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Crystallization and hydrogenation of a bulk metallic glass, $Zr_{50}Ti_{5}Al_{10}Cu_{22}Ni_{13}$

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Abstract

Glassy $Zr_{50}Ti_{5}Al_{10}Cu_{22}Ni_{13}$ alloy samples were prepared by HF melting and pouring into water-cooled copper mould of 6 mm diameter. The crystallization of these amorphous ingots has been studied by differential scanning calorimetry (DSC) measurements and in-situ neutron diffraction experiments showing that, by increasing temperature, intermediate (metastable) phases appear during heating. The structures of the intermediate and final phases have been determined by Rietveld refinements of X-ray and neutron diffraction data. The hydrogenation of the alloy has been performed by applying the H_2 gas pressure on the alloy annealed at different temperatures. The hydrogen uptake is different when applied on the amorphous, intermediate or final phases. The hydride ZrH_2 is formed when hydrogen pressure is applied on the amorphous or final phases, the hydride Zr_2NiH_4 is formed when the pressure is applied on the intermediate phase.

Keywords: Hydrogen storage materials; Amorphous materials; Solid-gas reactions; Neutron diffraction

1. Introduction

ZrTiAlCuNi metallic glasses are a new class of materials. They exhibit a high thermal stability corresponding to a wide undercooled liquid region before crystallization of binary intermetallic phases. There short range ordering involves many tetrahedral units, which are favorable for hydrogen storage. They show a bigger volume than the same crystallized materials involving new sites for hydrogen storage.

Previous studies on the hydrogenation of amorphous alloys have mainly been performed on ribbons obtained by melt spinning [1–9] in the Zr–Al–Ni–Cu system or in the Ti–Zr–Ni–Cu system [10]. Since the development of multi-component bulk metallic glasses [11,12], few studies have been devoted to the effects of hydrogen on these materials. Mainly the effects of hydrogen on the mechanical properties of Zr–Ti–Cu–Ni–Be alloys have been studied [13–15], damping properties in Zr–Al–Ni–Cu alloys [16] and the short-range chemical ordering in Zr–Ti–Cu–Ni–Al and Zr–Ti–Cu–Ni–Be [17]. We have recently prepared new bulk metallic glasses in the system Zr–Ti–Cu–Ni–Al in the form of cylinders with a 6 mm diameter [18,19]. We have studied the different phases appearing on heating by performing in-situ neutron diffraction studies and the aim of this study is to present the hydrogen absorption properties of $Zr_{50}Ti_{5}Al_{10}Cu_{22}Ni_{13}$ bulk metallic alloy by paying attention to the structure of the hydrogenated phases and to their higher hydrogen content.

2. Experimental details

Ingots of composition $Zr_{50}Ti_{5}Al_{10}Cu_{22}Ni_{13}$ were prepared from a mixture of the pure elements by HF induction melting in a water-cooled crucible in argon atmosphere. Heating under secondary vacuum at 1000 °C purified the zirconium provided by the CEZUS COMPANY. The ingots were melted by electromagnetic levitation and dropped into water-cooled copper mold of cylindrical shape (diameter 6 mm). Several rods were prepared from the same batch in order to perform the DSC and neutron diffraction experiments. The endothermic and exothermic reactions associated with glass transition and crystallization process were examined by differential scanning calorimetry (DSC) at different heating rates on a Netzsch DSC 404S calorime-

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ter under a flowing argon atmosphere. In order to prepare the hydrides with the maximum hydrogen content, the ingots, broken in small pieces, were placed into silica tubes and then into a stainless steel autoclave able to work under several few atmospheres of hydrogen gas pressure and up to 600 °C. After several evacuation and H_2 rinsing cycles, hydrogen gas was admitted into the reactor at 1 MPa pressure. In order to activate the sample, a first hydriding cycle was performed by slowly increasing temperature until H_2 absorption occurs. After this first H_2 uptake, the reactor was evacuated and the sample was cooled down to room temperature. The procedure was repeated and when H_2 absorption started, temperature was kept constant and the H_2 gas pressure increased to 3 MPa in order to reach the maximum hydrogen charge. Then the sample was cooled down to room temperature under H_2 pressure. The amount of the hydrogen uptake was measured by weighing the alloy before the experiment and the hydride after the reaction. All the samples (alloys and hydrides) were analyzed by powder X-ray diffraction using a Philips diffractometer ($\lambda_{Cu}=1.5418$ Å) equipped with a backscattering graphite monochromator. Neutron diffraction experiments were performed on the D20 diffractometer of ILL-Grenoble which is equipped with a 1600 cells position sensitive detector, covering an 160° 2θ range, and allowing recording a pattern every minute. The wavelength used was 2.424 Å.

3. Results

3.1. Structural study of the alloys

The $Zr_{50}Ti_5Al_{10}Cu_{22}Ni_{13}$ alloys formed after molding are cylinders of 6 mm in diameter and 60 mm in length; they present a shinning aspect and can be manipulated in air without corrosion. X-ray experiments are performed at room temperature on sections at the top and the bottom of the cylinder in order to check the homogeneity of the cylinder. A typical diffractogramme is shown in Fig. 1 with the typical bump of an amorphous compound.

By heating the amorphous compounds they present various crystallization that can be revealed by DSC measurements and in-situ neutron diffraction. We have performed both kinds of experiments by heating the sample at 2 K/min between room temperature and 820 °C. The DSC experiment is reported in Fig. 2. It shows the common features of bulk metallic glasses, with an endothermic reaction starting at $T_{g_1}=290$ °C and with various crystallizations at $T_{x_1}=427$ °C, $T_{x_2}=452$ °C and $T_{x_3}=513$ °C.

The neutron diffraction experiment is shown in Fig. 3, it shows an amorphous diffractogramme at room temperature, then two crystallization reactions appear at $T_{x_1}=423$ °C and $T_{x_3}=528$ °C. The first phase appearing above an amorphous bump is tetragonal Zr_2Ni, then this phase disappears and transforms to tetragonal Zr_2Cu, orthorhombic Zr_7Ni_{10} and cubic $ZrAl_2$.

3.2. Structural study of the hydrides

One sample has been heated, after activation, under 2 MPa of hydrogen gas pressure, the hydrogen uptake starts at 380 °C, we have stopped the heating at this plateau temperature and refilled the tank until no more pressure variation appears. The sample has then been cooled down at room temperature under 2 MPa and weighted. The hydrogen uptake corresponds to 90 hydrogen per formula unit ($Zr_{50}Ti_5Al_{10}Cu_{22}Ni_{13}H_{90}$). The sample was very brittle and transformed to a powder by grinding in a mortar. The X-ray diffraction pattern is reported in Fig. 4. The structure is tetragonal of the ThH_2 type with cell parameters $a=4.881(8)$ Å and $c=4.585(7)$ Å.

Another sample was heated to 480 °C under vacuum, and then cooled at room temperature in order to be transformed in the Zr_2Ni variety as shown in the DSC and neutron studies. The sample was then heated under 2 MPa of hydrogen gas pressure, the hydrogen uptake starts at 380 °C, we have stopped the heating at this plateau temperature and refilled the tank until no more pressure variation appears. The sample has then been cooled down at room temperature under 2 MPa and weighted. The hydrogen uptake corresponds to 97 hydrogen per formula unit ($Zr_{50}Ti_5Al_{10}Cu_{22}Ni_{13}H_{97}$). The sample was very

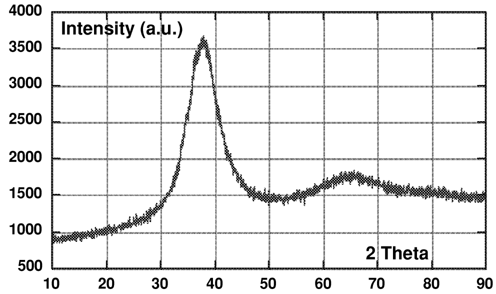

Fig. 1. RX Diffractogramme of $Zr_{50}Ti_5Al_{10}Cu_{22}Ni_{13}$ alloy.

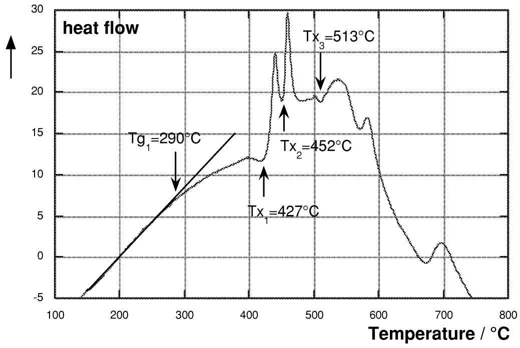

Fig. 2. DSC of $Zr_{50}Ti_5Al_{10}Cu_{22}Ni_{13}$ alloy recorded at 2 K/min.

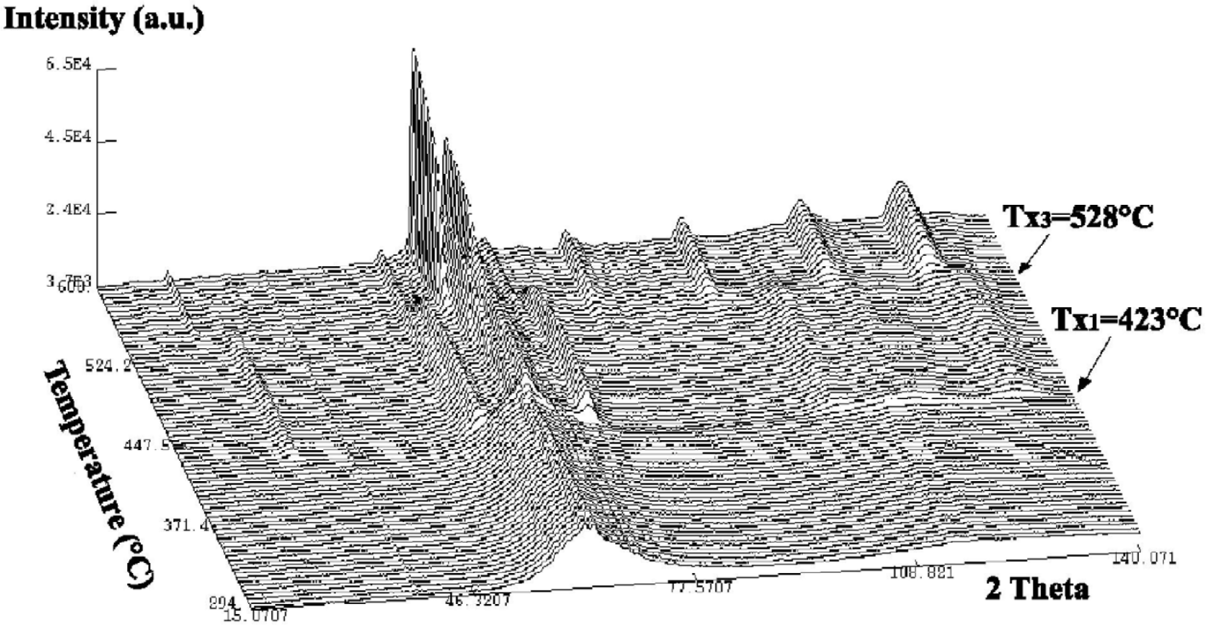

Fig. 3. Neutron diffraction experiment of the alloy $Zr_{50}Ti_5Al_{10}Cu_{22}Ni_{13}$ heated under vacuum between 295 and 600 °C.

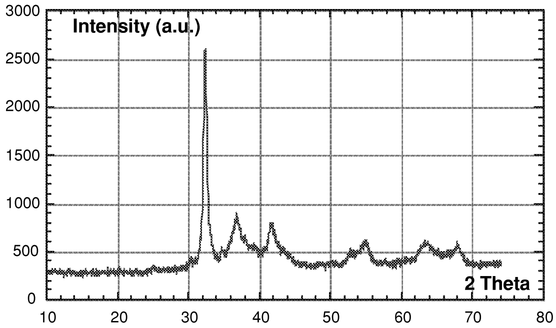

Fig. 4. X-ray diffractogramme of the hydride obtained at 380 °C of the bulk alloy.

brittle. The X-ray diffraction pattern is reported in Fig. 5. The structure is tetragonal of the Zr_2Ni type with cell parameters $a=6.971(8)$ Å and $c=5.535(7)$ Å. The alloy in the Zr_2Ni type had cell parameters $a=6.551(8)$ Å and $c=5.24(7)$ Å, that means that the volume increase between the alloy and the hydride is 19.5%. The entire alloy is not transformed to hydride and an amorphous bump is still present in the X-ray diffraction pattern of Fig. 5.

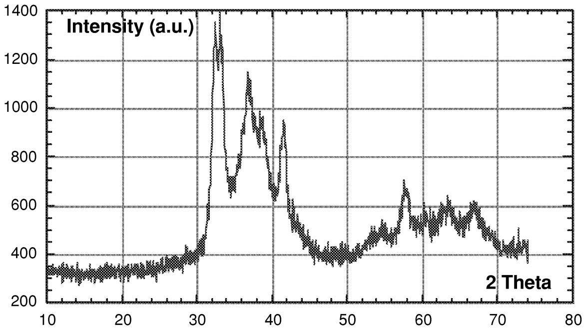

Fig. 5. X-ray diffractogramme of the hydride obtained at 380 °C after heating of the alloy at 480 °C.

4. Discussion and conclusion

It has been shown that bulk $Zr_{50}Ti_5Al_{10}Cu_{22}Ni_{13}$ metallic glasses can absorb hydrogen at 380 °C under 2 MPa of hydrogen gas pressure. Depending of the initial state of the alloy, different hydrides can be obtained. Starting from the amorphous state, hydrogenation leads to the formation of ε-ZrH_x. From the cell parameters obtained, we can deduce from Ref. [20] that the composition is close to ε-$ZrH_{1.70}$, that means that in the initial alloy, all the zirconium and a part of the titanium have been transformed to a hydride of formula $(Zr,Ti)H_{1.70}$, the aluminum, nickel and copper forming an alloy visible in the X-ray diffraction pattern at $2\theta=42°$.

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