Kinetics and Thermodynamics of Bulk Glass Formation in a Zr$_{52.5}$Cu$_{17.9}$Ni$_{14.6}$Al$_{10}$Ti$_5$ Alloy

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Zr$_{52.5}$Cu$_{17.9}$Ni$_{14.6}$Al$_{10}$Ti$_5$ bulk metallic glasses have been prepared by copper moulding. In order to obtain a fully amorphous sample, a careful control of the atmosphere conditions in the casting chamber was necessary. In particular, the presence of oxygen contamination promotes the nucleation of an fcc “big cube” phase, reducing glass formation. The crystallisation of bulk amorphous samples has been followed by DSC and values of about 4 kJ mol$^{-1}$ have been obtained for the heat release at about 740 K. By high temperature DSC, a metastable-to-stable phase transformation has been evidenced at 938 K, which gives a heat evolution of 1.12 kJ mol$^{-1}$. Melting and solidification of the alloy have been observed at 1070 K, giving an average value for the enthalpy change of about 8.2 kJ mol$^{-1}$. The temperature dependence of the entropy difference between undercooled liquid and equilibrium crystal phases has been described on the basis of different models for the specific heat difference ($\Delta C_p$) between the two phases. A best fitting of experimental data gives values of $\Delta C_p$ of about 21 J mol$^{-1}$ $\cdot$ K$^{-1}$ at the glass transition temperature (690 K), in good agreement with experimental values obtained from DSC measurements.

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1. Introduction

Zr-based alloys have a high glass forming ability (GFA) and a good glass stability. In fact, these alloys are characterised by a low critical cooling rate for glass formation ($R_c = 10^8 - 10^9$ K s$^{-1}$) and an interval ($\Delta T_x = T_x - T_g$) between the glass transition ($T_x$) and crystallisation ($T_g$) temperatures up to 100 K, so that bulk metallic glasses (BMG) may be prepared. In order to prepare fully amorphous bulk samples, the preparation conditions must be carefully controlled, avoiding the nucleation of crystal phases. The oxygen impurity level in these alloys has been found to play a crucial role in the GFA. In fact, the presence of oxygen promotes the nucleation of an fcc “big cube” phase, which promotes the crystallisation process of the undercooled melt.

Glass formation in metallic systems is generally described in terms of kinetics and thermodynamics arguments. The stability of undercooled liquid is strongly enhanced for alloys showing high viscosity, which reduces the atomic diffusivity necessary for the nucleation of crystal phases from a multicomponent system. In addition, the presence of a low free energy difference between the undercooled liquid and the corresponding crystal phases further reduces the nucleation frequency.

The aim of this paper is to study the kinetics and the thermodynamics of glass formation in a Zr$_{52.5}$Cu$_{17.9}$Ni$_{14.6}$Al$_{10}$Ti$_5$ alloy. Conditions necessary to prepare a fully amorphous BMG will be analysed and results will be explained on the basis of the effect of impurities on the nucleation of crystal phases. From experimental values of the heat of crystallisation obtained at different temperatures and from the heat of melting and solidification, the enthalpy difference between undercooled liquid and crystal phases will be estimated. Different models for the specific heat difference between undercooled liquid and crystal phases will be considered in order to fit experimental data.

2. Experimental Procedure

Alloy ingots, with nomination composition Zr$_{52.5}$Cu$_{17.9}$Ni$_{14.6}$Al$_{10}$Ti$_5$, have been prepared by arc melting a mixture of high purity elements under a Zr and Ti-gettered argon atmosphere. Each ingot has been melted three times in order to obtain a good composition homogeneity. Composition analyses have been carried out by SEM equipped with a microanalysis EDS.

The synthesis of bulk metallic glasses has been optimised using a wedge-shaped copper mould. In all cases the chamber was previously evacuated up to about $2 \times 10^{-2}$ Pa several times, in order to clean as much as possible the casting environment. Then the chamber was filled with pure Ar at 1.0 $\times$ 10$^5$ Pa and at 0.5 $\times$ 10$^5$ Pa. The melt was introduced into the copper mould with a constant overpressure of 2.5 $\times$ 10$^5$ Pa. From the wedge-shaped ingots, slides of 1 mm and 3 mm of diameter were selected for the analysis.

Structural characterisation at room temperature has been performed by X-ray diffraction (XRD) using Co K$_{\alpha}$ or Cu K$_{\alpha}$ radiation, in standard Bragg-Brentano geometry. The high flux high energy monochromatic radiation on ID11 beam line of the European Synchrotron Radiation Facilities (ESRF) has been employed for in-situ structural characterisation during heating up to melting temperature. The radiation has been selected using a nitrogen-cooled silicon monochromator. The energy of photons corresponds to an X-ray wave-length ($\lambda$) of 0.01304 nm. The quartz crucibles containing BMG samples were inserted inside an induction coil, vertically placed between the incident beam and a two-dimensional detector.
Both XRD and ESRF data are reported as a function of scattering vector $Q = 4\pi \sin \theta/\lambda$.

The crystallisation of amorphous alloys has been studied with a DSC (Perkin Elmer 7), both in isothermal and in scanning conditions, using standard Al pans under flowing Ar. The thermal analysis of samples, including melting and solidification of the alloy, has been also performed with a Setaram MultiHTC DSC cell, using alumina crucibles under flowing He. Samples were surrounded with alumina powder in order to avoid sticking to the walls. The calibration of both calorimeters has been performed by melting several pure elements.

### 3. Results and Discussion

The composition (at%) of master alloy checked by EDS analysis is Zr$_{52.5}$Cu$_{17.9}$Ni$_{13.9}$Al$_{6.9}$Ti$_{1.6}$ (typical error ±0.5–1.0 at%). The corresponding XRD pattern is shown in Fig. 1 (curve a). The identification of stable phase mixture is rather complicated: tetragonal Zr$_2$Cu, hexagonal Al$_2$NiZr$_6$ and tetragonal Zr$_2$Ni compounds have been found, together with unknown phases. The XRD patterns of BMG (3 mm) prepared in different conditions are also reported in Fig. 1 with unknown phases. The XRD patterns of BMG (3 mm) and tetragonal Zr$_2$Ni compounds have been found, together with 1.

<table>
<thead>
<tr>
<th>Ar pressure in the casting chamber $P/10^5$ Pa</th>
<th>Diameter $d$/mm</th>
<th>Glass transition temperature $T_g$/K</th>
<th>First peak temperature $T_{p1}$/K</th>
<th>Second peak temperature $T_{p2}$/K</th>
<th>Enthalpy of crystallisation $\Delta H_c$/kJ mol$^{-1}$</th>
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The synthesis of bulk metallic glasses in Zr-based alloys is very sensitive to the presence of oxygen contamination. For instance, doubling the oxygen content in the alloy, a time-shift of nearly one order of magnitude is observed in the TTT curves for glass-formation.\(^4\) The crucial role of oxygen in the nucleation of this phase has been demonstrated by the addition of small quantities of Y to Zr-based alloys.\(^3,7\) In fact, this element acts as a scavenger for the alloy, reduces the nucleation of the fcc “big cube” phase and increases significantly the glass formation. The effect of oxygen contamination can

![Fig. 1 XRD patterns of Zr$_{52.5}$Cu$_{17.9}$Ni$_{13.9}$Al$_{6.9}$Ti$_{1.6}$ master alloy (a) and after casting (φ3 mm) with 1.0 × 10$^5$ Pa of Ar (b) and 0.5 × 10$^5$ Pa of Ar (c) in the chamber. Intensity in logarithmic scale. Symbols: cross, big cube phase; circle, tetragonal NiZr$_2$; triangle, tetragonal CuZr$_2$; square, hexagonal Al$_2$NiZr$_6$.](image1)

![Fig. 2 DSC traces of Zr$_{52.5}$Cu$_{17.9}$Ni$_{13.9}$Al$_{6.9}$Ti$_{1.6}$ master alloy (a) and after casting (φ3 mm) with 1.0 × 10$^5$ Pa of Ar (b) and 0.5 × 10$^5$ Pa of Ar (c) in the chamber. The scanning rate was 10 K min$^{-1}$.](image2)
be described in terms of schematic TTT curves, as shown in Fig. 3. Considering that all oxygen impurities coming from the Ar in the chamber are incorporated into the molten alloy, a change from a pressure of $0.5 \times 10^5$ Pa to $1.0 \times 10^5$ Pa in the chamber may double the oxygen content into the sample, promoting the formation of the big cube. When the casting chamber is filled with $1.0 \times 10^5$ Pa of Ar, oxygen contamination cannot be fully avoided and the “big cube” oxygen-stabilised phase is easily nucleated. Filling the chamber with $0.5 \times 10^5$ Pa of Ar reduces the oxygen contamination, so that the TTT curve of the big cube phase is shifted to higher times and BMG formation is possible. Rapid solidification techniques may overcome the nucleation of all crystalline phases and produce easily a fully amorphous ribbons. 3) Recent examinations of BMG with nominal composition Zr$_{52.5}$Cu$_{17.9}$Ni$_{14.6}$Al$_{10}$Ti$_{5}$ prepared in various laboratories have revealed significant changes in the crystallisation behaviour. 8, 9) These differences may be explained in terms of small changes of composition and/or impurities level. In particular, small variations in the Ti and Al content modify the temperature and the mechanism of crystallisation.10) The formation of a significant amount of crystals of the big cube phase during quenching, leaves an amorphous matrix with different composition with respect to the starting master alloys. As a consequence, it crystallises with a different mechanism, evidenced by a single exothermic peak in the DSC trace (Fig. 2, curve a). Fully amorphous samples have a more similar crystallisation behaviour and slight differences observed in DSC traces (Fig. 2, curves b, c and d) may be due to small composition inhomogeneities or to the presence of quenched-in nuclei, which act as heterogeneous nucleation sites. The heat of crystallisation ($\Delta H_x$) is less sensitive to composition variation and a value of about 4 kJ·mol$^{-1}$ has been obtained for all fully amorphous samples (Table 1).

In order to study the thermodynamics of Zr$_{52.5}$Cu$_{17.9}$Ni$_{14.6}$Al$_{10}$Ti$_{5}$ alloy in undercooling conditions, the heat of crystallisation of the amorphous samples has been measured in different experimental conditions. As an example, the isothermal DSC trace obtained at 708 K is shown in Fig. 4. It shows two exothermal peaks partially overlapped. Similar curves have been obtained for annealing at different temperatures, even if the temperature range for isothermal measurements is rather limited. In fact, the annealing at temperatures lower than 708 K gives a very tiny signal, with a low reproducibility. On the contrary, an annealing at high temperatures does not allow the measurement of the whole heat of crystallisation, because of the missing of heat during the heating up of the sample in the DSC cell. The heat of crystallisation ($\Delta H_x$) has been also measured in scanning conditions, using different heating rates. In all cases the DSC trace is very similar to that shown in Fig. 2, where the crystallisation temperature progressively increases with increasing heating rate. In all cases, the DSC trace shows two exothermal peaks partially overlapped.

The melting and solidification behaviour has been followed by high temperature DSC, as shown in Fig. 5. The exothermal signal due to the crystallisation of the amorphous alloy is also reported for comparison. It is worth noting that, before melting, a tiny exothermic peak has been observed at about 938 K, which gives an heat evolution of 1.12 kJ·mol$^{-1}$. The melting of the alloy is evidenced by an endothermic peak at 1070 K due to an eutectic reaction, followed by a liquidus point at about 1150 K. On cooling, the liquid alloy shows a significant undercooling for the primary solidification and it fully solidi-
lies with a single peak at 1070 K. The undercooling of liquid glass forming alloys may be observed inside of the high temperature DSC cell: for instance, a Pd–Cu–P alloy has been undercooled for more than 200 K, whereas for Al-based alloys the undercooling is generally rather low. In fact, the presence of small oxide particles at the surface of the liquid alloy strongly promotes the heterogeneous nucleation of the solid phases. If the liquid alloy is overheated, oxide particles can be dissolved and a significant undercooling may be observed. In this case, the strong affinity of liquid Zr-based alloys with oxygen does not allow a strong undercooling inside of the HTDSC cell, even after an overheating of the sample up to 1473 K. An average value of 8.17 ± 0.24 kJ mol⁻¹ has been obtained for the enthalpy of melting (ΔHₘ) and of 8.28 ± 0.15 kJ mol⁻¹ for the enthalpy of solidification (ΔHₛ), in good agreement with previously reported results.

In order to confirm the phase transformations observed by thermal analysis, in-situ XRD experiments have been carried out at ESRF. The sample has been progressively heated by induction furnace and a full XRD spectrum has been recorded every 2 s. In Fig. 6, XRD patterns corresponding to selected runs are reported. The small halo centred at about 0.15 nm⁻¹ is due to the quartz crucible and it is evident in all spectra. The pattern of the as quenched sample obtained at room temperature is reported as a reference (Fig. 6, curve a). The absence of evident Bragg peaks confirms the fully amorphous structure of the sample. The first significant change in the XRD pattern has been observed for run 38, as reported in Fig. 6, curve b. The pattern has been identified as a tetragonal NiZr₂ and cubic AlNiZr phase mixture. The double peak observed in the DSC traces cannot be resolved with the in-situ XRD experiments, so that the exact crystallisation sequence cannot be identified from these data. After further annealing at higher temperature, a significant change of the whole XRD pattern is observed for run 64 (curve c in Fig. 6). In fact, some diffraction peaks disappear and some new peaks appear in the spectrum. They have been assigned to tetragonal CuZr₂ and hexagonal Al₃NiZr₆ phases. At still higher temperature, corresponding to run 132, the melting of alloy is clearly evidenced in the XRD pattern, even if some small fraction of Al₃NiZr₆ solid phase remains embedded in the liquid (curve d in Fig. 6). This sequence of XRD patterns is in good agreement with the thermal analysis shown in Fig. 5 where a phase transformation has been evidenced before melting and a liquidus point has been evidenced after the eutectic melting. The occurrence of an exothermic reaction after the main crystallisation event has been related, for a similar system, to the crystallisation of a residual amorphous phase. From the experimental XRD results, this phase transformation seems to be related to the decomposition of a metastable phase mixture into the stable phases, even if the simultaneous crystallisation of a residual amorphous phase cannot be excluded.

The enthalpy difference between the liquid phase and the solid mixture has been obtained from the experimental values of ΔHₛ, ΔHₘ and it is shown in Fig. 7 as a function of temperature. The enthalpies of melting and solidification have the same value, inside of the experimental error bar. In order to consider the same equilibrium phase mixture as a reference state for the solid, the experimental values for the crystallisation ΔHₛ obtained in isothermal and scanning mode in the temperature range 698–763 K, have been added to a constant value of 1.12 kJ mol⁻¹, corresponding to the heat of phase transformation observed at 985 K (Fig. 5).

An estimation of ΔC_p for temperatures close to Tₛ has been obtained from DSC traces obtained from scanning measurements. The experimental Tₛ value has been considered as the inflexion point of the DSC trace. For scanning rates lower than 10 K min⁻¹ the signal step at Tₛ is very noisy, whereas for scanning rates higher than 20 K min⁻¹, the exothermic peaks due to crystallisation partially overlap the signal due to glass transition, so that underestimated values have been obtained. The results are reported in Fig. 8 together with those obtained in with the same experimental procedure.

A thermodynamic description of the system in undercooling conditions can be obtained from the calorimetric data. In fact, the enthalpy related to the transition between undercooled liquid and solid phases can be fitted according to...
suitable models for the temperature dependence of the specific heat difference between the same phases in undercooling regime, $\Delta C_p(T)$. A general parametric description of the enthalpy difference between these phases is given by SGTE\(^{15}\) according to:

$$\Delta H = A + CT + DT^2 + ET^3 + FT^{-1}$$ (1)

which gives a specific heat difference expressed as:

$$\Delta C_p = C + 2DT + 3ET^2 - FT^{-2}$$ (2)

A linear behaviour for $\Delta C_p(T)$ (i.e. $E = F = 0$) has been found in Pd\(_{40}\)Ni\(_{40}\)P\(_{20}\)\(^{60}\) and in some other alloys.\(^{17}\) A polynomial description of $C_p$ has been already used to describe the thermodynamic properties of Zr\(_{52.5}\)Cu\(_{17.9}\)Ni\(_{14.6}\)Al\(_{10}\)Ti\(_{5}\) in undercooling conditions\(^{13}\) fitting experimental values of specific heat of the glassy and crystal phases obtained by DSC in step mode. The temperature dependence of $C_p$ for the solid phases was described with $C = F = 0$, according to\(^{18}\) whereas a function with $C = E = 0$ has been used for the $C_p$ of undercooled liquid. A good description of the free energy difference between the undercooled liquid and the solid phases, proposed by Dubay and Ramachandrarao (DR)\(^{19}\) following an hole theory for liquids, gives an enthalpy difference expressed as:

$$\Delta H = \Delta H_m + (1/4)\Delta C_p(T_m)[5T_m - 6T_m^2T^{-1} + T_m^3T^{-2}]$$

(3)

with

$$\Delta C_p(T_m) = (1/2)\Delta C_p(T_m)[3T_m^2T^{-2} - T_m^3T^{-3}]$$

(4)

The experimental values of the enthalpy difference between the liquid phase and the solid mixture have been fitted according to the previously mentioned models for $\Delta C_p(T)$ in the undercooking regime. The results of the fitting are shown in Fig. 7 and the corresponding calculated values of $\Delta C_p$ are shown, as a function of temperature, in Fig. 8. The numerical values of the fitting parameters are reported in Table 2. According to the description of DR, the single fitting parameter is $\Delta C_p(T_m)$, which turns out equal to 9.3 J·mol\(^{-1}\)·K\(^{-1}\) and leads to a value of $\Delta C_p$ of 16.6 J·mol\(^{-1}\)·K\(^{-1}\) at $T_g$. The linear and SGTE descriptions give lower values of $\Delta C_p$ at the melting point, which become higher on undercooling. They reach a value of 20.2 J·mol\(^{-1}\)·K\(^{-1}\) and 21.5 J·mol\(^{-1}\)·K\(^{-1}\) at $T_g$ for the linear and SGTE model, respectively. The different parametric description cannot be selected on the basis of the enthalpy data shown in Fig. 7. On the contrary, experimental $\Delta C_p$ values shown in Fig. 8 suggest that the SGTE description appears suitable for the thermodynamic description of undercooled Zr\(_{52.5}\)Cu\(_{17.9}\)Ni\(_{14.6}\)Al\(_{10}\)Ti\(_{5}\) liquid alloy. The increasing of $\Delta C_p$ on undercooling has been related to the good glass forming ability of the liquid alloys.\(^{20}\) In fact, a decreasing free energy difference between the undercooled liquid and the crystal phases strongly reduces the driving force for nucleation, promoting the glass formation.\(^{13}\)

### 4. Conclusions

The preparation of bulk metallic glasses by copper moulding of Zr\(_{52.5}\)Cu\(_{17.9}\)Ni\(_{14.6}\)Al\(_{10}\)Ti\(_{5}\) liquid alloy has been analysed from the kinetic and thermodynamic point of view. When protected Ar atmosphere is used in the casting chamber, oxygen contamination must be avoided, in order to delay the nucleation of the fcc big cube phase.

From calorimetric measurements of the heat of crystallisation, melting and solidification, the temperature dependence of the enthalpy difference between undercooled liquid and equilibrium crystal phases has been determined. The experimental data have been fitted with different models for specific heat difference between the same phases. The SGTE descrip-
tion appears suitable to describe the thermodynamics of undercooled Zr$_{52.5}$Cu$_{17.9}$Ni$_{14.6}$Al$_{10}$Ti$_{5}$ liquid alloy, which show a substantial glass forming ability.

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