 58, b in the range of 21 to 59, c is in the range of 5 to 17 in atomic percentages; ETM<sup>10</sup> is an early transition metal selected from the group of Hf; Nb, Ta, V, Cr, Mo, and W, and preferably from the group of Hf and Nb; TM is a transition metal selected from the group of Mn, Fe, Co, and Cu, and preferably from the group of Cu and Co; and AM is an additive material selected from the group of Si,<sup>15</sup> Sn, Ge, B, and Sb, and preferably from the group of Si and Sn. In such an embodiment the following constraints are given for the x, y and z fraction: x is less than 0.3, y is less than 0.3, z is less than 0.3, and the sum of x, y and z is less than about 0.5, and under the further constraint that the content of Ti content<sup>20</sup> is more than 8 atomic percent and Zr content is more than 13 atomic percent.

Preferably, the Ni-based alloys of the current invention are given by the formula:

 $(Ni_{1-x}TM_x)_a((Ti,Zr)_{1-y}ETM_y)_b(Al_{1-x}AM_x)_c,$ 

where a is in the range of from 37 to 49, b in the range of 38 to 52, c is in the range of 8 to 12 in atomic percentages; ETM is an early transition metal selected from the group of Hf, Nb, 30 Ta, V, Cr, Mo, and W, and preferably from the group of Hf and Nb; TM is a transition metal selected from the group of Mn, Fe, Co, and Cu, and preferably from the group of Cu and Co; and AM is an additive material selected from the group of Si, Sn, Ge, B, and Sb, and preferably from the group of Si and Sn. 35 In such an embodiment the following constraints are given for the x, y and z fraction: x is less than 0.2, y is less than 0.2, z is less than 0.2, and the sum of x, y and z is less than about 0.3, and under the further constraint that the content of Ti content is more than 13 atomic percent and Zr content is more than 25 40 atomic percent.

Still more preferably, the Ni-based alloys of the current invention are given by the formula:

 $(Ni_{1-x}TM_x)_a((Ti,Zr)_{1-y}ETM_y)_b(Al_{1-z}AM_z)_c,$ 

where a is in the range of from 39 to 47, b in the range of 42 to 48, c is in the range of 9 to 11 in atomic percentages; ETM is an early transition metal selected from the group of Hf, Nb, Ta, V, Cr, Mo, and W and preferably from the group of Hf and Nb; TM is a transition metal selected from the group of Mn, 50 Fe, Co, and Cu and preferably from the group of Cu and Co; and AM is an additive material selected from the group of Si, Sn, Ge, B, and Sb and preferably from the group of Si and Sn. In such an embodiment the following constraints are given for the x, y and z fraction: x is less than 0.1, y is less than 0.1, z is 55 less than 0.1, and the sum of x, y and z is less than about 0.2 and under the further constraint that the content of Ti content is more than 15 atomic percent and Zr content is more than 27 atomic percent.

For increased processability, the above mentioned alloys 60 are preferably selected to have five or more elemental components. It should be understood that the addition of the above mentioned additive alloying elements may have a varying degree of effectiveness for improving the processability within the spectrum of the alloy compositional ranges 65 described above and below, and that this should not be taken as a limitation of the current invention. 4

Other alloying elements can also be added, generally without any significant effect on processability when their total amount is limited to less than 2%. However, a higher amount of other elements can cause a degradation in the processability of the alloys, and in particular when compared to the processability of the exemplary alloy compositions described below. In limited and specific cases, the addition of other alloying elements may improve the processability of alloy compositions with marginal critical casting thicknesses of less than 1.0 mm. It should be understood that such alloy compositions are also included in the current invention.

Exemplary embodiments of the Ni-based alloys in accordance with the invention are described in the following:

In one exemplary embodiment of the invention the Ni-<sup>15</sup> based alloys have the following general formula:

$$Ni_{100-a-b-c}Ti_aZr_bAl_c$$

where 8<a<22, 13<b<37, 5<c<17.

In one preferred embodiment of the invention the Ni-based alloys have the following general formula

Ni100-a-b-cTiaZrbAlc,

where 13<a<20, 25<b<32, 8<c<12.

The most preferred embodiment of the ternary Ni-based alloys have the following general formula

 $Ni_{100-a-b-c}Ti_aZr_bAl_c$ ,

where 15<a<18, 27<b<30, 9<c<11.

Although higher order combinations of Ni-base alloys with five or more elemental components can be utilized in the current invention, in one particularly exemplary embodiment of the invention, the five component alloy system comprises combinations of Ni—Ti—Zr—Al—Cu, where the Ni content is from about 27 to 47 atomic percentage, the Ti content is from about 8 to 22 atomic percentage, the Zr content is from about 13 to about 37 atomic percent, the Cu content is up to 17 atomic percent, and the Al content is from about 5 to about 17 atomic percent.

To increase the ease of casting such alloys into larger bulk objects, and for increased processability, a formulation having a range of Ni content from about 37 to 44 atomic percentage, a range of Ti content from about 13 to 20 atomic percentage, a range of Zr content from about 25 to about 32 atomic percent, a range of Cu content from about 2 to 8 atomic percentage, and a range of Al content from about 2 to 8 atomic percentage, and a range of Al content from about 30 to 42 atomic percent is preferred. Still more preferable is a Nibased alloy having a range of Ni content from about 39 to 42 atomic percentage, a range of Zr content from about 15 to 18 atomic percentage, a range of Zr content from about 27 to about 30 atomic percent, a range of Cu content from about 3 to about 7 atomic percent and a range of Al content from about 9 to about 11 atomic percent.

It should be understood that other elements can be added to improve the ease of casting the five component Ni-based alloys of the invention into larger bulk objects or to increase the processability of the alloys. Additional alloying elements of potential interest are Co, Fe, and Mn, which can each be used as fractional replacements for Ni and Cu moiety; Hf; Nb, Ta, V, Cr, Mo and W, which can be used as fractional replacements for Zr and Ti moiety; and Si, Sn, Ge, B, and Sb, which can be used as fractional replacements for Al.

It should be understood that the addition of the above mentioned additive alloying elements may have a varying degree of effectiveness for improving the processability of the Ni-base alloys in the spectrum of compositional ranges

described above and below, and that this should not be taken as a limitation of the current invention.

Given the above discussion, in general, the Ni-base alloys based on the Ni—T—Zr—Cu—Al combination can be expressed by the following general formula (where a, b, c are 5 in atomic percentages and x, y, z are in fractions of whole):

 $((\operatorname{Ni}\operatorname{Cu})_{1-x}\operatorname{TM}_x)_a((\operatorname{Ti},\operatorname{Zr})_{1-y}\operatorname{ETM}_y)_b(\operatorname{Al}_{1-z}\operatorname{AM}_z)_c,$ 

where a is in the range of from 27 to 58, b in the range of 21 to 59, c is in the range of 5 to 17 in atomic percentages; ETM<sup>10</sup> is an early transition metal selected from the group of Hf, Nb, Ta, V, Cr, Mo, and W, and preferably from the group of Hf and Nb; TM is a transition metal selected from the group of Mn, Fe, and Co, and preferably Co; and AM is an additive material selected from the group of Si, Sn, Ge, B, and Sb, and preferably from the group of Si and Sn. In such an embodiment the following constraints are given for the x, y and z fraction: x is less than 0.3, y is less than 0.3, z is less than 0.3, and the sum of x, y and z is less than about 0.5, and under the further constraint that the content of Ti content is more than 8 atomic<sup>20</sup> percent, Zr content is more than 13 atomic percent and Cu content is less than 17 atomic percent.

Preferably, the Ni-based alloys of the current invention are given by the formula:

 $((Ni,Cu)_{1-x}TM_x)_a((Ti,Zr)_{1-y}ETM_y)_b(Al_{1-z}AM_z)_c,$ 

where a is in the range of from 37 to 49, b in the range of 38 to 52, c is in the range of 8 to 12 in atomic percentages; ETM is an early transition metal selected from the group of Hf, Nb, Ta, V, Cr, Mo, and W, and preferably from the group of Hf and Nb; TM is a transition metal selected from the group of Mn, Fe, and Co, and preferably Co; and AM is an additive material selected from the group of Si, Sn, Ge, B, and Sb, and preferably from the group of Si and Sn. In such an embodiment the following constraints are given for the x, y and z fraction: x is less than 0.2, y is less than 0.2, z is less than 0.2, and the sum of x, y and z is less than about 0.3, and under the further constraint that the content of Ti content is more than 13 atomic percent, Zr content is more than 25 atomic percent, 40

Still more preferably, the Ni-based alloys of the current invention are given by the formula:

 $((Ni,Cu)_{1-x}TM_x)_a((Ti,Zr)_{1-y}ETM_y)_b(Al_{1-z}AM_z)_c,$ 

where a is in the range of from 39 to 47, bin the range of 42 to 48, c is in the range of 9 to 11 in atomic percentages; ETM is an early transition metal selected from the group of Hf, Nb, Ta, V, Cr, Mo, and W, and preferably from the group of Hf and Nb; TM is a transition metal selected from the group of Mn, 50 Fe, and Co, and preferably Co; and AM is an additive material selected from the group of Si, Sn, Ge, B, and Sb, and preferably from the group of Si and Sn. In such an embodiment the following constraints are given for the x, y and z fraction: x is less than 0.1, y is less than 0.1, z is less than 0.1, and the sum 55 of x, y and z is less than about 0.2, and under the further constraint that the content of Ti content is more than 15 atomic percent, Zr content is more than 27 atomic percent, and Cu content is from about 3 to 7 atomic percentage.

Other alloying elements can also be added, generally without any significant effect on processability when their total amount is limited to less than 2%. However, a higher amount of other elements can cause a degradation in the processability of the alloys, an particularly when compared to the processability of the exemplary alloy compositions described 65 below. In limited and specific cases, the addition of other alloying elements may improve the processability of alloy

compositions with marginal critical casting thicknesses of less than 1.0 mm. It should be understood that such alloy compositions are also included in the current invention.

Exemplary embodiments of the Ni-based alloys in accordance with the invention are described in the following examples:

In one exemplary embodiment of the invention the Nibased alloys have the following general formula

Ni100-a-b-c-dTiaZrbAlcCud

where 8<a<22, 13<b<37, 5<c<17, and 0<d<17.

In one preferred embodiment of the invention the Ni- based alloys have the following general formula

Ni100-a-b-c-dTiaZrbAlcCud,

where 13<a<20, 25<b<32, 8<c<12, and 2<d<8.

The most preferred embodiment of the pentiary Ni-base alloys have the following general formula

 $Ni_{100-a-b-c-d}Ti_aZr_bAl_cCu_d$ 

where 15<a<18, 27<b<30, 9<c<11, and 3<d<7.

Alloys with these general formulations have been cast directly from the melt into copper molds to form fully amor-<sup>25</sup> phous strips or rods of thickness up to 6 mm. Examples of these bulk metallic glass forming alloys are given in Table 1, below.

TABLE 1

Alloy Composition (at %)	Critical Casting Thickness (mm)
Ni <sub>45</sub> Ti <sub>20</sub> Zr <sub>25</sub> Al <sub>10</sub>	2
Ni45Ti20Zr20Al10Hf5	2
Ni32 5Ti12 5Zr32 5Al10Cu12 5	3
$Ni_{33}Ti_{13}Zr_{32}Al_{10}Cu_{12}$	3
Ni <sub>37</sub> Ti <sub>18</sub> Zr <sub>20</sub> Al <sub>10</sub> Cu <sub>6</sub>	3
Ni40Ti16Zr23Al10CueHf5	3
Ni40Ti16Zr28Al11Cu5	3
$Ni_{40}Ti_{18}Zr_{26}Al_{10}Cu_{6}$	3
$Ni_{35}Ti_{14}Zr_{31}Al_{10}Cu_{10}$	4
Ni <sub>37</sub> Ti1 <sub>5</sub> Zr <sub>30</sub> Al <sub>10</sub> Cu <sub>8</sub>	4
Ni <sub>30</sub> Ti <sub>19</sub> Zr <sub>20</sub> Al <sub>10</sub> Cu <sub>4</sub>	4
Ni <sub>30 6</sub> Ti <sub>15 84</sub> Zr <sub>27 72</sub> Al <sub>0 0</sub> Cu <sub>5 04</sub> Si <sub>1</sub>	4
Ni40Ti16Zr28Al10Cuc	4
Ni40 5Ti16 2Tr28 2Al10Cu5	4
$Ni_{41}Ti_{16}Zr_{28}Al_{10}Cu_{5}$	4
$Ni_{41} = Ti_{10} Zr_{27} Al_{10} Cu_{35}$	4
$Ni_{42}Ti_{15}Zr_{28}Al_{10}Cu_{5}$	4
$Ni_{42}Ti_{10}Zr_{26}Al_{10}Cu_{2}$	4
$Ni_{38}$ $_{7}Ti_{17}$ $_{2}Zr_{20}$ $_{8}Al_{10}Cu_{43}$	5
$Ni_{20}Ti_{17}Zr_{20}Al_{10}Cu_5$	5
$N_{120}T_{117} + Z_{178} + A_{10}C_{10}$	5
$Ni_{39} = Ti_{16} = Zr_{29} = Al_{10}Cu_{4.4}$	5
$Ni_{40}Ti_{16}Zr_{20}Al_{10}Cu_5$	5
$Ni_{40}Ti_{17}Zr_{28}Al_{10}Cu_5$	5
$Ni_{40}Ti_{17}Zr_{29}Al_{10}Cu_4$	5
$Ni_{40}Ti_{17} z_{728} Al_{10}Cu_{4}$	5
$Ni_{40} Ti_{16} Zr_{28}Al_{10}Cu_{5}$	5
Ni40 5Ti16 75Zr28 25Al10Cu4 5	5
$Ni_{40.5}Ti_{1.7}Zr_{28.5}Al_{10}Cu_4$	5
$Ni_{41}Ti_{17}Zr_{28}Al_{10}Cu_4$	5
$Ni_{41}Ti_{17} z Zr_{27} Al_{10}Cu_{4}$	5
$Ni_{41} = Ti_{17} = Zr_{27} = Al_{10}Cu_{3} = S$	5
$Ni_{39}Ti_{16}Zr_{29}Al_{10}Cu_6$	6
Ni30Ti165Zr285Al10Cu6	6
Ni30 8Ti 15 02Zr27 86Alo 05Cu 5 07Si 0 5	6
Ni <sub>30 8</sub> Ti <sub>16 42</sub> Zr <sub>28 36</sub> Al <sub>9 95</sub> Cu <sub>5 97</sub> Si <sub>0 5</sub>	6
$Ni_{39} {}_{8}Ti_{16} {}_{42}Zr_{28} {}_{36}Al_{9} {}_{95}Cu_{4} {}_{97}Ge_{1}$	6
$Ni_{40}Ti_{16}SZr_{28}SAl_{10}Cu_{5}$	6
Ni40Ti165Zr285Al10Cu45Si05	6
$Ni_{40}Ti_{17}Zr_{28}Al_{10}Cu_{4.5}$	6
$Ni_{40}Ti_{17}Zr_{28}Al_{10}Cu_{45}Si_{05}$	6
Ni40 25 Ti 16 5Zr28 5Al 10Cu4 75	6
10120 1010 2010 IV TILD	

TABLE 1-continued

Alloy Composition (at %)	Critical Casting Thickness (mm)	
Ni40 3Ti 16 42Zr28 35Al 95Cu4 48Si 5	6	
Ni <sub>40.4</sub> Ti <sub>16.46</sub> Zr <sub>28.43</sub> Al <sub>9.97</sub> Cu <sub>4.49</sub> Si <sub>0.3</sub>	6	
Ni <sub>40.5</sub> Ti <sub>16.25</sub> Zr <sub>28.75</sub> Al <sub>10</sub> Cu <sub>4.5</sub>	6	
Ni <sub>40.5</sub> Ti <sub>16.5</sub> Zr <sub>28.5</sub> Al <sub>10</sub> Cu <sub>4.5</sub>	6	
Ni40.5Ti16.5Zr28.5Al10Cu4Sn1	6	
Ni <sub>40.5</sub> Ti <sub>17</sub> Zr <sub>28</sub> Al <sub>10</sub> Cu <sub>4.5</sub>	6	
Ni40.75Ti16.5Zr28.5Al10Cu4.25	6	
Ni <sub>41</sub> Ti <sub>165</sub> Zr <sub>285</sub> Al <sub>10</sub> Cu <sub>4</sub>	6	
$Ni_{41}Ti_{17}Zr_{28}Al_{10}Cu_4$	6	

The above table gives the maximum thickness for which 15 fully amorphous strips are obtained by metal mold casting using this exemplary formulation. Evidence of the amorphous nature of the cast strips can be determined by x-ray diffraction spectra. Typical x-ray diffraction spectra for fully amorphous alloy strips is provided in FIG. 1a.

The invention is also directed to methods of casting these alloys into three-dimensional bulk objects, while retaining a substantially amorphous atomic structure. In such an embodiment, the term three dimensional refers to an object having 25 dimensions of least 0.5 mm in each dimension. The term "substantially" as used herein in reference to the amorphous alloy (or glassy alloy) means that the metal alloys are at least fifty percent amorphous by volume. Preferably the metal alloy is at least ninety-five percent amorphous and most pref-30 erably about one hundred percent amorphous by volume.

In general, crystalline precipitates in bulk amorphous alloys are highly detrimental to their properties, especially to the toughness and strength, and as such generally preferred to 35 a minimum volume fraction possible. However, there are cases in which, ductile crystalline phases precipitate in-situ during the processing of bulk amorphous alloys forming a mixture of amorphous and crystalline phases, which are indeed beneficial to the properties of bulk amorphous alloys 40 especially to the toughness and ductility. These cases of mixed-phase alloys, where such beneficial precipitates coexist with amorphous phase are also included in the current invention. In one preferred embodiment of the invention, the precipitating crystalline phases have body-centered cubic 45 crystalline structure.

Another measurement of the processability of amorphous alloys can be described by defining a  $\Delta$ Tsc (super-cooled liquid region), which is a relative measure of the stability of the viscous liquid regime of the alloy above the glass transi- $_{50}$ tion.  $\Delta Tsc$  is defined as the difference between Tx, the onset temperature of crystallization, and Tsc, the onset temperature of the super-cooled liquid region. These values can be conveniently determined using standard calorimetric techniques such as DSC measurements at 20° C./min. For the purposes of 55 this disclosure, Tg, Tsc and Tx are determined from standard DSC (Differential Scanning Calorimetry) scans at 20° C./min. Tg is defined as the onset temperature of glass transition, Tsc is defined as the onset temperature of super-cooled liquid region, and Tx is defined as the onset temperature of 60 crystallization. Other heating rates such as 40° C./min, or 10° C./min can also be utilized while the basic physics of this technique are still valid. All the temperature units are in ° C.

Generally, a larger  $\Delta$ Tsc is associated with a lower critical cooling rate, though a significant amount of scatter exists at 65 As can be seen from the data, the Young's modulus for these ΔTsc values of more than 40° C. Bulk-solidifying amorphous alloys with a  $\Delta$ Tsc of more than 40° C., and preferably more

than 60° C., and still more preferably a  $\Delta$ Tsc of 90° C. and more are very desirable because of the relative ease of fabrication.

Typical examples of DSC scans for fully amorphous strips are given in FIG. 1b. The vertical arrows in FIG. 1b indicate the location of the observed glass transition and the observed crystallization temperature of an exemplary alloy which was cast up to 5 mm thick amorphous strips. Further, Table 2, 10 below gives the measured glass transition temperature and crystallization temperatures obtained for the alloys using Differential Scanning Calorimetry scans at heating rates of 10-20 K/s. The difference between Tg and Tx,  $\Delta T=Tx-Tg$ , is measure of the temperature range over which the supercooled liquid is stable against crystallization when the glass is heated above Tg. The value of  $\Delta T$  is a measure of the "processability" of the amorphous material upon subsequent heating. Values of this parameter are also given in Table 2, as reported  $_{20}$  values ranging up to  $\Delta T{\sim}50$  K are observed.

TABLE 2

Alloy Composition (Atomic %)	Critical Casting Thickness	Tg (K)	Tx (K)	ΔT (K)
Ni <sub>45</sub> Ti <sub>20</sub> Zr <sub>35</sub>	0.5	725	752	27
Ni <sub>45</sub> Ti <sub>20</sub> Zr <sub>27</sub> Al <sub>8</sub>	<0.5	761	802	41
Ni45Ti20Zr25Al10	2	773	818	45
Ni <sub>45</sub> Ti <sub>20</sub> Zr <sub>23</sub> Al <sub>12</sub>	<0.5	783	832	49
Ni <sub>40</sub> Ti <sub>16</sub> Zr <sub>28</sub> Al <sub>10</sub> Cu <sub>6</sub>	3.5	766	803	42
Ni40Ti17Zr28Al10Cu5	4	762	808	46
Ni40.5Ti16.5Zr28Al10Cu5	4	764	809	45
Ni40Ti16.5Zr28.5Al10Cu5	5	763	809	46
$Ni_{39.8}Ti_{15.92}Zr_{27.86}Al_{9.95}Cu_{5.97}Si_{0.5}$	5	768	815	47

To assess the strength and elastic properties of these new metallic glasses, we have carried out measurements of the Vickers Hardness and compression tests. Typical data are shown in Table 3, below. Typical values range from V.H.=700 to 900. Based on this data, and using empirical scaling rules, one can estimate the yield strength, Y.S. of these materials. Here we have used the approximate formula:

## $Y.S.=(V.H.)\times 3$

where the approximate yield strength is given in MPa and the Vickers Hardness is given in Kg/mm<sup>2</sup>. The yield strength values can be as high as 2.5 GPa and among the largest values of Y.S. of any bulk amorphous alloys reported to date.

Table 3 also gives values for Poisson ratio (v), shear modulus  $(\mu)$  and Young's modulus (E) of exemplary alloys. These elastic properties data were obtained by measuring the sound propagation velocities of plane waves (longitudinal and transverse,  $C_1$  and  $C_s$ , respectively) in the alloys, then using the following relations (valid for isotropic materials such as amorphous alloys):

v=(2-x)/(2-2x)=Poisson's ratio, where  $x=(C_1/C_s)^2$ 

 $\mu = \rho^* C_s^2$  = shear modulus, where  $\rho$  is density

 $E = \mu * 2(1 + \nu) =$  Young's modulus

new bulk amorphous alloys is relatively large, i.e., these are relatively "stiff" bulk amorphous alloys.

9

TARLE	3
$\mathbf{n}$	~

Alloy Composition (Atomic %)	Vickers Hardness	Yield Strength (GPa)	Poisson's ratio	Shear Modulus (GPa)	Young Modulus (GPa)
Ni <sub>45</sub> Ti <sub>20</sub> Zr <sub>25</sub> Al <sub>10</sub>	791	2.37	0.36	42.7	116
Ni <sub>40</sub> Ti <sub>16</sub> Zr <sub>28</sub> Al <sub>10</sub> Cu <sub>6</sub>	780	2.2	0.361	41.5	113
Ni <sub>40</sub> Ti <sub>17</sub> Zr <sub>28</sub> Al <sub>10</sub> Cu <sub>5</sub>	862	2.3	0.348	50.1	135.1
Ni40.5Ti16.5Zr28Al10Cu5	787	2.36	0.36	42.5	115.5
Ni40Ti16.5Zr28.5Al10Cu5	800	2.4	0.355	45.6	123.7
$Ni_{39.8}Ti_{15.92}Zr_{27.86}Al_{9.95}Cu_{5.97}Si_{0.5}$	829	2.49	0.36	43.5	118.2

In sum, the inventors discovered a new family of bulk metallic glass forming alloys having exceedingly high values 15 alloy has a Young's modulus of greater than 140 GPa. of hardness, elastic modulus (E), yield strength, and glass transition temperature, Tg. The values of these characteristic properties are among the highest reported for any known metallic alloys which form bulk metallic glass. Here, "bulk" is taken to mean that the alloys have a critical casting thick- <sup>20</sup> alloy is substantially amorphous. ness of the order of 0.5 mm or more. The properties of these new alloys make them ideal candidates for many engineering applications.

Although specific embodiments are disclosed herein, it is expected that persons skilled in the art can and will design  $^{25}$ alternative Ni-based alloys that are within the scope of the following claims either literally or under the Doctrine of Equivalents.

What is claimed is:

1. A glass forming alloy consisting of an alloy having a composition given by:

 $Ni_{100-a-b-c-d}$   $Ti_a Zr_b Al_c Cu_d$ , where 15<a<18, 27<b<30, 9<c<11.3<d<7.

2. The glass forming alloy described in claim 1 wherein the alloy has a  $\Delta$ Tsc of more than 40° C.

3. The glass forming alloy described in claim 1 wherein the alloy has a Vickers hardness greater than 700 Kg/mm<sup>2</sup>.

4. The glass forming alloy described in claim 1 wherein the alloy has a yield strength of greater than 2.5 GPa.

5. The glass forming alloy described in claim 1 wherein the

6. The glass forming alloy described in claim 1 wherein the alloy has a ratio of glass transition temperature to liquidus temperature of around 0.6 or more.

7. The glass forming alloy described in claim 1 wherein the

8. The glass forming alloy described in claim 1 wherein the alloy contains a ductile crystalline phase precipitate.

9. The glass forming alloy described in claim 1 wherein the critical cooling rate is less than about 1,000° C./sec.

10. A glass forming alloy consisting of an alloy having a composition given by:

 $Ni_{100-a-b-c-d}Ti_{a}Zr_{b}Al_{c}CU_{d}$ , where 15<a<18, 27<b<30, 9<c<11, 3<d<7, and a+b+c+d is in the range of from 58 to 61.

11. The glass forming alloy described in claim 10 wherein the critical cooling rate is less than about 1,000° C./sec.

12. A three dimensional article made from the alloy of claim 1 having an amorphous phase.

13. A three dimensional article made from the alloy of <sup>35</sup> claim 10 having an amorphous phase.

14. The glass forming alloy of claim 1 having a composition of Ni<sub>40</sub>Ti<sub>16</sub>Zr<sub>28</sub>Al<sub>10</sub>Cu<sub>6</sub>.

15. The glass forming alloy of claim 1 having a composition of  $Ni_{40}Ti_{17}Zr_{28}Al_{10}Cu_5$ .

## UNITED STATES PATENT AND TRADEMARK OFFICE CERTIFICATE OF CORRECTION

 PATENT NO.
 : 7,591,910 B2

 APPLICATION NO.
 : 10/535317

 DATED
 : September 22, 2009

 INVENTOR(S)
 : Xu et al.

Page 1 of 1

It is certified that error appears in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

On the Title Page:

The first or sole Notice should read --

Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 327 days.

Signed and Sealed this

Twenty-first Day of September, 2010

Jand J.K -gApos

David J. Kappos Director of the United States Patent and Trademark Office

## UNITED STATES PATENT AND TRADEMARK OFFICE CERTIFICATE OF CORRECTION

PATENT NO.: 7,591,910 B2APPLICATION NO.: 10/535317DATED: September 22, 2009INVENTOR(S): Donghua Xu et al.

Page 1 of 1

It is certified that error appears in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

Column 1, line 5 Insert after the "Title" and before the "Field of the Invention" -- STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH OR DEVELOPMENT The U.S. Government has certain rights in this invention pursuant to Grant No. DAAD19-01-1-0525 awarded by the United States Army Research Office. --

In the Claims

Column 9, Claim 1, line 34 After

After "11," Insert -- and --

Signed and Sealed this

Twenty-first Day of December, 2010

Jand J. Kgppos

David J. Kappos Director of the United States Patent and Trademark Office