ESRF	**Experiment title:** Crystal, Quasicrystal and Metastable Phase Selection in Bulk Metallic Glasses and their Undercooled Melts	**Experiment number**: ME-181
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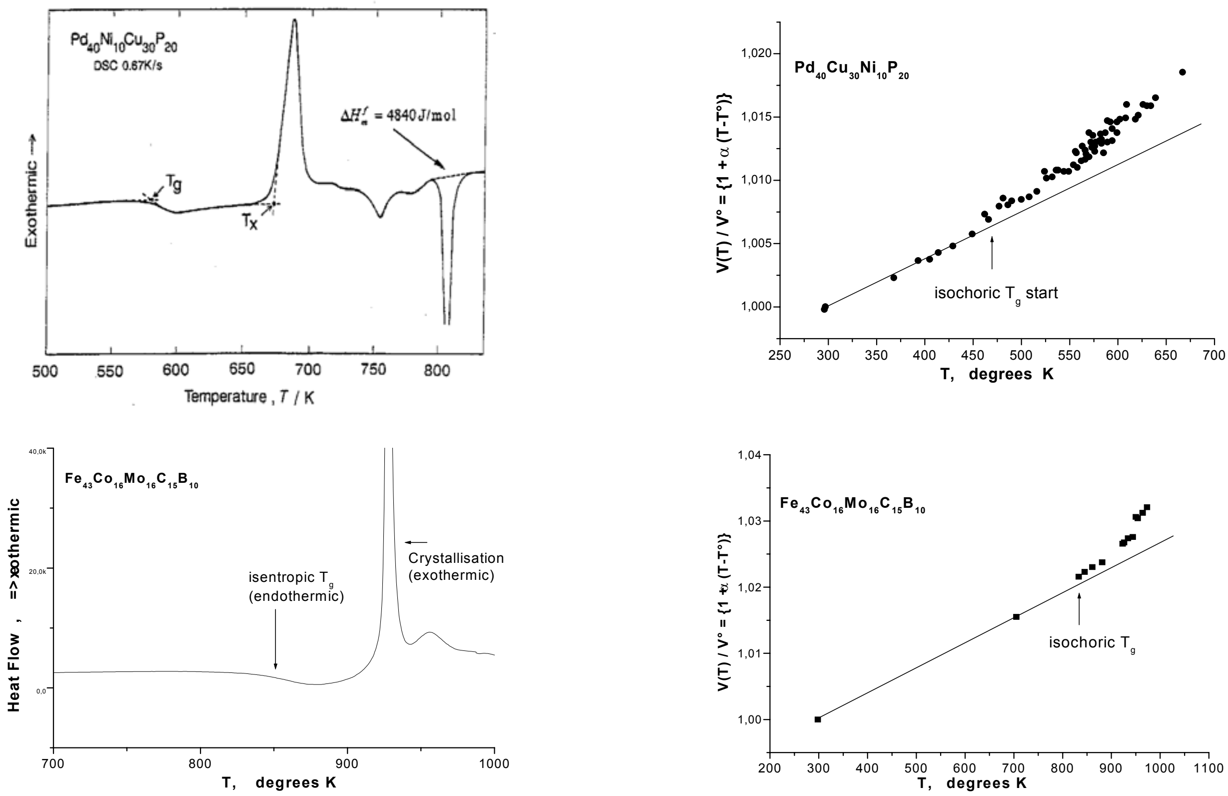
Report:

Introduction: Bulk metallic glasses constitute a new class of materials mostly discovered by the team of the co-proposer Akihisa Inoue of Tohoku University since 1989. They are muticomponent alloys that can be amorphized by ingot casting from the liquid state in thicknesses from several mm to centimeters. They were developped by careful additions of selected elements to well known glass-forming near-eutectic alloys such as ZrCu, FeB, PdNiP or lanthanide-Ni with the aim of depressing the liquidus temperatures T_l and increasing the temperature range $\Delta T = T_X - T_g$ between the glass transition at T_g and crystallisation at T_X. The state of the alloy in this temperature range, referred to as the supercooled liquid, is of technological importance because it undergoes Newtonian viscous flow that allows shaping of the alloy at fairly low temperatures (often between 300 and 500 C).
The first metallic glass-forming alloys discovered by Paul Duwez required cooling rates of the order of 10^6 degrees/s to suppress nucleation and growth of crystals and attain the glassy state. The new bulk metallic glasses require cooling rates in the range of 10 to 100 K/s thus allowing time for in-situ diffraction studies of their transformations. However crystal nucleation can occur heterogeneously on the surfaces or homogeneously inside such that conventional diffraction in reflection is inadequate and high energy high intensity beams are needed for diffraction in transmission.

The present project (following HS-299 and HS-822), which has enabled *in-situ examination of phase transformations and glass transition in bulk glass-forming alloys at the ESRF*, is part of a broader European and international research effort towards a better (more funamental and more quantitative) understanding of these new materials, understanding that has so far been largely empirical.
The opportunities at the ESRF and the fruitfull collaboration with the ID11 team have allowed us to obtain thermodynamic (phase diagram information) and structural results of funamental importance (quasi-crystal nucleation) as well as of significance for optimisation of preparation processes and mechanical and magnetic properties of bulk metallic glasses. The participation of the ESRF team being collaborative through EU fellowships (as compared to supportive only), the results have lead to a large number of joint publications. Due to this report's space limitations, the next page gives examples of the *most recent* results only.

Ground-breaking results: The first study of the glass transition in metallic glasses by diffraction

The exact nature of the glass transition in metallic glasses is still under debate mainly because it can only be studied by calorimetric techniques which show an endothermic event corresponding to a specific heat ΔC_p difference between the glassy and supercooled liquid states. This can be referred to as the “isentropic T_g” occuring to avoid the Kauzmann paradox (see Physics of Amorphous Materials, S.R. Elliott). The specific heat change ΔC_p is expected to be accompanied by changes in the compressibility $\Delta\kappa_T$ and the thermal expansion coefficient $\Delta\alpha_T$., the three properties being related through the constant R of Prigogine and Defay in $R = \Delta\kappa_T{*}\Delta C_p/\{TV{*}\Delta\alpha_T^2\}$. During heating of a glass below Tg, there is no atomic mobility for structural change and an isostructural thermal expansion coefficient α_T is easily obtained by diffraction data hence an “isochoric T_g” which may or may not be at the same temperature should be detectable by diffraction. The problem was that near T_g, metallic glasses are unstable and crystallise during the diffraction experiment. This limitation does not occur in bulk metallic glasses with large supercooled regions $\Delta T = T_X\text{-}T_g$. The ID11 facilities combined with the quality of our innoculent free, bulk glasses has allowed this collaborative project to become the first capable of comparing “isentropic T_g” with “isochoric T_g”. The next figures show isentropic T_g (measured by DSC) and isochoric Tg (from diffraction data) for two of several bulk metallic glasses recently studied. Several papers are in preparation for presentation and discussion of recent finding.



Left: Isentropic T_g determined calorimetry Right: Isochoric T_g determined from diffraction data

Recent joint publications with the participation of the ESRF :

* FeNiB-based metallic glasses with fcc crystallisation products, *Journal of Non-Crystalline Solids, Volume 304, Issues 1-3, June 2002, Pages 44-50* by A. R. Yavari, W. J. Botta Filho, C. A. D. Rodrigues, A. L. Greer, J. L. Uriarte, G. Huenen, G. Vaughan, A. Inoue.

*Metastable phases in Zr-based bulk glass-forming alloys detected using a synchrotron beam in transmission, *Materials Science and Engineering A, Volumes 304-306, 31 May 2001, Pages 34-38* by A. R. Yavari, A. Le Moulec, A. Inoue, Walter J. Botta F., G. Vaughan and **Å**. Kvick.

* Metastable phases, quasicrystals and solid solutions in Zr-based bulk glass-forming alloys, *Scripta Materialia, Volume 44, Issues 8-9, 18 May 2001, Pages 1239-1244,* by A. R. Yavari, A. Inoue, T. Zhang, W. J. Botta F., **Å**. Kvick

* Processing of bulk glass forming alloys in high energy synchrotron beams, *Annales Chimie Matériaux, 2002 in press*, by A.R. Yavari, A. Le Moulec, A. Inoue, G. Vaughan, Å. Kvick.

* In-the-Beam Metallic Glass Formation Monitored by High-Energy Synchrotron Radiation, *Scripta Mater. 2002 in press*, by J.L. Uriarte , A.R.Yavari , N. Nishiyama , G. Heunen , G. Vaughan , Å. Kvick, A. Inoue