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Quasicrystal Formation in the system $Zr_{75-x}Ti_xCu_{25-y}Ni_y$

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Abstract

During the crystallization study of the bulk metallic glass $Zr_{46.8}Ti_{8.2}Cu_{7.5}Ni_{10}Be_{27.5}$ (Vit4) we have demonstrated that the primary crystals appearing during isothermal annealing in the glass region, above T_g and before T_x, were of quasicrystalline nature and beryllium free. The formula of the quasicrystalline phase so obtained and determined by electron techniques (EDX and EELS) was $Zr_{63}Ti_{14.4}Ni_{12.4}Cu_{10.2}$. We have synthesized phases in the system $Zr_{75-x}Ti_xCu_{25-y}Ni_y$ by melt spinning and obtained either amorphous or quasicrystalline phases. For the amorphous phases, we have studied the crystallization by in-situ neutron diffraction and obtained quasicrystals as primary crystals. Neutron and X-ray diffraction, DSC studies are presented.

Introduction

Bulk metallic glasses and quasicrystalline phases have attracted a lot of attention this last decade, and among them the family ZrTiCuNiBe presents the best performances in matter of glass forming ability over cost [1]. However these phases are metastable and several studies deal with the inherent instability of the amorphous state, as this instability modifies the mechanical properties. In particular when these alloys are heated in the supercooled liquid region, decomposition appears and is different for each alloy composition. For the alloy $Zr_{46.25}Ti_{8.25}Cu_{7.5}Ni_{10}Be_{27.5}$ (called Vit4), no phase separation appears prior to crystallization and Wanderka et al. [2,3] reported that a quasicrystalline phase is formed in the first step of crystallization, followed by a decomposition of this phase at higher temperatures. Formation of quasicrystals during devitrification of metallic glasses has been also observed in rapidly quenched alloys $Pd_{60}U_{20}Si_{20}$ [4], $Ti_{45}Zr_{38}Ni_{17}$ [5], or bulk metallic glasses $Zr_{65}Ni_{10}Ag_{10}Al_{7.5}Ni_{7.5}$ [6], ZrNiCuAl [7,8] and ZrTiCuNi [9]. During the crystallization study of the bulk metallic glass $Zr_{46.8}Ti_{8.2}Cu_{7.5}Ni_{10}Be_{27.5}$ (Vit4) [10,11] we have demonstrated that the primary crystals appearing during isothermal annealing in the glass region, above T_g and before T_x, were of quasicrystalline nature and beryllium free. The formula of the quasicrystalline phase so obtained and determined by electron techniques (EDX and EELS) was $Zr_{63}Ti_{14.4}Ni_{12.4}Cu_{10.2}$. So we have extended this study of beryllium free phases to the system $Zr_{75-x}Ti_xCu_{25-y}Ni_y$ in order to study the stability domain of these new quasicrystalline phases.

Experimental details

Metallic alloys $Zr_{75-x}Ti_xCu_{25-y}Ni_y$ samples were prepared from a mixture of the pure elements by induction melting in a water-cooled copper crucible under argon gas. The ingots were remelted by electromagnetic levitation several times. Ribbons were obtained by the melt-spinning technique at a constant copper wheel speed of 21 ms^{-1}, injected under argon by a cordierite rectangular nose of 7 by 0.4 mm and producing ribbons with a thickness of 50 μm and a width of 7 mm.

The endothermic and exothermic reactions associated with glass transition, crystallization and melting processes were examined by DSC at different heating rates on a Netzsch DSC 404S calorimeter under a flowing argon atmosphere. Neutron diffraction experiments were performed on the D1B diffractometer of ILL-Grenoble which is equipped with a 400 cells position sensitive

detector, covering an 80° 2-theta range, and allowing recording a pattern every 5 minutes. The experiments were performed in a dedicated furnace with a vanadium resistor under a secondary vacuum. The wavelength used was 0.2524 nm. The data presented are corrected of the background, sample container and furnace contributions.

Results and discussion

The first ribbon produced and analyzed was the composition determined during our study of the decomposition of the Vit4 bulk metallic glass, $Zr_{63}Ti_{14.4}Ni_{12.4}Cu_{10.2}$[10]. It is amorphous by X-ray and neutron diffraction. The DSC experiment performed at 2K/min is reported in figure 1a, it shows three exothermic peaks at 576, 609 and 656 K reported as Tx_1, Tx_2 and Tx_3 on the figure. We have performed an in-situ neutron diffraction experiment by heating the ribbon between 300 and 670 K. The three dimensional plot is reported in figure 1b.
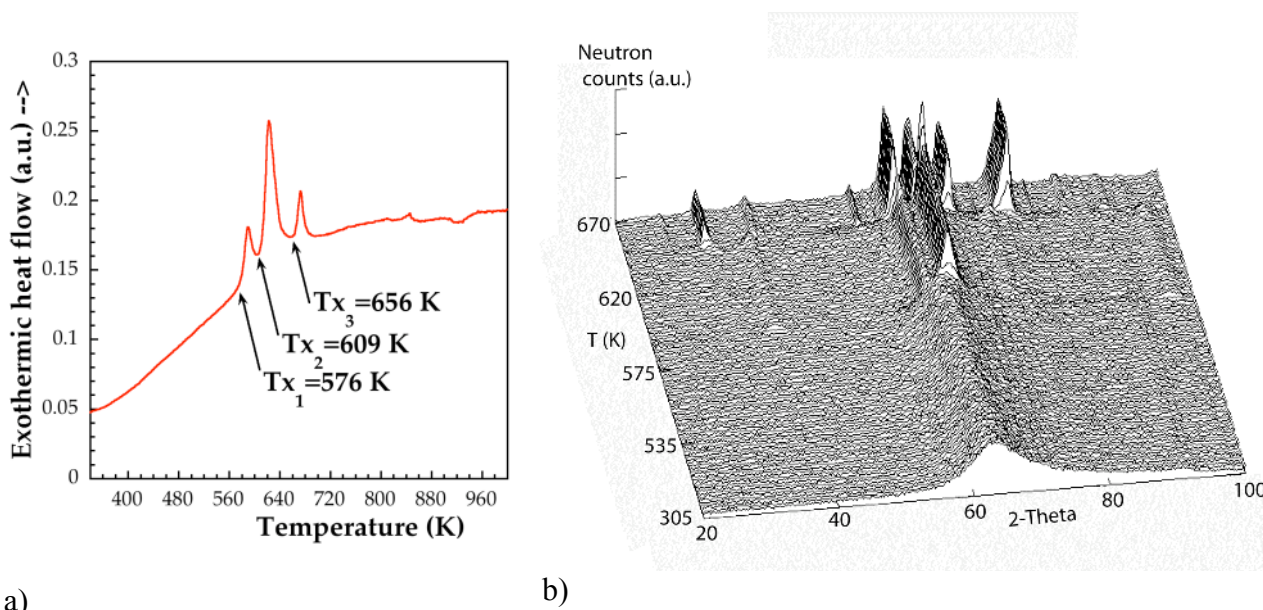

a)   b)

Figure 1: *a) DSC scan performed at 2K/min on the $Zr_{63}Ti_{14.4}Ni_{12.4}Cu_{10.2}$ alloy. b) 3D plot of the in-situ neutron diffraction experiment of the $Zr_{63}Ti_{14.4}Ni_{12.4}Cu_{10.2}$ alloy heated at 2K/min.*

At room temperature the sample is characterized by an amorphous bump centered around d = 0.232 nm, then at 610 K a series of peaks appears with two main contributions at d_1 = 0.252 nm and d_2 = 0.239 nm, this series of peaks disappears at 655 K to give new peaks that are stable up to 670 K. The phase formed at 610 K is very close to the one observed in Vit4 during the crystallization experiment [10], confirming that composition determined by chemical analysis is a composition that allows preparing quasicrystals. No diffraction peak is associated to the first event Tx_1 in the DSC experiment. We have then produced ribbons by increasing the content in titanium in the system $Zr_{75-x}Ti_xNi_{15}Cu_{10}$ from x=10 to 60. All the ribbons have been produced in the same conditions at a constant speed of 21 ms^{-1}. The X-ray diffraction patterns of the samples so obtained are reported in figure 2. By increasing the titanium content, the amorphous nature of the ribbons decreases up to x=25 where peaks are appearing at positions of the quasicrystal lines observed in the previous crystallization study. By increasing the titanium content, there is a superposition of an amorphous bump and of the lines due to the quasicrystalline particles. For the composition x=60 there is no more amorphous bump and the peak position have been indexed in the figure 3a with the six indices used for icosahedral phases [12].

It is also possible to produce the quasicrystalline phase by crystallization of the amorphous phase as seen in the in-situ neutron diffraction study. As an example we report in figure 3b the X-ray diffraction pattern of an amorphous sample as produced by melt spinning and crystallized at 583 K

during 360 minutes, but longer exposition, for example 720 minutes, or higher temperature, for example 603 K, leads to crystallization of other phases (Zr$_2$Cu).
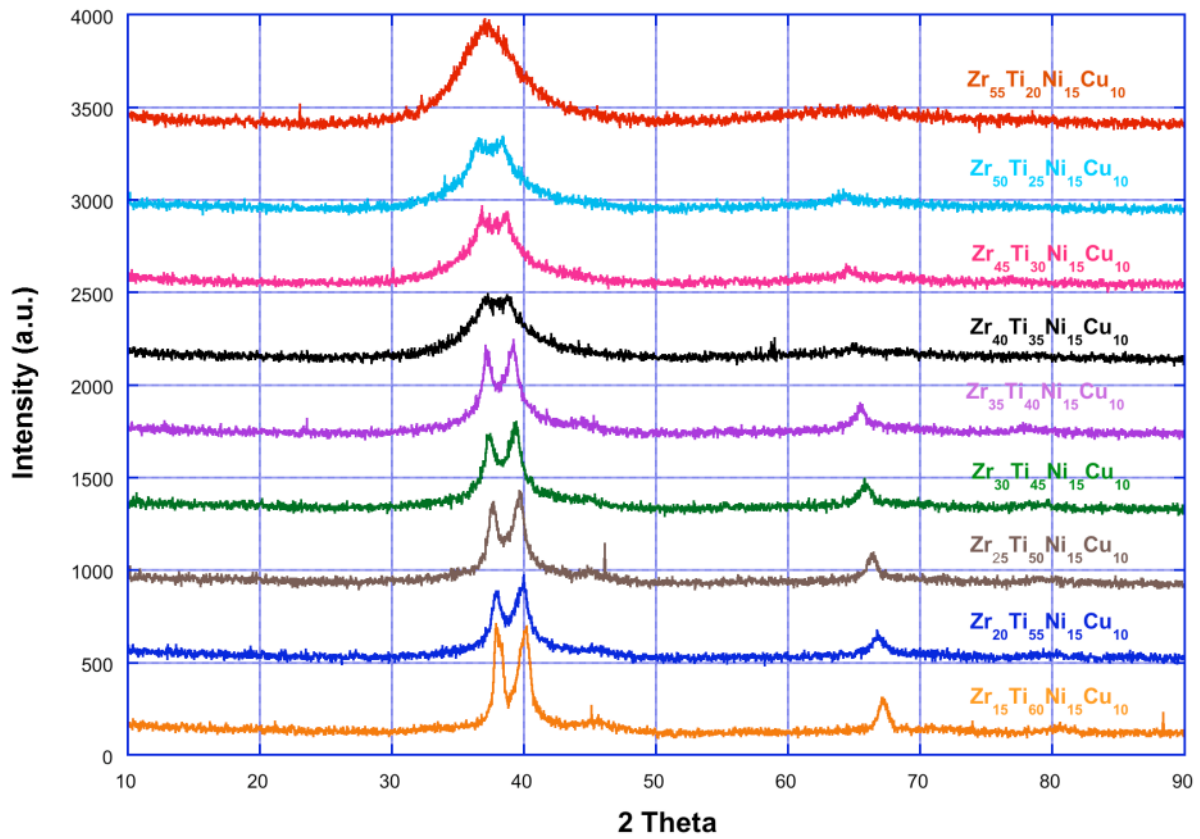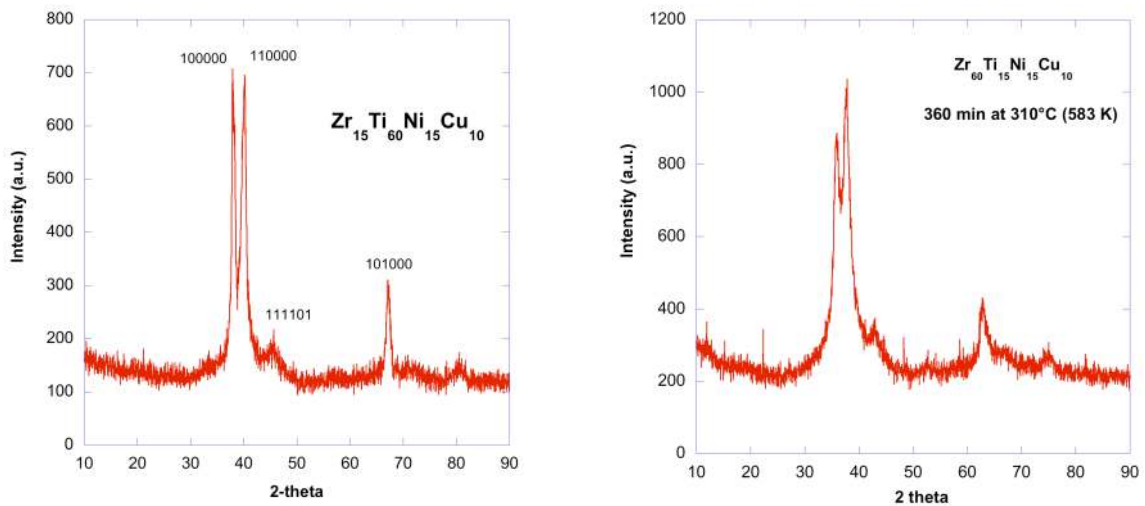

Figure 2: *X-ray diffraction patterns of the phases formed directly by melt spinning in the system Zr$_{75-x}$Ti$_x$Ni$_{15}$Cu$_{15}$ from x=20 to 60*

a)   b)

Figure 3: *X-ray diffraction patterns of: a) the phase formed directly by melt spinning for the alloy Zr$_{15}$Ti$_{60}$Ni$_{15}$Cu$_{15}$. b) The alloy Zr$_{60}$Ti$_{15}$Ni$_{15}$Cu$_{15}$ after annealing at 583K for 360 minutes.*

On figure 2, it is possible to note that the peak positions shift to higher angles when the titanium increases, meaning that the cell parameter a$_{6D}$ of the quasicrystalline lattice is decreasing when the titanium content is increasing. The lattice parameter a$_{6D}$ in six-dimensional (6D) reciprocal hypercubic space, is related to the absolute diffraction vector value Q by the expression:

$$Q = \frac{4\pi \sin\theta}{\lambda} = \frac{2\pi}{a_{6D}} \left(\frac{N + M\tau}{2(2+\tau)} \right)^{1/2}$$

Where τ is the irrational golden mean. The quasicrystal parameter in 3D space a_q is related to a_{6D} by the expression:

$$a_q = \frac{a_{6D}}{2^{1/2}}$$

In the system studied, a_q varies from 0.4673 nm for x=25 to 0.4517 nm for x=60.

Conclusion

The amorphous to quasicrystalline (QC) phase transformation in the $Zr_{63}Ti_{14.4}Ni_{12.4}Cu_{10.2}$ alloy has been studied by in-situ powder neutron diffraction, the transformation occurs at 610 K, but the phase formed is metastable and decomposes at 655 K. By changing the titanium composition in the system $Zr_{75-x}Ti_xNi_{15}Cu_{10}$ from x=10 to 60, it was possible to obtain QC particles for compositions above x=25. The composition with the sharper peaks is $Zr_{15}Ti_{60}Ni_{15}Cu_{10}$, the alloy presents a quasilattice parameter a_q = 0.4517 nm, close to other icosahedral QC phases as $Zr_{41.5}Ti_{41.5}Ni_{17}$ (0.5209 nm) and $Zr_{27}Ti_{53}Ni_{20}$ (0.5118 nm) [13], or 0.4843 nm in $Zr_{65}Al_{7.5}Ni_{10}Cu_{7.5}Ag_{10}$ [14]. It was also possible to produce QC phases by annealing the amorphous phases obtained for x < 25 in the system $Zr_{75-x}Ti_xNi_{15}Cu_{10}$, but these phases have not so sharp diffraction peaks, certainly due to the relative short time possible for annealing, longer times leading to crystallization of other phases more stable as Zr_2Cu.

Acknowledgments

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