METAL ALLOY AND USE THEREOF

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ABSTRACT
A metallic alloy comprising Ti, Zr, Nb, containing an amorphous phase and a quasicrystalline phase and is represented by the formula:

\[ Ti_{1-x}Zr_xNb_{1-x}M_y \]

wherein:
M represents an element selected from a group consisting of Ni, Co, Fe, Mn,
1 represents impurities,
coefficients a, b, c, d, e represent atomic %, and are equal to: 40 ≤ a ≤ 55, 5 ≤ b ≤ 30, 5 ≤ c ≤ 25, 5 ≤ d ≤ 30, e ≤ 1.
Tape obtained by melt spinning on a copper wheel (2500rpm)

\[ \text{Ti}_{50} \text{Zr}_{25} \text{Fe}_{25} \]

\[ \text{Ti}_{50} \text{Zr}_{15} \text{Nb}_{15} \text{Co}_{20} \]

\[ \text{Ti}_{40} \text{Zr}_{25} \text{Nb}_{10} \text{Ni}_{17} \]

Diffraction angle 2\( \theta \) (degrees)

Fig. 1
Fig. 2
Fig. 3
Fig. 4
Potential vs. Ag/AgCl (V)

Current density (A/cm²)

Fig. 5
Fig. 7
Fig. 8
METAL ALLOY AND USE THEREOF

BACKGROUND

[0001] The object of the invention is a metal alloy, useful in particular as a biomaterial.

[0002] Biomaterials must imperatively obey to specific criteria regarding the physical, chemical and mechanical properties, such as mechanical durability, chemical inertness, resistance to corrosion, bio-adhesion.

[0003] Titanium alloys have demonstrated superior biocompatibility among candidate metallic biomaterials however this class of alloys exhibits inferior tribological properties than those of for example Cr—Co—Mo alloys.

[0004] The mechanical properties and biocompatibility of titanium alloys can be improved by forming them as metallic glass having amorphous or nanocrystalline structure. Recent progresses in the field of research has demonstrated that amorphous and quasicrystalline phases can be prepared for several compositions based on combinations of titanium, zirconium and metals such as palladium, cobalt, nickel, copper: Ti—Zr—(Ni,Co,Pd), Ti—Zr—(Ni,Pd), Ti—Zr—(Ni,Co) and Ti—Zr—Co. However, these metallic glasses did not comply with all requirements of biocompatibility. Moreover, palladium is an expensive material. An exemplary metallic glass of this type is Ti₄₀Zr₂₀Cu₃₀Pd₁₄ described in publications: Fengxian Qin, Masahiro Yoshimura, Xinning Wang, Shengli Zhu, Asahi Kawashima, Katsuhiko Asami and Akihisa Inoue “Corrosion Behavior of a Ti-Based Bulk Metallic Glass and Its Crystalline Alloys” (MATERIALS TRANSACTIONS, Vol. 48 (2007), No. 7, pp. 1855-1858) and F. X. Qin, X. M. Wang and A. Inoue “Effect of annealing on microstructure and mechanical property of a Ti—Zr—Cu—Pd bulk metallic glass” (Intermetallics, Volume 15, Issue 10, October 2007, Pages 1337-1342). Recent research works concentrate on metallic glasses based on titanium and zirconium, such as Zr₂₅Nd₃₀Cu₃₀Zr₁₀₀₋₅₀₅₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄₅₋₄
wherein:

[0023] M represents an element selected from a group consisting of Ni, Co, Fe, Mn,

[0024] 1 represents impurities,

[0025] coefficients a, b, c, d, e represent atomic %, and are equal to: 40 ≤ a ≤ 55, 5 ≤ b ≤ 30, 5 ≤ c ≤ 25, 5 ≤ d ≤ 30, e ≤ 1.

[0026] The amorphous phase provides good corrosion resistance and the quasicrystalline phase provides high hardness of the alloy.

[0027] Preparing alloys comprising an amorphous phase and quasicrystalline phase, comprising Ni, Co, Fe, Mn, depends on various factors, such as the electron structure of the elements. For alloys according to the invention, there are maintained appropriate concentrations of metals of groups 4 and 5 (i.e. Ti, Zr, Nb) and groups 7 to 10 (i.e. Ni, Co, Fe and Mn). The used elements Ni, Co, Fe 1 Mn are easily accessible and affordable. Optionally, Ni could be replaced by Pd and Pt, Co by Rh and Ir, Fe by Ru and Os, Mn by Tc and Re, but these elements are not common (Tc is not present in the Earth soil) and are expensive. Cu has not been used due to low corrosion resistance.

[0028] The structure of the layers as analyzed by X-ray diffraction indicated the formation of icosahedral quasicrystalline phase, as shown in FIG. 1. The quasicrystalline phase, i.e. a form of a solid body, in which atoms are aligned in a seemingly regular, but a nonperiodic structure, which makes it impossible to distinguish their elementary cells, has been formed by quasicrystals having sizes from a few nanometers to about 100 micrometers, embedded in an amorphous matrix. The volume fraction of the icosahedral quasicrystalline phase in the metallic glass is dependent on the alloy composition and can be adjusted in order to comply with the desired properties, ranging from 1 to 80%. The volume fraction of the icosahedral quasicrystalline phase can be controlled by the alloy composition and the speed of cooling (which can be adjusted e.g. by changing the speed of rotation in the melt spinning method).

[0029] The alloy according to the invention shows excellent corrosion resistance, and therefore is very suitable for use in medicine as part of implants.

[0030] The corrosion properties of the alloy according to the invention have been investigated in simulated physiological solution at 37° C. (aerated Hanks' balanced salt solution; 8 NaCl, 0.4 KCl, 0.35 NaHCO3, 0.25 NaHPO4*H2O, 0.06 Na2HPO4*H2O, 0.19 CaCl2*2H2O, 0.19 MgCl2, 0.06MgSO4*7H2O, 1. g/l) by means of potentiodynamic test. The layers exhibit a low value of the corrosion current density in the range (1-5)*10^-6 A/cm² i and passivation current density in the range (5-7)*10^-6 A/cm². The corrosion current density has been measured by a Tafel extrapolation method, wherein exemplary plots for various embodiments of the alloys are presented in FIGS. 2-9.

[0031] The alloy according to the invention exhibits high wear resistance and increased hardness, as indicated by the measurements below:

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Vickers microhardness</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti₆₅Zr₁₅Fe₂₅</td>
<td>375</td>
</tr>
<tr>
<td>Ti₆₅Zr₁₅Mn₂₅</td>
<td>344</td>
</tr>
</tbody>
</table>

[0032] As indicated by the measurements in the table above, partial replacement of Fe and Mn by Nb increases the hardness of the alloys by 30% for Fe alloys and by 40% for Mn alloys.

[0033] In addition, the alloys according to the invention, as shown in FIGS. 3-9, are characterized by a wide range of passivation, i.e. from 1.0 to 1.5V in contrast to an alloy which does not contain niobium, as shown in FIG. 10, for which the range of passivation equals only 0.2 V. This property is particularly important in relation to corrosion, i.e. then titanium is in contact with other metallic materials.

[0034] The partial replacement of Zr by Nb provides an extension of the passivation region to a large value of the potential up to about 1.5V.

[0035] The alloy according to the invention can be manufactured by the methods known for metallic glasses, for example by the melt spinning method described by Cahn [W. Cahn, Physical Metallurgy, Third edition, Elsevier Science Publishers B.V., 1985] and Liebermann [Liebermann H. and Graham C., Production Of Amorphous Alloy Ribbons And Effects Of Apparatus Parameters On Ribbon Dimensions, IEEE Transactions on Magnetics, Vol Mag-12, No 6, 1976, pp. 921-923], by rapid cooling by squeezing as described in the Polish patent application PL384142 or by melt spinning according to the Polish patent application PL378301, as well as by thermal sputtering—cooling from a gaseous phase or by ion sputtering techniques.

We claim:

1. A metallic alloy comprising Ti, Zr, Nb, characterized in that it contains an amorphous phase and a quasicrystalline phase and is represented by the formula:

$$\text{Ti}_{x}\text{Zr}_{y}\text{Nb}_{z}\text{M}_{l}\text{n}$$

wherein:

M represents an element selected from a group consisting of Ni, Co, Fe, Mn,

1 represents impurities,

coefficients a, b, c, d, e represent atomic %, and are equal to: 40 ≤ a ≤ 55, 5 ≤ b ≤ 30, 5 ≤ c ≤ 25, 5 ≤ d ≤ 30, e ≤ 1.

2. The metallic alloy according to claim 1, characterized in that the quasicrystalline phase is formed by icosahedral crystals.

3. The metallic alloy according to claim 1, characterized in that the quasicrystalline phase is formed by quasicrystals having size ranging from a few nanometers to 100 micrometers.

4. The metallic alloy according to claim 1, characterized in that it is formed by a method of the group containing melt spinning, rapid cooling by squeezing, thermal sputtering—cooling from a gaseous phase, ion sputtering techniques.

5. Use of the alloy according to claim 1 for manufacturing a product intended as an implant for human or animal body.

6. An implant for implantation in the human or animal body comprising an alloy according to claim 1.