Microstructure evolution upon devitrification and crystallization studies of Ti-Hf-Zr-Cu-Ni-Sn-Si glassy alloy

J.L. Soubeyroux a, J.J. Blandin b and J.N. Mei a,c

a Institut Néel/CRETA, CNRS Grenoble, 25 Avenue des Martyrs, BP 166, 38042 Grenoble Cedex 9, France.
bGrenoble-INP, SIMAP-GPM2, CNRS, 38402 Saint-Martin d’Hères Cedex, France.
cState Key Laboratory of Solidification Processing, Northwestern Polytechnical University, Xi’an, 710072, Shaanxi, China.

jean-louis.soubeyroux@grenoble.cnrs.fr

Abstract. The phase components and microstructure of as-cast Ti41.5Cu37.5Ni7.5Zr2.5Sn5Hf5Si1 glass forming alloy was investigated by differential scanning calorimetry (DSC), scanning electron microscopy and in-situ neutron diffraction studies. For diameters above 3 mm the samples present small crystals identified as the Ti5Sn3Cu and cubic Ti(CuNi) phases. Crystallization studies in the DSC furnace and in-situ neutron diffraction reveal that the cubic titanium phase is TiNi(Cu) with the Pm-3m space group and not the β-Ti phase. The evolution of phases above Tg show that the TiNi phase is metastable and decomposes at Tg=727 K to form the γ-TiCu phase. The Ti5Sn3Cu phase does not evolve in this temperature range. At room temperature by compression measurements, the alloy with 2 mm diameter shows a high failure limit of 2120 MPa with 2.1% of plasticity.

1. Introduction

Much attention is actually paid to find and to study Ti-based bulk metallic glasses (BMG) due to their high specific strength, low weight and low cost [1-8]. Development of these BMG can expend the field of their applications. Among the Be-free Ti-based system studied, ternaries Ti50-(Cu,Ni)50 alloys [9-10] have been shown to present a glass transition temperature when elaborated as ribbons. Ma et al. [11] have improved the glass forming ability (GFA) by substituting Ti with Zr and Hf and Cu by Si to form the Ti42.5Cu42.5Ni7.5Hf5Zr2.5Si1 BMG by conventional mould casting and they succeed to form amorphous samples up to a 5mm diameter.

Huang et al. [12] have recently improved the GFA of this alloy by studying the effects of the Sn to Cu substitution and the compound Ti42.5Cu37.5Ni7.5Hf5Zr2.5Si1Sn5 has been demonstrated to be the best Be-free BMG found in the titanium-copper system today and presents a critical diameter of 6 mm. In a previous paper [13] we have presented the sample synthesis and DSC crystallization kinetics studies. In this paper, we present the phase components and microstructure studies of the as-cast Ti42.5Cu37.5Ni7.5Hf5Zr2.5Si1Sn5 alloy by SEM/EDS and in-situ neutron diffraction experiments. Preliminary compression test experiments are also presented.
2. Experimental procedure

Ingots with nominal composition Ti<sub>42.5</sub>Cu<sub>37.5</sub>Ni<sub>7.5</sub>Hf<sub>5</sub>Zr<sub>2.5</sub>Si<sub>1</sub>Sn<sub>5</sub> were prepared by HF-melting the mixture of the pure Ti, Cu, Ni, Hf, Zr, Si and Sn elements in a copper cold crucible. Bulk alloys in a cylindrical form with 40 mm in length and 2 or 4 mm in diameter (named Φ2 and Φ4) were prepared by injection method in a copper mould under argon gas. Alloys’ oxygen content was measured <400 ppm. The phase components and microstructure were obtained by scanning electron microscopy (SEM) (JEOL-5600LV equipped for energy-dispersive X-ray spectrometry (EDS)). Thermal properties were measured by differential scanning calorimetry (DSC) (NETZSCH DSC 404S) at a heating rate of 2 K/min under flowing argon gas in order to be compared with neutron experiments. In-situ neutron diffraction was studied on the D1B-CRG diffractometer at Institute Laue Langevin in Grenoble at the 2.524Å wavelength, spectra during continuous heating at 2K/min under vacuum were recorded every 5 minutes using a position sensitive detector covering 80° in 2-theta. Data treatment was done with the LAMP and FULLPROF programs of ILL [14].

3. Results and discussion

For Φ2 alloy, the SEM and X-ray patterns indicate that the as-cast alloy consists of fully amorphous phase. For Φ4 alloy, the SEM and X-ray patterns show tiny crystals of an extra phase that were attributed to the TiNi(Cu) or β-Ti phase quenched from high temperature and a second phase (Ti<sub>5</sub>Sn<sub>3</sub>Cu). The bcc (Ti,Cu,Ni) phase has been found in a great number of Ti-based BMGs and reported as a β-Ti phase [15, 16] or a TiNi (CsCl-type) phase [17,18].

In the SEM images of Φ4 sample shown in figure 1, white particles are observed in back scattering mode (average typical size is 5 μm) with a “flower-like” shape and are not very widespread in the glassy matrix with a darker grey zone around, the chemical element percentages of these small crystals measured by EDS are given in table 1. The white flowers are enriched in tin and could correspond to the Ti<sub>5</sub>Sn<sub>3</sub>Cu crystallized phase not observed by XRD. The dark grey zone is lower in tin and should correspond to the TiNi(Cu) structure, the light grey zone (matrix) has a composition very close to the initial glass composition.

![Figure 1. SEM image of the Φ4 sample.](image)

| Table 1. EDS analysis of the different grey zones of the Φ4 sample (the overlap of the energies of Si and Hf lowers the Hf content and enhances the Si content). |
|------------------|---|---|---|---|---|---|---|
| elements         | Ti | Zr | Hf | Cu | Ni | Si | Sn |
| Initial (master ingot) | 41.5 | 2.5 | 5.0 | 37.5 | 7.5 | 1.0 | 5.0 |
| White flowers    | 42.05 | 3.85 | 2.65 | 29.35 | 5.35 | 4.5 | 12.25 |
| Dark grey zone   | 43.15 | 2.78 | 2.48 | 36.7 | 7.9 | 3.65 | 3.35 |
| Light grey zone  | 42.6 | 2.65 | 3.45 | 35.9 | 6.6 | 3.35 | 5.45 |

Table 2 gives the thermal parameters obtained with DSC traces and compared to previous studies on the same alloy [12, 13], the DSC traces at 2K/min have been measured to compare with neutron diffraction in-situ studies performed at the same heating rate on Φ4 samples. The two studies at
20K/min are very close and show that the same composition has been prepared and that the small crystals have no influence on the thermal properties of the vitreous matrix.

| Table 2. DSC thermal parameters extracted from experiments performed at 2 and 20K/min and compared to previous studies on the same alloy prepared as a 6 or 4 mm sample [12, 13]. |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Alloy           | T_{x1} | T_{x2} | T_{l} | ΔT_{c1} | T_{g} | γ | δ |
| This study (2K/min) | 675     | 727   | 803   | 1173   | 52   | 0.575 | 0.393 | 1.460 |
| Ref [13] (20K/min) | 694     | 756   | 820   | 1183   | 62   | 0.587 | 0.403 | 1.546 |
| Huang [12] (20K/min) | 693     | 757   | 820   | 1176   | 64   | 0.59  | 0.405 | 1.569 |

Mechanical testing was carried out in compression at room temperature on the Φ=2 mm samples. The measured parameters were a fracture stress σ_f = 2120 MPa, an elastic strain ε_s = 2%. These values are also in agreement with previously reported ones on the same composition [12]. The Young modulus was measured thanks to ultrasonic techniques and E_Y = 86 MPa. The microhardness was also measured and a value of 645 HV was found.

In order to study the crystallization process by an ex-situ method, Φ4 samples have been heated in the DSC apparatus at 716K slightly above T_g (T_g=694K) at a constant heating rate (20K/min) then maintained at this temperature for annealing at different times then quenched in air; two other samples were heated at the same heating rate: one was maintained 5 min at 769K, this temperature being at the end of the first crystallization DSC peak, and the other one was maintained at 873K, this temperature being at the end of the second crystallization DSC peak. X-ray patterns of these samples show broad amorphous peak with the cubic TiNi(Cu) phase peak intensities increasing with time and the hexagonal Ti_{5}Sn_{3}Cu phase appearing more clearly, the pattern recorded after the first crystallization peak (769K) having the same properties, the cell parameter of this cubic phase (a=0.3090(2) nm) is not evolving with crystallization in all these samples. The sample recorded after the second DSC event at 800 K can be indexed with two main phases, the tetragonal γ-TiCu phase with parameters a=0.3120(1) nm and c=0.5920(3) nm and the hexagonal Ti_{5}Sn_{3}Cu phase with parameters a=0.8020(3) nm and c=0.5583(2) nm. The γ-TiCu phase replacing the cubic TiNi(Cu) phase with close cell parameters (a(γ-TiCu)=a(TiNi); c(γ-TiCu)=2a(TiNi)), it is suggested that the second peak in the DSC scan is the transformation of the metastable cubic TiNi(Cu) phase in tetragonal γ-TiCu phase. The β-Ti phase is bcc with space group Im3m and implies no ordering between the atoms at the 0,0,0 position and the centered ½,½,½ ones. X-ray are not able to show this ordering for contiguous elements among the 3d metal series. We will see in the following experiments with neutron diffraction studies that titanium occupies mainly the 0,0,0 position and Cu and Ni, the centered ½,½,½ one, so that the (100) and (111) peaks are present, leading to the Pm-3m space group.

Neutron diffraction patterns have been recorded on Φ4 samples. The constant heating at 2K/min up to 920K and after a plateau at this temperature is presented in figure 2 as a 3D plot with 2-theta along the x-axis, the temperature (or time) along the y-axis and the intensity of the neutron counts along the z-axis. Neutron diffraction technique measures the whole volume of the sample, so it is possible to observe three different components of diffraction, a bump centered at 2θ=73° corresponding to the amorphous part of the sample, small lines around 2θ=22 and 42° and indexed as the Ti_{5}Sn_{3}Cu phase and 3 stronger lines indexed as (100), (110) and (111) of a cubic phase. The neutron diffraction pattern at the beginning of the experiment (without any thermal treatment) and the corresponding X-ray diffraction pattern have been both refined with a model of two phases, Ti_{5}Sn_{3}Cu (SP=P6_3/mmc ; a=0.8117(7) nm, c=0.5605(8) nm) and TiNi(Cu) (SP=Pm-3m ; a = 0.3117(1) nm) with Ti at the 0,0,0 position and Ni,Cu at the ½,½,½ position. The result of these refinements gives a good refinement with the 3 peaks (100), (110) and (111) and X-ray diffraction pattern with the (110) peak only. Copper, nickel and titanium have a too close number of electrons to observe this ordering by X-ray, but the high neutron contrast between scattering lengths of titanium (-0.34) compared to copper (0.77) and nickel (1.03) evidences this ordering. During the heating at 2K/min, two transformations of phases occur, the first at T_{x1}=737K with the appearance of a new set of lines indexed as the γ-TiCu phase and
an Sn₁₃Cu₃₉-like phase. At 803K, the cubic TiCu phase decomposes to transform into the γ-TiCu phase. The lines corresponding to the Ti₅Sn₃Cu phase don’t change during this heating process and have the same intensity at the end of the experiment as at the beginning. As previously done, the neutron diffraction pattern at the end of the neutron diffraction experiment recorded at room temperature and the same sample measured by X-ray diffraction have been refined with a model of 3 phases: γ-TiCu (SG=P4/nmm ; a=0.3153(2)nm, c=0.5972(3) nm), Ti₅Sn₃Cu (SP=P6₃/mmc ; a=0.8125(7) nm, c=0.5631(8) nm) et Sn₁₁Cu₃₉ (SP=F-43m ; a=1.8086(5)).

Figure 2. Neutron thermodiffractogram recorded at λ=0.2524 nm during a constant heating at 2K/min of the Φ4 sample.

4. Conclusions
Ti₄₁.₅Cu₃₇.₅Ni₇.₅Zr₂.₅Sn₂.Hf₀.₅Si₀.₅ glasses have been prepared as fully amorphous cylinders of 2 mm in diameter and with some particles (Ti₅Sn₃Cu and TiNi(Cu)) in the 4 mm sample. Ex-situ crystallization in the DSC furnace and in-situ neutron diffraction experiments have been analyzed as a function of annealing time and temperature. The first phase to crystallize in this system is a cubic non-centered phase of TiNi(Cu) formula with space group Pm-3m presenting an ordering between titanium and the other 3d metals. By heating the sample above Tₓ₁=737K, the cubic TiNi(Cu) phase transforms to tetragonal γ-TiCu(Ni), the transformation is finished at Tₓ₂=803K when no more peaks of the cubic phase are visible. The Ti₅Sn₃Cu phase shown since the glass formation does not evolve during the heat treatment but the TiNi phase develops around the Ti₅Sn₃Cu nucleus. At the second crystallization event of the DSC curve, a cubic phase with the Sn₁₁Cu₃₉-like phase appears with a low intensity. Preliminary mechanical tests at room temperature show a high failure limit of 2120 MPa. Additional mechanical tests as a function of temperature are under way.

Acknowledgements
This work was supported by the New Century Excellent Person Supporting Project of China (521020301) and China Scholarship Council.

References
[1] T. Zhang, A. Inoue, Mat. Trans., JIM, 40 (1999) 301
[2] T. Zhang, A. Inoue, Mat. Sci. Eng., A304-306 (2001) 771
[3] C. Ma, S. Ishihara, H. Soejima, N. Nishiyama, A. Inoue, Mat. Trans., 45 (2004) 1802
[4] H. Men, S. Pang, A. Inoue, T. Zhang, Mat. Trans.,46 (2005) 2218
[5] G. Wang, Y.H. Liu, P. Yu, D.Q. Zhao, M.X. Pan, W.H. Wang, Appl. Phys. Lett., 89 (2006) 251909
[6] K.B. Kim, J. Das, S. Venkataraman, S. Yi J. Eckert, Appl. Phys. Lett., 89 (2006) 71908
[7] S.L. Zhu, X.M. Wang, F.X. Qin, A. Inoue, Mat. Trans., 48 (2007) 163
[8] S.L. Zhu, X.M. Wang, F.X. Qin, M. Yoshimura, A. Inoue, Mat. Trans., 48 (2007) 2445
[9] T. Zhang, A. Inoue, T. Masumoto, Mater. Sci. Eng., A181/182 (1994) 1423
[10] T. Zhang, A. Inoue, Mat. Trans., JIM 39 (1998) 1001
[11] C. Ma, H. Soejima, S. Ishihara, K. Amiya, N. Nishiyama, A. Inoue, Mat. Trans., 45, 11 (2004) 3223
[12] Y.J. Huang, J. Shen, J.F. Sun, X.B. Yu, J. Alloys Comp., 427 (2007) 171
[13] J.N. Mei, J.L. Soubeyroux, J.S. Li, J.J. Blandin, H.C. Kou, H.Z. Fu, L. Zhou, Acta Materialia, submitted.
[14] J. Rodriguez-Carvajal, Physica B, (1993), 192
[15] G. He, J. Eckert, W. Löser, L. Schultz, Mat. Res. Soc. Symp. Proc., 754 (2003) CC11.12.1
[16] B.B. Sun, M.L. Sui, Y.M. Wang, G. He, J. Eckert, E. Ma, Acta Mater., 54 (2006) 1349-1357
[17] T.G. Woodcock, M. Kusy, S. Mato, G. Alcala, J. Thomas, W. Löser, A. Gebert, J. Eckert, L. Schultz., Acta Mater., 53 (2005) 5141-5149
[18] M. Calin, L.C. Zhang and J. Eckert, Scripta Mater., 57 (2007) 1101-1104