Abstract: Composite phase structures of early transition metal-based metallic alloys, including those consisting of crystalline, quasicrystalline and amorphous phases, can be obtained in a controllable way upon direct (in-situ) cooling (solidification) of the alloy, realized either by adjusting the alloy compositions at a fixed cooling rate or by changing the cooling rates for a given alloy composition. Some embodiments are based on the addition of later transition metals, mainly of Cu with Ni or Fe with Co in early transition metal based (mainly Ti and Zr or Hf and Nb) metallic alloys. If cooling rate is on the scale of 10⁻⁵ °C/s, a wholly amorphous structure is obtained for most of the compositions. At reduced cooling rates, composite structures with different kinds of phases can be achieved. Ni addition promotes the formation of quasicrystalline phases, especially for Ti-rich alloy compositions with Beryllium. A critical percentage of Ni addition exists below which no quasicrystalline phases will be formed. This critical Ni percentage varies closely with the relative Ti-Zr content, decreasing with increasing relative Ti content. Additions of Cu, Co and Fe do not facilitate the formation of quasicrystalline phase, instead formation of amorphous and/or crystalline phases are obtained. Thus, the additions of the different components can be controllably varied to achieve different kinds of desired phase structures. Other materials properties can also be controlled.

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

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TIZR-BASED METALLIC ALLOYS: CONTROLLABLE COMPOSITE PHASE STRUCTURES AND RELATED PROPERTIES

5 CROSS-REFERENCE TO RELATED APPLICATIONS

This application claims benefit of priority under 35 U.S.C. § 119(e) from U.S. Patent Application No. 60/689,813, filed June 13, 2005, the entire disclosure of which is hereby incorporated by reference herein.

10 GOVERNMENT SUPPORT

Work described herein was supported by Federal Government Grant No. N00014-01-1-0961 awarded by the Defense Advanced Research Projects Agency. The Government has certain rights in the invention.

FIELD OF THE INVENTION

The present invention relates to controlling composite phase structures in metallic alloys. More particularly, the present invention relates to, but not limited thereto, controlling composite phase structures early transition metal based metallic alloys as well as related properties either by adjustments of the alloy composition at a fixed cooling rate or by different cooling rates.
BACKGROUND OF THE INVENTION

Some embodiments of this invention focus on the formation of controllable composite phase structures in early transition metal based (mainly of Ti and Zr) metallic alloys as well as related properties. Control of the different desired structures can be achieved either by cooling the alloy melts of a given composition at different cooling rates or by adjustment of the alloy composition at a fixed cooling rate.

Thermodynamically, amorphous and/or quasicrystalline phases are in a metastable state compared with their equilibrium crystalline counterparts. Hence there is always a tendency for the crystalline phases to form from the alloy melt upon cooling, provided that the cooling rate is sufficiently slow. In this sense, the formation of amorphous or quasicrystalline phases upon cooling faces the same challenge, that is, avoiding the formation of equilibrium crystalline phases. In addition to the effort of making the alloy melt more thermodynamically stable at lowered temperatures, much more work (research) has been done dealing with the crystallization kinetics. Early work, done by Turnbull, suggested that a nucleation rate less than $10^{-6}/\text{cm}^3\cdot\text{s}$ will avoid the formation of crystalline phases, with an assumption that growth occurs fast, once the nucleation rate is higher than this value, the resulting alloy will be fully crystallized. Later, researchers combined the nucleation and growth of crystalline phases together and developed TTT diagrams to predict the avoidance of crystalline phases upon cooling.

More recently, work done on La alloys has confirmed that once the growth of crystalline phases can be slowed down, one may obtain alloys with a dominant volume fraction of non-equilibrium phases (in this case, amorphous phase) at lowered cooling rates, even if the nucleation is not avoidable.
Exploration and synthesis of non-equilibrium phases (here we mean amorphous and quasicrystalline phases) have been one of the challenging projects in materials science field over the past several decades. Compared with the first report of a quasicrystalline structure in Al-Mn alloys in 1984, the study of amorphous structures can be traced back to the work of Duwez at Caltech in the 1960s. Studies of quasicrystalline and glassy alloys were also motivated by the technological properties of these materials as functional and structural materials. The results so far have been fruitful. Large-sized quasicrystalline samples (or, at least the quasicrystalline phases are dominant in volume fraction) have been prepared in Al-, Mg- and Cd-based alloys. In addition, formation of amorphous phases, both brittle and ductile, in various sample dimensions, has been reported extensively. In terms of sample size, Zr-, Pd-, Y- and Fe-based metallic alloys are able to form a wholly amorphous phase with the shortest dimension over 1 cm, as well as forming “glassy ingot” samples, that is, the as-made ingot is in a fully amorphous state. Most of amorphous alloys obtained are brittle, showing no deformability at room temperature. While Zr- and some of the Ti- and Cu-based metallic glasses show some degree of ductility, which are believed to be promising as structural materials. The development of these two kinds of non-equilibrium structures followed two parallel lines and had not been correlated until the late 1980s, when Poon and Shiflet at UVA discovered the Al-rich amorphous alloy during their exploration of Al-rich quasicrystalline formation alloys. Even in that case, there is no overlapping of chemical compositions in terms of forming amorphous and quasicrystalline phases alternatively. More links between amorphous and quasicrystalline phases have been found between these two classes of structures since then, as exemplified by recent reports that in bulk metallic glass forming alloys, quasicrystalline phases are usually found in the initial annealing stage of the amorphous alloys.
Although the pursuit of monolithic non-equilibrium phases can lead to fundamental understanding of material properties, improvements of structural properties are usually achieved in multi-phase materials. In fact, according to one of the concluding statements in a report written by a panel of the National Research Council on materials research, "monolithic structural materials composed of metal alloys are not likely to enjoy major improvements in any of several mechanical properties." This document refers to the discoveries and productions of new metal alloys that should include, but are not limited to, the non-equilibrium phase (amorphous and quasicrystalline phases) alloys we write about here. As also revealed in the literature, a monolithic metallic glass, even if it is ductile, can only stand very limited plastic deformation before the final fracture, typically less than 2%, especially when tested in tension mode. The reason for this low ductility is that once deformation occurs, shear bands form in the deformation slip area and propagate quickly and easily through the whole sample cross-section, leading to the final fracture of the sample. The method used to solve this problem is similar to that used in crystalline structured materials, that is, by introducing a second phase, which can either hinder or pin down the swift spread of the shear band. As a result, any further deformation will take place through the occurrence of shear bands elsewhere in the sample and the elongation is therefore improved. There are generally two ways to generate such a composite structure. One is to introduce external fine particles during solidification of the glass-forming alloy melt, as described in an US patent 5,368,658 (hereby incorporated by reference herein in its entirety). The other is to form a second phase, as will be discussed in this invention, which in-situ precipitates during solidification of the alloy melt, or alternatively, to form a second phase by annealing the as-prepared amorphous alloys at appropriate temperatures. This second phase can be either crystalline or quasicrystalline.

As will be seen in this invention, by adjustment of the alloy composition and/or by
changing the cooling rate of the alloy melt, one can obtain different kinds of composite phase structures in a controllable way.

The present invention provides the important advantage of controlling composite phase structures and related properties of metallic alloys through a predetermined transition metal ratio or through control of the cooling rate.

We selected Ti as a base element to start with, on consideration that Ti alloys have a wide application potential in different fields, such as, the medical and aerospace industries. By obtaining various desired phase structures in a controllable way, we aimed at developing low mass density (due to the low density of Ti) metallic alloys with promising mechanical and other kinds of properties. The current invention originated from our study of the effect of later transition metal additions, mainly of Cu and Ni (Fe and Co are also evaluated), on the formation of different composite phase structures, including crystalline, quasicrystalline and amorphous phases, in early transition metal based (mainly of Ti and Zr; Hf and Nb are also included) metallic alloys upon cooling of the alloy melts. Zr and Be was introduced based on our knowledge of the atomic size effect on the glass forming ability.

TiZr alloys are found to show a tendency of forming quasicrystalline structure upon cooling when Ni is introduced. It was further found that the introduction of Be strengthens this tendency, which is especially true for the Ti-rich alloys. For the Zr-rich alloys, somehow, the quasicrystalline phase structure seems not as easy to form as in the case of Ti-rich alloys with the occurrence of Ni. There exists a critical Ni percentage, below which no quasicrystalline phase is formed; this critical Ni percentage is higher for the Zr-rich alloys. Coupled with this is that the addition of Ni to replace some percentage of Cu lowers the melting points of the alloys over the whole composition range, but more
substantially in the Zr-rich alloys than in the Ti-rich ones. As a result of those two factors, it is apparent that the addition of Ni improves the glass forming ability of the Zr-rich alloys to a larger degree than in the Ti-rich alloys. Based on all of these discoveries and understandings, one can intentionally introduce different elemental components in different relative contents with aims of forming a range of different but desired phase structures. As an example, one can introduced more Ni to replace Cu if a quasicrystalline phase is sought. On the other hand, the Ni addition seems always detrimental to the thermal stability of the amorphous and/or supercooled liquid structure no matter what the relative content of Ti and Zr is. When the contents of all the other components are fixed, the supercooled liquid region and the onset crystallization temperature of the amorphous containing alloys decrease consistently with increasing the Ni content at the expense of Cu. The Ni-poor or even Ni-free amorphous containing alloys show wider supercooled liquid region and higher thermal resistance against crystallization than Ni-richer alloys. Therefore, for the purpose of maximum processability of the amorphous-containing alloys, one can choose more Cu-rich alloys to utilize the wide supercooled liquid region.

Based on the above understandings, for the TiZr-based metallic alloys, on both Ti-rich and Zr-rich sides, in order to achieve a composite structure of amorphous plus crystalline phases, one has to select to work on Cu-rich alloys; if any Ni is involved, its content must be lower than the critical Ni percentage for formation of quasicrystalline phase, which decreases with increasing the relative content of Ti over the overall earth transition metal content. This is especially important for the Ti-rich metallic alloys because of the sensitivity of the formation of quasicrystalline phase with Ni additions. On the other hand, introducing more Ni into the TiZr-based alloys enhances the formation of
amorphous-quasicrystalline composite structures, which is equally important in terms of mechanical properties when compared with amorphous-crystalline composite structure.

If the cooling rate of the alloy melt is fast enough in both of the cases above, a wholly amorphous phase structure can be obtained by avoiding formation of crystalline and/or quasicrystalline phases. It was found that Zr-rich alloys usually exhibit a larger glass forming ability that the Ti-rich ones. In addition to the early transition metal Ti and Zr and the late transition metal Cu and Ni, other early transition metals (Groups IIIB-VIB), mainly of Hf and Nb, and late transition metals (Groups VIIIB, VIIIIB and IB), mainly of Fe and Co, may also be included. The general mass density of the current invention alloys is in the range of 5-7 grams/cc. Previous patent (No. 5,288,344) reported the ZrTi-based amorphous alloys with an approximately equal Ni and Cu content, where a relative atomic fraction of 0.35-0.65 between Ni and Cu was claimed preferably in terms of glass forming ability.

The alloy compositions that lead to the different composite phase structures claimed in this invention can be summarized by the formula, \((\text{Ti}_a\text{Zr}_{1-x})_b(\text{Cu}_y\text{Ni}_{1-y})_b\text{Be}_c\), where \(a\), \(b\) and \(c\) are atomic percentages and in the range of about 50-70, 10-30 and 10-30 at.\%, respectively; while \(x\) and \(y\) are atomic fractions and about 0.1 ≤ \(x\) ≤ 0.9 and about 0 ≤ \(y\) ≤ 0.35 and/or about 0.65 ≤ \(y\) ≤ 1, respectively.

The formation of different composite phase structures may be controlled either by adjustment of the alloy compositions at a fixed cooling rate or by changing the cooling rate for a given alloy composition. For the time being, the control of cooling rates is quite qualitative rather than quantitative, therefore, more quantitative control of the cooling rates will need to be developed later. A fixed cooling rate can be realized by making alloy samples with roughly the same size, such as by casting ingot buttons with similar masses.
(assuming a similar mass density for all alloys), same diameter cylinder-shaped rods, or ribbon samples with a similar thickness made by melt-spinning at the same rpm. Similarly, realization of different cooling (solidification) rates for a given alloy composition can be carried out using different cooling methods. In this invention, melt-spinning, injection casting and cooling directly in the furnace have been employed, which covers cooling rates ranging from about $10^3$ down to $10^2 \degree \text{C}/\text{s}$ or lower.

At a cooling rate of about $10^3 \degree \text{C}/\text{s}$ or higher, a monolithic amorphous phase can be formed from the melt for most of the alloy compositions claimed in this invention. The glass transition temperatures are around 330 to 360$\degree \text{C}$ and increase with decreasing the combined TiZr content. If the cooling rate is lowered to the range of about $10^2 \degree \text{C}/\text{s}$ or lower, which is estimated to be comparable to the cooling rates available in forming injection-cast samples or as-cast ingots, it was found that, for alloys with increased levels of Cu ($0.65 < y \leq 1$), amorphous ingots up to 5 grams are readily formed upon casting of the alloys in the Ti-rich side ($0.5 \leq x \leq 0.9$). If a monolithic amorphous phase failed to form, the composite structure is then composed of amorphous and crystalline phases with $y$ in the range of about 0.75-1; and amorphous plus quasicrystalline phases will be obtained if $y$ is in the range of about 0.65-0.75. In comparison, for the Zr-rich alloys ($0.1 \leq x \leq 0.5$), amorphous ingots of up to 10 grams with a wholly amorphous phase can be formed. If a wholly amorphous structure is not obtained, the composite structure will be amorphous plus crystalline phases; and no formation of quasicrystalline phase can be observed with $y$ in the whole range of about 0.65-1. On the other hand, for the Ni-rich alloys ($0 \leq y < 0.35$), either a monolithic amorphous phase or a composite structure consisting of amorphous and quasicrystalline phases is formed, depending on the relative Ti-Zr and Cu-Ni contents and cooling rates. At a fixed cooling rate where a composite
structure is formed, the volume fraction of quasicrystalline phase increases with increasing the relative content of Ti and Ni at the expense of Zr and Cu, respectively, in the whole range of \(0.1 < x < 0.9\) and \(0 \leq y < 0.35\). Especially at the Ti-rich side with \(0.5 < x < 0.9\), with increasing the relative content of Ti (to replace Zr) as well as Ni (to replace Cu), the formation of quasicrystalline phases becomes more dominant and a single quasicrystalline phase is formed in the as-cast ingot when Cu is totally replaced with Ni.

Although the composite structural alloys utilize similar elemental components as those of commercial Zr-based metallic glasses, the two materials differ significantly in the optimal compositional ranges obtained. Furthermore, because of the similarities in elemental components and melting temperatures between the two materials, the processing procedure currently employed for Zr-based alloys are expected to be directly adaptable to the commercial production of the current alloys. By adjusting alloy compositions according to the current invention, or alternatively, by varying the cooling rate in a more controllable way, various desired composite phase structures can be readily produced.

Properties currently under evaluation include mechanical properties (tensile and compressive strength, shock impact toughness) and corrosion resistance. Preliminary result of microhardness and elastic moduli measurements of representative alloys are tabulated in the Detailed Description Section.

None of the patents and patent applications described above provides the important advantage of controlling composite phase structures and related properties of metallic alloys through a predetermined transition metal ratio or through control of the cooling rate.
SUMMARY OF THE INVENTION

An unique approach to provide the important advantage of controlling composite phase structures and related properties of metallic alloys through a predetermined transition metal ratio or through control of the cooling rate.

In one aspect, an embodiment of the present invention provides a method of controlling the composite phase structures and related properties of metallic alloys comprising: selecting an alloy; and controlling composite phase structures and related properties of the metallic alloy by predetermined transition metal ratio.

The method wherein the alloy further comprises at least two early transition metals, at least one late transition metal, and beryllium.

The alloy wherein the early transition metal includes Ti, Zr, Hf, Nb, V, and other early transition metals selected from Group IIIB and Group IVB.

The alloy wherein the late transition metal includes Cu, Ni, Fe, Co, and other late transition metals selected from Groups VIIIB, VIIIB, or IB.

The alloy is represented by the formula: \[(\text{Ti}_a \text{Zr}_{1-a})_b (\text{Cu}_x \text{Ni}_{1-x})_c \text{Be}_d\], wherein a is an atomic percentage from 50 to 70; b is an atomic percentage from 10 to 30; c is an atomic percentage from 10 to 30; x is an atomic fraction that satisfies the relation \(0.1 \leq x \leq 0.9\); and y is an atomic fraction that satisfies either the relation \(0 \leq y < 0.35\) or \(0.65 < y \leq 1\).
The method wherein the controlling composite phase structures and related properties of the metallic alloy by predetermined transition metal ratio further comprises selecting the ratio of Cu to Ni where higher Cu addition at the expense of Ni results in a wider supercooled liquid region with less glass forming ability.

The method wherein below a critical Ni percentage no quasicrystalline phase forms.

The method wherein the critical Ni percentage varies with the relative Ti-Zr content and the critical Ni percentage decreases with increasing relative Ti content over the overall earth transition metal content.

The method wherein increasing the content of Ti relative to Zr and increasing the content of Ni relative to Cu increases the volume fraction of quasicrystalline phases.

The alloy wherein said processed article is provided by at least one of the following processing methods: conventional injection casting, die casting, squeeze casting, suction casting, strip casting, and other state-of-the-art casting techniques currently employed in research labs and industries.

The alloy is processable into, but are not limited thereto 1) ship, submarine (e.g., watercrafts), space station and vehicle, land-craft and aircraft frames and parts, 2) building structures, 3) armor penetrators, armor penetrating projectiles or kinetic energy projectiles, 4) protection armors, armor composites, or laminate armor, 5) engineering, construction, and medical materials and tools and devices, 6) corrosion and wear-resistant coatings, 7) cell phone and personal digital assistant (PDA) casings, housings and components, 8) electronics and computer casings, housings, and components, 9) cable armor, 10) composite power shaft, 11) laminate composite: laminate with other structural
alloys for aerospace, marine, and land transportation applications, and 12) actuators and other utilization that require the combination of specific properties realizable by the present invention alloys.

The alloy provides an ideal system to study the fundamental issues related to glass transition and glass forming ability as well as phase transition between amorphous, crystalline and quasicrystalline phases.

In another aspect, a method of controlling the composite phase structures and related properties of metallic alloys comprising: selecting an alloy; heating an alloy above the melting point of the alloy; and controlling composite phase structures and related properties of the metallic alloy through control of the cooling rate of the alloy.

The method wherein the alloy comprises at least two early transition metals, at least one late transition metal, and beryllium.

The alloy wherein the early transition metal includes Ti, Zr, Hf, Nb, V, and other early transition metals selected from Group IIIB and Group IVB.

The alloy wherein the late transition metal includes Cu, Ni, Fe, Co, and other late transition metals selected from Groups VIIB, VIIIB, or IB.

The alloy wherein the alloy is represented by the formula: \((\text{Ti}_a\text{Zr}_{1-a})(\text{Cu}_b\text{Ni}_c)(\text{Be}_y)\), wherein a is an atomic percentage from 50 to 70; b is an atomic percentage from 10 to 30; c is an atomic percentage from 10 to 30; x is an atomic fraction that satisfies the relation \(0.1 \leq x \leq 0.9\); and \(y\) is an atomic fraction that satisfies either the relation \(0 \leq y < 0.35\) or \(0.65 < y \leq 1\).
The method wherein control of the cooling rate further comprises selecting a high cooling rate for greater likelihood of forming a monolithic amorphous phase in the selected alloy.

The method wherein control of the cooling rate further comprises selecting a low cooling rate for forming composite structures with different kinds of phases in the selected alloy.

The method wherein a low cooling rate for a Ti-rich alloy results in monolithic amorphous phase, amorphous with quasicrystalline phases, or amorphous with crystalline phases with increasing levels of Cu.

The alloy wherein said processed article is provided by at least one of the following processing methods: conventional injection casting, die casting, squeeze casting, suction casting, strip casting, and other state-of-the-art casting techniques currently employed in research labs and industries.

The alloy is processable into, but are not limited thereto 1) ship, submarine (e.g., watercrafts), space station and vehicle, land-craft and aircraft frames and parts, 2) building structures, 3) armor penetrators, armor penetrating projectiles or kinetic energy projectiles, 4) protection armors, armor composites, or laminate armor, 5) engineering, construction, and medical materials and tools and devices, 6) corrosion and wear-resistant coatings, 7) cell phone and personal digital assistant (PDA) casings, housings and components, 8) electronics and computer casings, housings, and components, 9) cable armor, 10) composite power shaft, 11) laminate composite: laminate with other structural alloys for aerospace, marine, and land transportation applications, and 12) actuators and
other utilization that require the combination of specific properties realizable by the present invention alloys.

The alloy provides an ideal system to study the fundamental issues related to glass transition and glass forming ability as well as phase transition between amorphous, crystalline and quasicrystalline phases.

The alloy wherein said processed article is provided by at least one of the following processing methods: conventional injection casting, die casting, squeeze casting, suction casting, strip casting, and other state-of-the-art casting techniques currently employed in research labs and industries.

BRIEF DESCRIPTION OF THE DRAWING FIGURES

The foregoing and other objects, features, and advantages of the present invention, as well as the invention itself, will be more fully understood from the following description of preferred embodiments, when read together with the accompanying drawings, in which:

FIG. 1a and 1b show X-ray diffraction patterns to show the formation of different phases for given alloy compositions at different cooling rates Ti$_{40}$Zr$_{25}$Cu$_{11}$Ni$_8$Be$_{20}$ and Ti$_{40}$Zr$_{25}$Cu$_{13}$Be$_{20}$ alloys, respectively;

FIG. 2a and 2b show X-ray diffraction patterns to show the formation of different phases in 2 gram as-made ingots for Ti$_{40}$Zr$_{25}$Cu$_{15.3}$Ni$_8$Be$_{20}$ and Ti$_{40}$Zr$_{25}$Cu$_{15.3}$Ni$_8$Be$_{20}$ alloys, respectively; and
FIG. 3 shows the differential thermal analysis curves to show the effect of Cu addition on the width of the supercooled liquid region of representative alloy compositions.

FIG. 4. shows SEM image of the fracture surface of Ti₄₀Zr₂₅Cu₁₂Ni₃Be₂₀ amorphous rod under tension.

FIG. 5. shows strain-stress curve of Ti₄₀Zr₂₅Cu₁₂Ni₃Be₂₀ amorphous specimen under compression. The specimen surface was carefully polished and laser-treated.

DETAILED DESCRIPTION OF THE INVENTION

Hereinafter, certain embodiments of the present invention will be described in detail with reference to the accompanying drawing figures.

In the following description, the matters defined in the description, such as a detailed methods and elements, are provided only to assist in a comprehensive understanding of the invention. Thus, it is apparent that the present invention can be carried out without those defined matters. Also, well-known functions are not described in detail since they would obscure the invention in unnecessary detail.

Ingot preparation – Alloy ingots were prepared by melting mixtures of commercial grade component elements, with purities of about 99.5 at.% or above, in an arc-furnace or induction furnace under flowing protective gas atmosphere. In order to ensure the homogeneity of the composition, alloy ingots were melted repeatedly, at least four times. For the alloys containing Zr, Ti and Ni and other components with high
melting temperatures, the raw materials are pre-melted to make an intermediate alloy and then melted together with the other components.

*Control of composite phase structures*—Evaluation of the ability to form various desired phase structures including the amorphous phase in the invention alloys starts from the preparation of the alloy ingots. Usually a about 2 gram ingot was made as the first step. Then a piece of sample was cut from the core part of the ingot and used for X-ray diffraction. If the prepared ingot was found to be in a fully amorphous state with a weight of about 2 grams, then a larger ingot of about 5 grams was made and the same procedure was repeated to examine its microstructure. The next benchmark of the sample weight was set to about 10 grams. For those alloys not forming a fully amorphous phase in a about 2 gram ingot, the upper limit of forming ability of composite structure was explored by making larger sized ingots up to about 10 grams. In order to explore the lower end of the forming ability of composite structures, smaller sized ingots (1 gram) were made or injection casting was employed to examine where a monolithic amorphous phase is formed. For injection casting, the alloys was induction-melted in a quartz tube under a partial vacuum atmosphere and ejected into water-cooled copper block with cylinder-shaped cavities having diameters of about 1, 2 and 5 mm. Generally, with \( 0.1 < x < 0.5 \) and for \( 0.65 < y < 1 \), Zr-rich amorphous ingots with weight of at least 2 grams can be readily formed after melting the components together and the glass forming ability was found to increase with decreasing \( x \) within \( 0.2 < x < 0.5 \); for \( 0 \leq y < 0.35 \), composite structures of amorphous and quasicrystalline phases can be formed with the ingot weight up to 10 grams and the volume fraction of the quasicrystalline phase increases with the increase of the ingot weight and the increase of \( x \) within 0.2 - 0.5. For Ti-rich alloys with \( 0.5 < x < 0.9 \), when \( 0.75 < y \leq 1 \), amorphous ingots with a weight of at least 2 grams can
be formed and the glass forming ability increases with increasing x within this range; when the cooling rate is lowered to below the critical cooling rate for forming the monolithic amorphous phase, a composite structure of amorphous and crystalline phases can be obtained in this composition range; for $0.65 < y < 0.75$, composite structure of amorphous plus quasicrystalline phases can be formed in the ingot and the volume fraction of quasicrystalline phase increases with increasing x and decreasing y, however, the amorphous phase still serves as the matrix; when $0 \leq y < 0.35$, by decreasing the y value, the quasicrystalline phase becomes more dominant in volume fraction over the amorphous phase. A single quasicrystalline phase can be formed in the ingots when y reaches 0. Melt-spinning techniques were employed for alloy compositions that failed to obtain the desired phase structure even by casting. It was found that most of the compositions are able to form a monolithic amorphous phase. The cooling rate of this technique is in the range of about $10^3 \, ^\circ\text{C/s}$ or above, depending on the rotating speed of the copper wheel employed.

**Processability** – Owing to the controllable formation of different phase structures, the current alloys are highly processable. They can be produced into various forms with the desired composite or monolithic phase structures, such as amorphous foils by splat quenching, amorphous thin ribbons by melt spinning, amorphous powders by gas atomization, or rod-, sheet- or plate-shaped samples with amorphous, crystalline and quasicrystalline composite phase structures by casting. The casting can be carried out using conventional injection casting, die casting, squeeze casting, suction casting and strip casting, as well as other state-of-art casting techniques currently employed in research lab and industries. It is very promising for these alloys to be cast directly into the desired near net shapes without the need for further machining. In view of the importance
of being able to directly cast the alloy melt into different shapes, one can also utilize the
deformability of the amorphous containing composite alloys in the supercooled liquid
region to form near net shape products. More importantly, by controlling the cooling rates
of the casting process, one can at the same time obtain various desired phase structures in
the as-cast composite samples. The desired phase structure can also be obtained by
adjusting the alloy compositions and/or by subsequent annealing of the as-cast amorphous
containing alloys at appropriate temperatures.

**Exploration and evaluation of properties** – The current alloys are ductile at
room temperature when a fully amorphous phase is obtained or the amorphous phase
dominates in volume fraction. The ribbon shaped samples do not break when they are
bent by 180°. The as-cast amorphous rod can be bent close to about 90° for small size
samples and do not break. Compared with monolithic amorphous structures, composite
structures composing of amorphous, crystalline and quasicrystalline phases are of more
interest in terms of applications as structural materials. On consideration of the similar
elemental species of the current invention alloys to those claimed in an issued patent (No.
5,288,344), comparable mechanical properties could be reasonably expected, except that
the current invention alloys exhibit a controllable formation of different kinds of
composite structures and a high glass forming ability in the Ti-rich alloy compositions.
The mechanical properties, including tensile and compressive strength, shock impact
toughness, microhardness and bulk and elastic modulus are currently being evaluated.
The evaluation of corrosion resistance is also being carried out. Other properties, such as
wear resistance, fatigue strength, bio-chemical properties are worth exploration and
evaluation as well.
Application domain - Because of the good combination of high thermal stability, reasonably low mass density and good mechanical properties, it is expected that the current invention alloys to be used as structural materials where high strength properties are required, such as structural materials in aeronautics and astronautics industries. It can also be used in many other ways. As examples, the current alloys can be used as a coating on other matrix materials (or called surface modification), which is realized by locally melting the surface layer of the material and cooling down to form an amorphous layer; ceramic particles or fibers and/or refractory metal particles can be introduced into the alloy melt, a composite of amorphous alloy matrix with hard particles/fibers embedded can then be obtained; The present invention alloys may be used in many application areas. Some products and services of which some embodiments of the present invention can be implemented include, but are not limited thereto 1) ship, submarine (e.g., watercrafts), space station and vehicle, land-craft and aircraft frames and parts, 2) building structures, 3) armor penetrators, armor penetrating projectiles or kinetic energy projectiles, 4) protection armors, armor composites, or laminate armor, 5) engineering, construction, and medical materials and tools and devices, 6) corrosion and wear-resistant coatings, 7) cell phone and personal digital assistant PDA) casings, housings and components, 8) electronics and computer casings, housings, and components, 9) cable armor, 10) composite power shaft, 11) laminate composite: laminate with other structural alloys for aerospace, marine, and land transportation applications, 12) actuators and other utilization that require the combination of specific properties realizable by the present invention alloys. The current invention alloys may also have other useful functional applications in addition to their mechanical properties. As important as its potential practical application, from the point of scientific view, the current alloys provide an ideal system to study the fundamental issues related to glass
transition and glass forming ability as well as phase transition between amorphous, crystalline and quasicrystalline phases.

**Detailed description of the phase structure control of invention alloys**

In general, different composite phase structures of the alloys in this invention can be achieved in a controllable way either by adjusting the alloy compositions at a fixed cooling rate or by changing the cooling rates for a given alloy composition. The alloys employed comprise at least two early transition metals, at least one late transition metal and beryllium. Early transition metals include mainly Ti and Zr, but can also include Hf, Nb and V as well as other early transition metals selected from IIIB-VIB. Late transition metals include mainly Cu and Ni, but can also include Fe and Co as well as other late transition metals selected from VIIB, VIIIB and IB. Cu and Ni are introduced with an unbalanced relative content. In the current invention, the Cu or Ni content is in the range of 0-0.35 of the total Cu+Ni content. Selections of Cu and Ni contents are based on our recent knowledge about quasicrystalline formation in TiZrNi alloys. We found that, when the addition of Ni exceeds a certain critical content, the formation of quasicrystalline phases is unavoidable. This is especially true for the Ti-rich alloys. The alloys with Ni contents beyond this critical value tend to form into an amorphous-quasicrystalline composite structure if a monolithic amorphous structure is not formed. Combined with careful control of the cooling rates, one can modify the microstructure of the composite samples that may show better mechanical properties than the monolithic amorphous phase.

To more efficiently describe the different phase structures and related alloy compositions in this invention, the following composition formula are introduced: (TiₓZrᵧ₋ₓ)(CuₐNi₁₋ₐ)ₐBeₐ, where a, b and c are atomic percentages and in the range of 50-70, 10-
30 and 10-30 at.%, respectively; while x and y are atomic fractions and 0.1 ≤ x ≤ 0.9 and 0 ≤ y < 0.35 and/or 0.65 < y ≤ 1, respectively.

The evaluation of the ability of forming various desired phase structures upon a fixed cooling rate was carried out on as-made ingots starting with an ingot weight of 2 grams. The characterization of phase structures was done by means of X-ray diffraction, differential scanning calorimeter and differential thermal analysis. For the Ti-rich alloys with 0.6 < x < 0.9, 0.8 < y ≤ 1 is required for the formation of a about 2 gram ingot with a monolithic amorphous phase; 0.65 < y < 0.8 leads to the formation of composite structure of amorphous plus quasicrystalline phases with the amorphous phase as the matrix; for 0 ≤ y < 0.35, a composite structure of quasicrystalline plus amorphous phase can be formed with the quasicrystalline phase as the matrix, the volume fraction of quasicrystalline phase becomes more dominant with decreasing y values and finally a single quasicrystalline phase can be formed when y reaches 0. For the alloys with approximately equal content of Ti and Zr, that is, 0.4 < x < 0.6, 2 gram alloy ingots with wholly amorphous phase can be formed with 0.65 < y ≤ 1; when y is in the range of 0-0.35, a composite structure of amorphous plus quasicrystalline phases can be obtained and the volume fraction of quasicrystalline phase increases with decreasing y values. For the Zr-rich alloys with 0 < x < 0.4, the formation of a about 2 gram wholly amorphous ingot can be verified with 0.65 < y ≤ 1; when y covers the range of about 0 to 0.35, a composite structure of amorphous plus quasicrystalline phases can be readily formed with the amorphous phase as the matrix.

For the purpose of controllable formation of the desired phase structure, it was found that this can be achieved either by adjusting of the chemical composition of the alloys at a given cooling rate or changing cooling rates for a given alloy composition.
Although quantitative control of the cooling rates is not currently available, one can qualitatively obtain a certain cooling rate by making ingots of the same size, or one can obtain different cooling rates by making different sizes of ingots or using different casting techniques, such as injection casting and melt spinning.

Referring to FIG. 1a and 1b, they show X-ray diffraction patterns to show the formation of different phases for given alloy compositions at different cooling rates Ti₄₀Zr₂₅Cu₁₁Ni₄Be₂₀ and Ti₄₀Zr₂₅Cu₁₃Be₂₀ alloys, respectively. The different cooling rates were realized by making ingots with different weights or casting rods in different diameters. By comparing a and b, one can see the addition of 4 at.% Ni to replace Cu leads to the formation of different phase structures, that is, from amorphous plus crystalline phases to amorphous plus quasicrystalline phases, as marked in the figure.

Referring to FIG. 2a and 2b, they show X-ray diffraction patterns to show the formation of different phases in 2 gram as-made ingots of different alloy compositions as marked in the figure. In order to ensure a roughly comparable cooling rate for all the compositions, ingots with a similar mass of about 2 grams were made for Ti₄₀Zr₂₅(CuNi)₁₃Be₂₀ and Ti₂₀Zr₄₅(CuNi)₁₃Be₂₀ alloys.

It is worth noting that, although the Ti₄₀Zr₃₀Ni₁₃Be₁₅ alloy is brittle when the quasicrystalline phase is dominant in volume fraction, which forms in the as-made ingot and as-cast rod samples, it becomes ductile in the ribbon sample which is in an fully amorphous state. This is a common feature of the alloys in this invention that those with a monolithic amorphous phase are ductile. With the introduction of crystalline or quasicrystalline phases within a certain volume fraction, the composite samples may still remain ductile and, at the same time, more importantly, the fracture strength and elongation are expected to be improved further, which are the major drawback for
monolithic amorphous alloys, no matter whether they are brittle or ductile. The reason for that is that the crystalline or quasicrystalline phases may serve as hindering barriers mitigating the propagation of shear bands. When the crystalline or quasicrystalline phases exceed a certain volume fraction or when they dominate in volume fraction, the alloy samples become brittle and are no longer ideal for use as structural materials. The different cooling rates were realized by making different sizes of alloy ingot. The determination of volume fraction of quasicrystalline phase was done using differential scanning calorimeter, with the wholly amorphous sample as a standard.

For the purpose of good processability, the width of the supercooled liquid region is one of the important parameters for amorphous containing alloys. A wider supercooled liquid region allows a longer processing time in this temperature window without the occurrence of crystallization. It has been found in this invention that the alloys with higher additions of Cu at the expense of Ni possess a wider supercooled liquid region, which is especially true for the Zr-rich alloys. Referring to FIG. 3, it shows differential thermal analysis curves to show the effect of Cu addition on the width of the supercooled liquid region of representative alloy compositions, as marked in the figure. Therefore, these alloys with more Cu are highly desirable to serve this purpose, although their glass forming ability might not be as good as those alloys with less Cu.

For the purpose of obtaining materials with high specific strength, the Ti-rich alloys with a monolithic amorphous phase, and more importantly, with composite structures composed of amorphous, crystalline and quasicrystalline phases, are of high interest owing to the low density of Ti. In addition to that, the fact that Ti-rich alloys are able to form up to 5 gram amorphous ingots, as well as amorphous-based composite
structures, means that these alloys are practical for production of large sized amorphous and composite materials.

Representative alloy compositions are listed in Tables I-III, together with their glass transition temperature, onset crystallization temperature, phase structures and related forming ability for those specific phase structures. These alloys are grouped into Tables I-III based on phase structures obtained in ingots directly from the furnace, rods made by injection casting and ribbons by melt-spinning, namely Table I, composite structure composing of amorphous and crystalline phases, Table II, composite structure composing of amorphous and quasicrystalline phases, Table III, amorphous alloys. All the alloy compositions are given in atomic percentages. The temperatures are given in degrees Centigrade. Note that for the purpose of obtaining an amorphous phase, only the upper limit of glass forming ability needs to be explored, because at the lower limit, ribbon samples made by melt spinning were found to be in a wholly amorphous state for all the alloy compositions in this invention. To minimize the amount of work, the evaluation of forming ability range of different phase structures starts with the ingot weight of 2 grams. If the 2 gram as-made ingot was found in a fully amorphous state, then a 5 gram ingot was made. If the 5 gram ingot was not in a fully amorphous state, the upper limit of glass forming ability is between about 2-5 grams, at the same time, it is also the lower limit for forming a composite structure. A larger sized ingot with weight of 10 grams was then made to explore the upper limit of the formation of composite phase structures. If a fully amorphous phase was formed for the 5 gram ingot, then a 10 gram ingot was made. If the 10 gram ingot was found not in a fully amorphous state, then the upper limit of glass forming ability was between about 5-10 grams. At the same time, 5-10 grams are also the lower limit of forming a composite structure and the upper limit for
forming a composite structure was not pursued further and marked with about 10 grams. If a fully amorphous phase was formed in the 10 gram ingot, the glass forming ability was taken as 10 grams and the lower limit of forming a composite structure was marked with >10 grams, the upper limit column was left blank. Upper bounds for both glass forming ability and composite phase forming ability were not pursued further. If the alloys failed to form a fully amorphous phase in 2 gram ingots, larger sized ingots were made to explore the upper limit of forming composite phase structures up to an ingot weight of about 10 grams, the exploration follows procedure mentioned above. To explore the upper limit of glass forming ability, or one can say, the lower limit of forming a composite phase structure, we make smaller sized ingots (1 gram) or employ injection casting to examine where a monolithic amorphous phase is formed. For injection casting, 5 mm in diameter was the maximum size of as-cast rods we tested. The smaller rod diameter sizes include 2 and 1 mm. If the 1 mm diameter rod was not in a fully amorphous state, then ribbon sample by melt-spinning at different rpm was made and the phase structure was examined.
Table I. Compositions of composite structure composing of amorphous and crystalline phases and the forming ability range of this composite phase structure.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Tg</th>
<th>Tx</th>
<th>∆T</th>
<th>Forming ability range</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Lower limit</td>
</tr>
<tr>
<td>Ti₆₀Zr₂₀Cu₁₄Be₁₆</td>
<td>296</td>
<td>352</td>
<td>56</td>
<td>2 mm</td>
</tr>
<tr>
<td>Ti₆₀Zr₂₀Cu₁₄Be₁₆</td>
<td>312</td>
<td>367</td>
<td>55</td>
<td>2 mm</td>
</tr>
<tr>
<td>Ti₆₂Zr₂₀Cu₁₄Be₁₆</td>
<td>290</td>
<td>340</td>
<td>50</td>
<td>3 mm</td>
</tr>
<tr>
<td>Ti₅₂Zr₂₀Cu₁₄Be₁₆</td>
<td>300</td>
<td>340</td>
<td>40</td>
<td>2 mm</td>
</tr>
<tr>
<td>Ti₄₅Zr₂₅Cu₁₄Ni₁₀Be₁₆</td>
<td>290</td>
<td>335</td>
<td>45</td>
<td>3 mm</td>
</tr>
<tr>
<td>Ti₄₂Zr₂₅Cu₁₄Be₁₆</td>
<td>324</td>
<td>357</td>
<td>33</td>
<td>2 mm</td>
</tr>
<tr>
<td>Ti₄₀Zr₂₀Cu₁₄Be₂₀</td>
<td>342</td>
<td>397</td>
<td>55</td>
<td>1 gram</td>
</tr>
<tr>
<td>Ti₄₀Zr₂₀Cu₁₄Be₂₀</td>
<td>327</td>
<td>384</td>
<td>57</td>
<td>5 mm</td>
</tr>
<tr>
<td>Ti₄₀Zr₂₀Cu₁₄Be₂₀</td>
<td>337</td>
<td>376</td>
<td>39</td>
<td>1 gram</td>
</tr>
<tr>
<td>Ti₄₀Zr₂₀Cu₁₄Be₂₀</td>
<td>330</td>
<td>380</td>
<td>50</td>
<td>5 mm</td>
</tr>
<tr>
<td>Ti₄₀Zr₂₀Cu₁₄Be₂₀</td>
<td>334</td>
<td>388</td>
<td>54</td>
<td>5 mm</td>
</tr>
<tr>
<td>Ti₄₀Zr₂₀Cu₁₄Be₂₀</td>
<td>364</td>
<td>422</td>
<td>58</td>
<td>2 mm</td>
</tr>
<tr>
<td>Ti₄₀Zr₂₀Cu₁₄Ni₁₀Be₂₀</td>
<td>333</td>
<td>375</td>
<td>42</td>
<td>2 grams</td>
</tr>
<tr>
<td>Ti₄₀Zr₁₅Cu₁₄Be₂₀</td>
<td>343</td>
<td>386</td>
<td>43</td>
<td>2 mm</td>
</tr>
<tr>
<td>Ti₄₀Zr₁₅Cu₁₄Be₂₀</td>
<td>336</td>
<td>392</td>
<td>56</td>
<td>2 mm</td>
</tr>
<tr>
<td>Ti₄₀Zr₁₅Cu₁₄Be₂₀</td>
<td>321</td>
<td>345</td>
<td>24</td>
<td>1 mm</td>
</tr>
<tr>
<td>Ti₄₀Zr₁₅Cu₁₄Ni₁₀Be₂₀</td>
<td>345</td>
<td>386</td>
<td>41</td>
<td>2 mm</td>
</tr>
<tr>
<td>Ti₄₀Zr₂₀Cu₁₄Ni₁₀Be₂₀</td>
<td>327</td>
<td>372</td>
<td>45</td>
<td>1 gram</td>
</tr>
<tr>
<td>Ti₄₀Zr₂₀Cu₁₄Ni₁₀Be₂₀</td>
<td>326</td>
<td>372</td>
<td>46</td>
<td>2 grams</td>
</tr>
<tr>
<td>Ti₄₀Zr₂₀Cu₁₄Ni₁₀Be₂₀</td>
<td>331</td>
<td>372</td>
<td>41</td>
<td>5 grams</td>
</tr>
<tr>
<td>Ti₄₀Zr₂₀Cu₁₄Be₂₀</td>
<td>342</td>
<td>368</td>
<td>26</td>
<td>1 grams</td>
</tr>
<tr>
<td>Ti₄₀Zr₂₀Cu₁₄Be₂₀</td>
<td>330</td>
<td>396</td>
<td>66</td>
<td>1 grams</td>
</tr>
<tr>
<td>Ti₄₀Zr₂₀Cu₁₄Ni₁₀Be₂₀</td>
<td>330</td>
<td>371</td>
<td>41</td>
<td>&gt;10 grams</td>
</tr>
<tr>
<td>Ti₄₀Zr₉₄Cu₂₂₂Be₂₂₂₅</td>
<td>348</td>
<td>456</td>
<td>108</td>
<td>2 grams</td>
</tr>
<tr>
<td>Ti₄₀Zr₉₄Cu₂₂₂Be₂₀</td>
<td>342</td>
<td>402</td>
<td>60</td>
<td>5 grams</td>
</tr>
<tr>
<td>Ti₄₀Zr₉₄Cu₂₂₂Be₂₀</td>
<td>353</td>
<td>401</td>
<td>48</td>
<td>5 grams</td>
</tr>
<tr>
<td>Ti₄₀Zr₉₄Cu₂₂₂Be₂₀</td>
<td>321</td>
<td>371</td>
<td>50</td>
<td>ribbon</td>
</tr>
<tr>
<td>Ti₄₀Nb₁₀Zr₂₀Cu₁₄Ni₁₀Be₂₀</td>
<td>347</td>
<td>395</td>
<td>48</td>
<td>2 grams</td>
</tr>
<tr>
<td>Ti₄₀Zr₉₄Cu₁₄Fe₉Be₂₀</td>
<td>350</td>
<td>379</td>
<td>29</td>
<td>5 mm</td>
</tr>
<tr>
<td>Ti₄₀Zr₉₄Cu₁₄Co₂Be₂₀</td>
<td>346</td>
<td>374</td>
<td>28</td>
<td>1 gram</td>
</tr>
</tbody>
</table>
Table II. Compositions of composite structure composing of amorphous and quasicrystalline phases and the forming ability range of this composite phase structure.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Tg</th>
<th>T_x</th>
<th>ΔT</th>
<th>Forming ability range</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Lower limit</td>
</tr>
<tr>
<td>Ti_{40}Zr_{30}Ni_{16}Be_{15}</td>
<td>288</td>
<td>337</td>
<td>30</td>
<td>1 mm</td>
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<tr>
<td>Ti_{40}Zr_{35}Cu_{10}Ni_{15}Be_{15}</td>
<td>300</td>
<td>340</td>
<td>40</td>
<td>1 mm</td>
</tr>
<tr>
<td>Ti_{40}Zr_{35}Cu_{10}Ni_{15}Be_{16}</td>
<td>300</td>
<td>342</td>
<td>42</td>
<td>2 mm</td>
</tr>
<tr>
<td>Ti_{40}Zr_{35}Cu_{10}Ni_{15}Be_{17}</td>
<td>312</td>
<td>350</td>
<td>38</td>
<td>3 mm</td>
</tr>
<tr>
<td>Ti_{40}Zr_{35}Cu_{10}Ni_{15}Be_{20}</td>
<td>333</td>
<td>366</td>
<td>33</td>
<td>1 gram</td>
</tr>
<tr>
<td>Ti_{40}Zr_{35}Cu_{10}Ni_{15}Be_{20}</td>
<td>340</td>
<td>363</td>
<td>23</td>
<td>1 gram</td>
</tr>
<tr>
<td>Ti_{40}Zr_{35}Ni_{15}Be_{15}</td>
<td>347</td>
<td>374</td>
<td>27</td>
<td>1 gram</td>
</tr>
<tr>
<td>Ti_{40}Zr_{45}Cu_{10}Ni_{15}Be_{20}</td>
<td>348</td>
<td>371</td>
<td>23</td>
<td>5 grams</td>
</tr>
<tr>
<td>Ti_{40}Zr_{45}Ni_{15}Be_{20}</td>
<td>347</td>
<td>374</td>
<td>27</td>
<td>1 gram</td>
</tr>
<tr>
<td>Ti_{40}Zr_{45}Cu_{10}Ni_{15}Be_{20}</td>
<td>342</td>
<td>402</td>
<td>60</td>
<td>5 grams</td>
</tr>
</tbody>
</table>
Table III. Glass forming alloy compositions and the upper limit of glass forming ability.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Tg</th>
<th>Tx</th>
<th>ΔT</th>
<th>Glass forming ability</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tla0.3Zr0.7Ni15Be15</td>
<td></td>
<td>350</td>
<td>56</td>
<td>2 mm</td>
</tr>
<tr>
<td>Tla0.3Zr0.7Cu15Be15</td>
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<td>352</td>
<td>55</td>
<td>2 mm</td>
</tr>
<tr>
<td>Tla0.3Zr0.7Cu15Be15</td>
<td>312</td>
<td>367</td>
<td>55</td>
<td>2 mm</td>
</tr>
<tr>
<td>Tla0.3Zr0.7Cu15Be15</td>
<td>324</td>
<td>357</td>
<td>33</td>
<td>2 mm</td>
</tr>
<tr>
<td>Tla0.3Zr0.7Cu15Be15</td>
<td>342</td>
<td>397</td>
<td>55</td>
<td>1 gram</td>
</tr>
<tr>
<td>Tla0.3Zr0.7Cu15Be15</td>
<td>327</td>
<td>384</td>
<td>57</td>
<td>5 mm</td>
</tr>
<tr>
<td>Tla0.3Zr0.7Cu15Be15</td>
<td>337</td>
<td>376</td>
<td>39</td>
<td>1 gram</td>
</tr>
<tr>
<td>Tla0.3Zr0.7Cu15Be15</td>
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<td>380</td>
<td>50</td>
<td>5 mm</td>
</tr>
<tr>
<td>Tla0.3Zr0.7Cu15Be15</td>
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<td>382</td>
<td>51</td>
<td>5 mm</td>
</tr>
<tr>
<td>Tla0.3Zr0.7Cu15Be15</td>
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<td>388</td>
<td>54</td>
<td>5 mm</td>
</tr>
<tr>
<td>Tla0.3Zr0.7Cu15Be15</td>
<td>364</td>
<td>422</td>
<td>58</td>
<td>2 mm</td>
</tr>
<tr>
<td>Tla0.3Zr0.7Cu15Ni15Be20</td>
<td>333</td>
<td>375</td>
<td>42</td>
<td>2-5 grams</td>
</tr>
<tr>
<td>Tla0.3Zr0.7Cu15Ni15Be20</td>
<td>343</td>
<td>386</td>
<td>43</td>
<td>1 mm</td>
</tr>
<tr>
<td>Tla0.3Zr0.7Cu15Ni15Be20</td>
<td>336</td>
<td>392</td>
<td>56</td>
<td>2 mm</td>
</tr>
<tr>
<td>Tla0.3Zr0.7Cu15Ni15Be20</td>
<td>321</td>
<td>345</td>
<td>24</td>
<td>ribbon</td>
</tr>
<tr>
<td>Tla0.3Zr0.7Cu15Ni15Be20</td>
<td>345</td>
<td>386</td>
<td>41</td>
<td>2 mm</td>
</tr>
<tr>
<td>Tla0.3Zr0.7Cu15Ni15Be20</td>
<td>327</td>
<td>372</td>
<td>45</td>
<td>2-5 grams</td>
</tr>
<tr>
<td>Tla0.3Zr0.7Cu15Ni15Be20</td>
<td>326</td>
<td>372</td>
<td>46</td>
<td>2-5 grams</td>
</tr>
<tr>
<td>Tla0.3Zr0.7Cu15Ni15Be20</td>
<td>331</td>
<td>372</td>
<td>41</td>
<td>5-10 grams</td>
</tr>
<tr>
<td>Tla0.3Zr0.7Cu15Ni15Be20</td>
<td>333</td>
<td>366</td>
<td>33</td>
<td>1 gram</td>
</tr>
<tr>
<td>Tla0.3Zr0.7Cu15Ni15Be20</td>
<td></td>
<td>370</td>
<td></td>
<td>5 mm</td>
</tr>
<tr>
<td>Tla0.3Zr0.7Cu15Ni15Be20</td>
<td>342</td>
<td>368</td>
<td>26</td>
<td>2-5 grams</td>
</tr>
<tr>
<td>Tla0.3Zr0.7Cu15Ni15Be20</td>
<td>340</td>
<td>363</td>
<td>23</td>
<td>5 mm</td>
</tr>
<tr>
<td>Tla0.3Zr0.7Cu15Ni15Be20</td>
<td>347</td>
<td>376</td>
<td>29</td>
<td>2-5 mm</td>
</tr>
<tr>
<td>Tla0.3Zr0.7Cu15Ni15Be20</td>
<td>330</td>
<td>396</td>
<td>66</td>
<td>2-5 grams</td>
</tr>
<tr>
<td>Tla0.3Zr0.7Cu15Ni15Be20</td>
<td>330</td>
<td>371</td>
<td>41</td>
<td>10 grams</td>
</tr>
<tr>
<td>Tla0.3Zr0.7Cu15Ni15Be20</td>
<td>348</td>
<td>371</td>
<td>23</td>
<td>5-10 grams</td>
</tr>
<tr>
<td>Tla0.3Zr0.7Cu15Ni15Be20</td>
<td>347</td>
<td>374</td>
<td>27</td>
<td>5 mm</td>
</tr>
<tr>
<td>Tla0.3Zr0.7Cu15Ni15Be20</td>
<td>342</td>
<td>402</td>
<td>60</td>
<td>5 grams</td>
</tr>
<tr>
<td>Tla0.3Hf0.7Zr0.3Cu17Ni15Be20</td>
<td>353</td>
<td>401</td>
<td>48</td>
<td>5 grams</td>
</tr>
<tr>
<td>Tla0.3V2Zr0.7Cu17Ni15Be20</td>
<td>321</td>
<td>371</td>
<td>50</td>
<td>ribbon</td>
</tr>
<tr>
<td>Tla0.3Nbx0.3Zr0.7Cu15Ni15Be20</td>
<td>347</td>
<td>395</td>
<td>48</td>
<td>2-5 grams</td>
</tr>
<tr>
<td>Tla0.3Zr0.7Cu17Fe3Be20</td>
<td>350</td>
<td>379</td>
<td>29</td>
<td>1 gram</td>
</tr>
<tr>
<td>Tla0.3Zr0.7Cu17Co3Be20</td>
<td>346</td>
<td>374</td>
<td>28</td>
<td>2-5 grams</td>
</tr>
</tbody>
</table>
Table IV. Microhardness and elastic moduli measurements of representative alloy compositions, which were done on as-made ingots with a weight of 2 grams unless noted. The values of Vicher’s hardness are given in this table. Seven microhardness tests were done for each sample. Five out of the seven data in the middle was used to obtain the hardness value. A, C and Q represent amorphous, crystalline and quasicrystalline phases, respectively.

<table>
<thead>
<tr>
<th>Composition (at.%)</th>
<th>Phase structure</th>
<th>Vicker's hardness</th>
<th>Young's modulus</th>
<th>Bulk modulus</th>
<th>Shear modulus</th>
<th>Poisson ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti₆₀Zr₂₅Cu₁₅Be₂₀</td>
<td>A+C</td>
<td>548</td>
<td>100</td>
<td>104</td>
<td>37</td>
<td>0.34</td>
</tr>
<tr>
<td>Ti₆₀Zr₂₅Cu₁₅Ni₁₀Be₂₀</td>
<td>A</td>
<td>497</td>
<td>101</td>
<td>100</td>
<td>38</td>
<td>0.33</td>
</tr>
<tr>
<td>Ti₆₀Zr₂₅Cu₁₅Ni₁₀Be₂₀</td>
<td>A+Q</td>
<td>503</td>
<td>99</td>
<td>106</td>
<td>36</td>
<td>0.34</td>
</tr>
<tr>
<td>Ti₆₀Zr₄₅Cu₁₅Be₂₀</td>
<td>A+traceC</td>
<td>466</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ti₆₀Zr₄₅Cu₁₅Ni₁₀Be₂₀</td>
<td>A</td>
<td>478</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ti₆₀Zr₄₅Cu₁₅Ni₁₀Be₂₀ (10 grams)</td>
<td>A+Q</td>
<td>483</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

While the invention has been shown and described with reference to certain embodiments thereof, it will be understood by those skilled in the art that various changes in form and details may be made therein without departing from the spirit and scope of the invention as defined by the appended claims. The examples and embodiments described herein are for illustrative purposes only and are not limiting.
CLAIMS:

We claim:

1. A method of controlling the composite phase structures and related properties of metallic alloys comprising:
   selecting an alloy; and
   controlling composite phase structures and related properties of the metallic alloy by predetermined transition metal ratio.

2. A method according to claim 1 wherein the alloy further comprises at least two early transition metals, at least one late transition metal, and beryllium.

3. An alloy according to claim 2 wherein the early transition metal includes Ti, Zr, Hf, Nb, V, and other early transition metals selected from Group IIIB and Group IVB.

4. An alloy according to claim 2 wherein the late transition metal includes Cu, Ni, Fe, Co, and other late transition metals selected from Groups VIIB, VIIIB, or IB.

5. An alloy according to claim 2 wherein the alloy is represented by the formula:

   \[(\text{Ti}_{a}\text{Zr}_{1-a})(\text{Cu}_{b}\text{Ni}_{1-b})\text{Be}_{c}\]

   wherein \(a\) is an atomic percentage from 50 to 70;
   \(b\) is an atomic percentage from 10 to 30;
   \(c\) is an atomic percentage from 10 to 30;
x is an atomic fraction that satisfies the relation $0.1 \leq x \leq 0.9$; and

$y$ is an atomic fraction that satisfies either the relation $0 \leq y < 0.35$ or $0.65 < y \leq 1$.

6. A method according to claim 1 wherein the controlling composite phase structures and related properties of the metallic alloy by predetermined transition metal ratio further comprises selecting the ratio of Cu to Ni where higher Cu addition at the expense of Ni results in a wider supercooled liquid region with less glass forming ability.

7. A method according to claim 6 wherein below a critical Ni percentage no quasicrystalline phase forms.

8. A method according to claim 7 wherein the critical Ni percentage varies with the relative Ti-Zr content and the critical Ni percentage decreases with increasing relative Ti content over the overall earth transition metal content.

9. A method according to claim 8 wherein increasing the content of Ti relative to Zr and increasing the content of Ni relative to Cu increases the volume fraction of quasicrystalline phases.

10. An alloy according to claim 2, wherein said processed article is provided by at least one of the following processing methods: conventional injection casting, die casting, squeeze casting, suction casting, strip casting, and other state-of-the-art casting techniques currently employed in research labs and industries.
11. An alloy according to claim 2, wherein said alloy is processable into, but are not limited thereto

1) ship, submarine (e.g., watercrafts), space station and vehicle, land-craft and aircraft frames and parts,

2) building structures,

3) armor penetrators, armor penetrating projectiles or kinetic energy projectiles,

4) protection armors, armor composites, or laminate armor,

5) engineering, construction, and medical materials and tools and devices,

6) corrosion and wear-resistant coatings,

7) cell phone and personal digital assistant (PDA) casings, housings and components,

8) electronics and computer casings, housings, and components,

9) cable armor,

10) composite power shaft,

11) laminate composite: laminate with other structural alloys for aerospace, marine, and land transportation applications, and

12) actuators and other utilization that require the combination of specific properties realizable by the present invention alloys.

12. An alloy according to claim 2, wherein said alloy provides an ideal system to study the fundamental issues related to glass transition and glass forming ability as well as phase transition between amorphous, crystalline and quasicrystalline phases.
13. A method of controlling the composite phase structures and related properties of metallic alloys comprising:

selecting an alloy;

heating an alloy above the melting point of the alloy; and

controlling composite phase structures and related properties of the metallic alloy through control of the cooling rate of the alloy.

14. A method according to claim 13 wherein the alloy comprises at least two early transition metals, at least one late transition metal, and beryllium.

15. An alloy according to claim 14 wherein the early transition metal includes Ti, Zr, Hf, Nb, V, and other early transition metals selected from Group IIIB and Group IVB.

16. An alloy according to claim 14 wherein the late transition metal includes Cu, Ni, Fe, Co, and other late transition metals selected from Groups VIIB, VIIIB, or IB.

17. An alloy according to claim 14 wherein the alloy is represented by the formula:

\[(\text{Ti}_x\text{Zr}_{1-x})_a(\text{Cu}_y\text{Ni}_{1-y})_b\text{Be}_c,\]

wherein \(a\) is an atomic percentage from 50 to 70;

\(b\) is an atomic percentage from 10 to 30;

\(c\) is an atomic percentage from 10 to 30;

\(x\) is an atomic fraction that satisfies the relation \(0.1 \leq x \leq 0.9\); and
y is an atomic fraction that satisfies either the relation $0 \leq y < 0.35$ or $0.65 < y \leq 1$.

18. A method according to claim 13, wherein control of the cooling rate further comprises selecting a high cooling rate for greater likelihood of forming a monolithic amorphous phase in the selected alloy.

19. A method according to claim 13, wherein control of the cooling rate further comprises selecting a low cooling rate for forming composite structures with different kinds of phases in the selected alloy.

20. A method according to claim 19, wherein a low cooling rate for a Ti-rich alloy results in monolithic amorphous phase, amorphous with quasicrystalline phases, or amorphous with crystalline phases with increasing levels of Cu.

21. An alloy according to claim 14, wherein said processed article is provided by at least one of the following processing methods: conventional injection casting, die casting, squeeze casting, suction casting, strip casting, and other state-of-the-art casting techniques currently employed in research labs and industries.

22. An alloy according to claim 14, wherein said alloy is processable into, but are not limited thereto

1) ship, submarine (e.g., watercrafts), space station and vehicle, land-craft and aircraft frames and parts,

2) building structures,
3) armor penetrators, armor penetrating projectiles or kinetic energy projectiles,
4) protection armors, armor composites, or laminate armor,
5) engineering, construction, and medical materials and tools and devices,
6) corrosion and wear-resistant coatings,
7) cell phone and personal digital assistant (PDA) casings, housings and components,
8) electronics and computer casings, housings, and components,
9) cable armor,
10) composite power shaft,
11) laminate composite: laminate with other structural alloys for aerospace, marine, and land transportation applications, and
12) actuators and other utilization that require the combination of specific properties realizable by the present invention alloys.

23. An alloy according to claim 14, wherein said alloy provides an ideal system to study the fundamental issues related to glass transition and glass forming ability as well as phase transition between amorphous, crystalline and quasicrystalline phases.

24. An alloy according to claim 14, wherein said processed article is provided by at least one of the following processing methods: conventional injection casting, die casting, squeeze casting, suction casting, strip casting, and other state-of-the-art casting techniques currently employed in research labs and industries.
FIG. 1A

Ti40Zr25Cu11Ni4Be20

- quasicrystalline phase

Intensity (arb. unit)

5 grams ingot
2 grams ingot
1 gram ingot

FIG. 1B

Ti40Zr25Cu15Be20

2 grams ingot
1 gram ingot
5 mm rod

2-Theta (degree)
FIG. 2A

FIG. 2B
FIG. 3

Heat Flow (arb. unit)

Ti₂₀Zr₄₀Ni₁₅Be₂₀

Ti₂₀Zr₄₅Cu₁₅Be₂₀

Ti₁₃₈Zr₄₁₂Cu₁₂₅Ni₁₀Be₂₂₅ (Vit1)

Ti₁₃₈Zr₄₁₂Cu₂ₒ₅Be₂₂₅

Temperature (°C)

FIG. 4
FIG. 5