ESRF	**Experiment title:** CRYSTAL NUCLEATION AND METASTABLE PHASE SELECTION IN BULK METALLIC GLASSES AND THEIR UNDERCOOLED MELTS	**Experiment number:** HS-822
Beamline:	**Date of experiment:** Long term project from: Jan 99 to: Dec 2000	**Date of report:** August 8, 2000
Shifts:	**Local contact(s):** Dr Gavin Vaughan	*Received at ESRF:*

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Report:

In order to achieve the task of in-situ examination of phase transformations in bulk glass-forming alloys at the ESRF, the proposers' strategy has been as follows [1-2]:

1) In order to *detect nucleation in the bulk*, signal from heterogeneous crystal nucleation and growth on the surfaces must be minimized. This requires diffraction in transmission through thick samples. Conventional diffraction measurements in transmission require acquisition times that are too long for the kinetics in the undercooled liquid, even for most high flux neutron beams. High energy beams on ID11 in the transmission through our samples (cut to 3 mm thickness) yield *a diffraction pattern per second* with the potential to detect transient and metastable states.

2) As the total *transformation time is of the order of one minute above* T_g, and heating must be stopped at wish in order to recover the partially transformed sample for TEM and other characterisations, conventional heating (by convection, conduction or radiation) cannot be used. An *induction heating device* using a HF generator and accessories for remote temperature control was therefore acquired and put in operation on ID11.

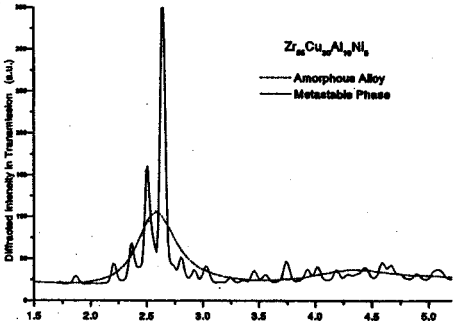
Results: We start with the rapid heating of $Zr_{55}Cu_{30}Al_{10}Ni_5$ bulk glass [1]. Diffraction patterns show the emergence of the Bragg peaks of a metastable crystalline phase referred to as MS1. When the heating is stopped at this point and the sample examined by TEM, a nanograin stucture on a scale of 20 nm is observed [3]. MS1 has recently been indexed as a tetragonal phase [4].As the heating continues, this metastable phase transforms over a time of 4 seconds to tetragonal Zr_2Cu [1].

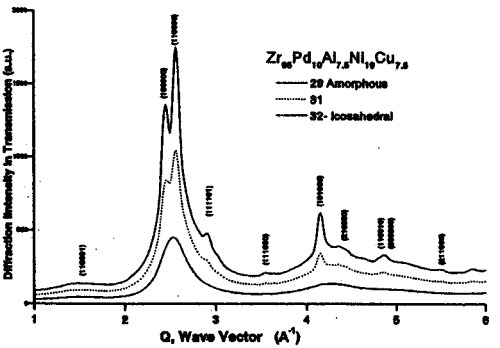
When the total Zr content is raised to near 70% as in $Zr_{69.5}Cu_{12}Al_{7.5}Ni_{11}$, MS1 again forms from the amorphous phase during heating but then remains stable until just before melting.

When instead of Zr addition, titanium is added as in $Zr_{55}Ti_4Cu_{25}Al_{10}Ni_6$, upon fast heating, the amorphous phase transforms to a different metastable crystalline structure MS2. If the heating is stopped for TEM examination of MS2, a nano-twinned fine grain stucture is observed [5].

When Pd is added in small amounts such as in $Zr_{55}Pd_5Cu_{20}Al_{10}Ni_{10}$, the amorphous phase again crystallizes into MS1 and subsequently at higher temperatures transforms to tetragonal Zr_2Cu as for the $Zr_{55}Cu_{30}Al_{10}Ni_5$ bulk glass but with slower kinetics perhaps indicating a diffusion controlled process [6].

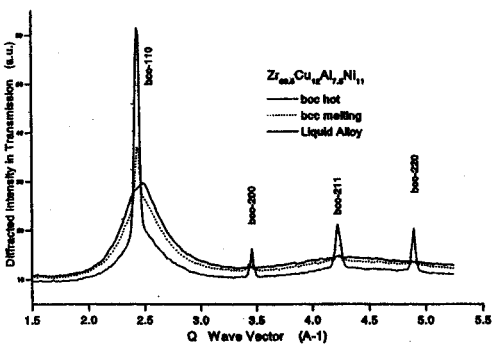
When higher Pd and Zr contents are added as in $Zr_{65}Pd_{10}Cu_{7.5}Al_{7.5}Ni_{10}$, the glassy alloy crystallizes differently. Instead of MS1, the glassy state first transforms to an icosahedral quasicrystalline (QC) state [7]. We have observed in-the-beam transformation of this metallic glass to the *i*-phase state during heating.

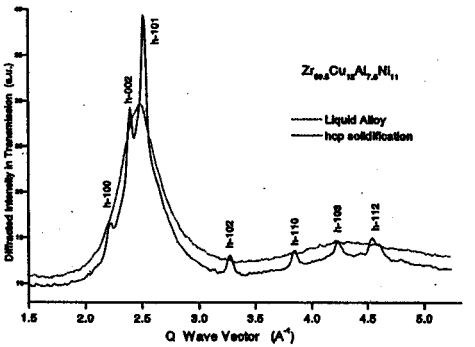




Finally, the $Zr_{69.5}Cu_{12}Al_{7.5}Ni_{11}$ alloy was found to form α-hcp and β-bcc solid solutions at high temperatures [5]. The ingots retain the α-hcp structure that transforms to β-bcc at higher temperatures. While Al is significantly soluble in both α-Zr and β-Zr, Ni is less so and Cu does not significantly dissolve. The existence of such wide phase fields for α-Zr and β-Zr in the quaternary $Zr_{69.5}Cu_{12}Al_{7.5}Ni_{11}$ is therefore surprising.

Here we show the melting of β-bcc $Zr_{69.5}Cu_{12}Al_{7.5}Ni_{11}$. When the melt is cooled, the diffraction pattern shows that β-bcc is bypassed and the α-hcp phase forms. Of course at higher cooling rates, instead of α-hcp, the glassy state is retained. The presence of such high-temperature solid solution phase fields reduces the ease of glass formation which classically is known to be associated with absence of solid solubility (necessitating diffusion-controlled decomposition) and near-eutectic compositions.





Conclusions: When heated at rates of the order of the cooling rates required for glass formation, all the Zr-based bulk metallic glasses studied first crystallize into metastable crystalline structures. It is suggested that these metastable phases have lower specific volumes resulting in faster formation kinetics than those of equilibrium phases thus winning the phase selection at high supercoolings [8-9]. Depending on the composition, two different metastable structures occur. The metastable phases can be quasicrystalline as icosahedral phase formation is strongly favored by noble metal addition (here Pd). Increasing the Zr content to near 70 at.% results in the appearance of high temperature α and β-Zr type solid solution phase fields that reduce the ease of glass formation and the maximum attainable glassy thicknesses. Further work is needed in this exciting field using the now very effective setup developed on ID11

References

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