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ESRF

Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

Once completed, the report should be submitted electronically to the User Office using the **Electronic Report Submission Application:**

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Reports supporting requests for additional beam time

Reports can now be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

Reports on experiments relating to long term projects

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

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All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

Deadlines for submission of Experimental Reports

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.

ESRF	**Experiment title:** Studies of crystalline phases in magnetic amorphous alloys	**Experiment number**: 28-01-813
Beamline:	**Date of experiment**: from: 29/08/2008 to: 02/09/2008	**Date of report**: 10/03/2009
Shifts:	**Local contact(s)**: Paul Thompson	*Received at ESRF:*

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Report:

Introduction: Kinetic experiments have afforded the opportunity to understand the evolution of crystalline phases as a material crystallises from an amorphous state. The purpose of this work was to exploit a kinetic diffraction technique in order to investigate two current questions regarding metallic glasses that are of considerable technological importance:

(i) **$Pd_{40}Ni_{(40-x)}Fe_xP_2$:** Amorphous metallic alloys are normally prepared as melt spun ribbons or sputtered films, making use of the quenching technique or evaporation technique respectively. More recently alloys have also been formed as 'bulk' metallic glasses (BMG's) in mm dimensions. Although for conventional amorphous ribbons glass-formation is determined by the use of exceptionally high cooling rates, for BMGs this aspect is less essential. For these alloys the constituent atoms have a tendency to form microclusters, and the fact that these cannot readily enlarge into macroscopic crystals results in an (almost) amorphous state. For $0 \leq x \leq 20$ the alloy series $Pd_{40}Ni_{(40-x)}Fe_xP_2$ can be formed as BMGs with an unusually wide range of magnetic properties depending on composition and temperature [1]. The physical properties of these amorphous alloys are clearly related to the possible existence and structure of such clusters or nanocrystals, with the magnetic properties related to the relative concentrations of the metallic elements in these regions.

(ii) **$Co_xFe_{(80-x)}B_{20}$:** This range of alloys based on the classical ferromagnetic amorphous alloy, $Fe_{80}B_{20}$, has recently been used as the insulating component in magnetic tunnel junctions (MTJ's). These consist of ferromagnetic/insulating oxide/ferromagnetic trilayers – materials for which room temperature tunnelling magnetoresistance ratio (TMR) can be as high as 200% (and even possibly 400%). The ratio is greatest with crystalline components, but it is impossible to grow the correct Co or Fe orientations ((001) bcc Fe or Co) without an expensive single crystal substrate. However with amorphous CoFeB as the first layer it is possible to obtain high quality MgO with an (001) texture – after which annealing the complete trilayer gives top-of-the-range TMR. Previous XRD and TEM studies indicate that the CoFeB layer induces crystallisation and lattice matching with MgO during annealing [2]. However, there appears to be no previous studies on the bulk amorphous alloys themselves. We draw attention to the contrast between the two series in that for

PdNiFeP we are trying to *avoid* crystallisation, whereas in tunnel junctions CoFeB is used to *induce* crystallisation.

Results:

Experiments were performed on melt spun ribbons of the two alloy series to monitor the transition from the amorphous to the crystalline state. The specimens were mounted in the heating stage of a Displex temperature controller and heated from room temperature to 800K concentrating on regions above 500K. Both the $Co_xFe_{(80-x)}B_{20}$ specimens were heated at a rate of 1.2K/min with spectra collected every 2K. Two of the three $Pd_{40}Ni_{(40-x)}Fe_xP_{20}$ samples were heated at a rate of 0.6K/min with spectra collected every 1K, and the third at a rate 3K/min with data collection every 5K. Data sets were collected using the MAR CCD camera. Using the software ESA project [3] the images were integrated over the entire pixel range yielding intensity versus 2θ as a function of temperature. From these scans it is possible to see the evolution of the crystalline phases with the increase in temperature for each sample.

Figure 1(a) shows the variation in 1D diffraction patterns at a constant temperature for samples of different composition. Bearing in mind that the $Pd_{40}Ni_{30}Fe_{10}P_{20}$ composition was treated under a different heating profile than the other two, these images show that different phases are formed for each of the samples.
Figure 1(b) shows the phase formation for $Pd_{40}Ni_{22.5}Fe_{17.5}P_{20}$ as it is ramped from 600 to 800K. Each of the curves shows the formation of different sets of peaks suggesting that the recrystallisation is through multiple phases.

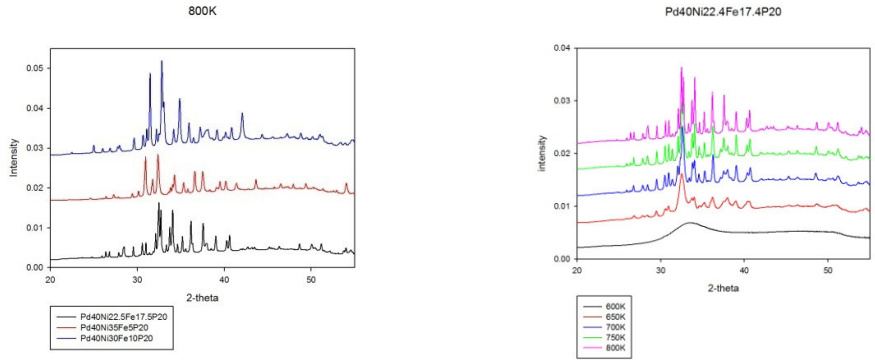

Figure 1: *recrystallisation images of $Pd_{40}Ni_{(40-x)}Fe_xP_{20}$ series (a) comparison of all compositions at the final temperature of 800K and, (b) the evolution of the crystalline phases*

Figure 2 shows equivalent data for the $Co_xFe_{(80-x)}B_{20}$ series. Both compositions have a sharp dominant peak at 2θ ~ 36˚ forming at 632K. As both α-Fe and CoFe solid solutions have (110) Bragg peaks at this position the confirmation of which phase is indicated by the data (if not both) requires that we identify other peaks associated with these phases. In a forthcoming run we intend to perform a much slower ramp collecting data at shorter time intervals, to focus on the formation of individual phases.

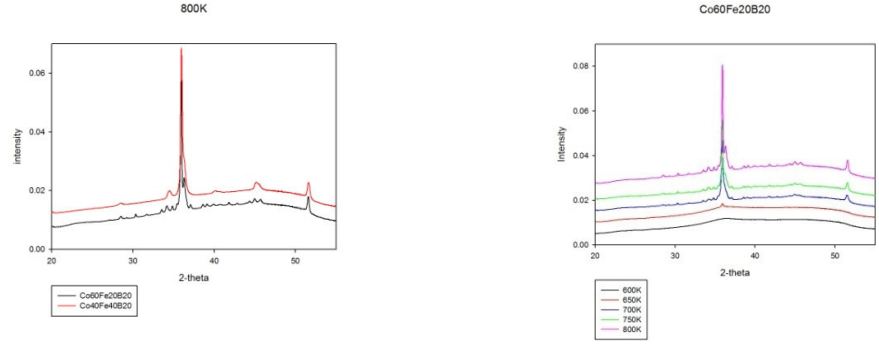

Figure 2: *recrystallisation images of $Co_xFe_{(80-x)}B_{20}$ series (a) comparison of both compositions at the final temperature of 800K and, (b) the evolution of the crystalline phases in $Co_{60}Fe_{20}B_{20}$*

For both alloy series the phases will be established using profile matching techniques. In a forthcoming extension of this work Rietveld Refinement software will be used to identify the chemical composition and structure of each. In the work outlined above beam refills meant that each of the samples underwent short temperature holds at arbitrary points during recrystallisation. This variation in heating profiles makes it difficult to assign changes in the crystallisation to either temperature or compositional changes, and in our next experiment we intend to collect data almost continuously every mK over a relatively narrow temperature range to avoid discontinuities during beam refills.

Summary:

- We have attained the heating profiles from RT to 800K of several compositions of two important series of amorphous alloys.
- The first, $Pd_{40}Ni_{(40-x)}Fe_xP_{20}$, is an alloy series with a wide range of magnetic properties that can be formed as a bulk metallic glass (BMG).
- The second, $Co_xFe_{(80-x)}B_{20}$, was an addition to the original proposal as it has recently become a key ingredient in the crystallisation of magnetic tunnel junctions.
- Further work is still required on the nature and structure of enlarged clusters or nanocrystals that have a major influence on the physical properties of BMGs.

References

1. Shen TD, Schwarz RB and Thompson JD, *Paramagnetism, superparamagnetism and spin-glass behavior in bulk amorphous PdNiFeP alloys,* J Applied Physics, 1999, **85**: 4110-4119
2. Takeuchi T, et al, *Crystallization of amorphous CoFeB ferromagnetic layers in CoFeB/MgO/CoFeB magnetic tunnel junctions.* Japanese Journal of Applied Physics Part 2-Letters & Express Letters, 2007. **46**: L623-L626.
3. Adriaens A, et al, *Insights into electrolytic stabilization with weak polarization as treatment for archaeological copper objects.* Analytical and Bioanalytical Chemistry, 2007. **387**(3): 861-868.