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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:**

http://193.49.43.2:8080/smis/servlet/UserUtils?start

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.

Published papers

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 nanocrystals in amorphous alloys by X-ray diffraction	**Experiment number**: 28-01-738
Beamline: BM28	**Date of experiment**: from: 13/10/05 to:17/10/05	**Date of report**: 31/10/2006
Shifts:	**Local contact(s)**: Dr. Danny Mannix	*Received at ESRF:*

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Report:

Introduction

Amorphous alloys were first developed over 40 years ago but due to cooling rates exceeding 105 – 106 K/s normally took the form of thin ribbons severely limiting possible applications. However starting in the late 1980s methods were developed in Japan and the USA for forming amorphous alloys of mm thicknesses or greater – alloys now known as 'bulk metallic glasses' or BMGs. A major review article outlining the development of these materials has recently appeared in Materials Science and Engineering. (WH Wang, C Dong and CH Shek, Materials Science and Engineering, R44, 45-89 (2004), [1]). Regarding possible applications we note that BMGs have a number of very attractive properties such as low density, high strengthto- weight ratio, low corrosion resistance and negligible mechanical hysteresis loss. Likewise such materials have an unusual range of magnetic properties from the high coercivities of ferromagnetic NdFe-based alloys to an unusually low coercivity in the annealed multielement alloy, FeAlGaPCBSi. However it is also recognised that in the presence of nanocrystals there can be a wide variation in all of those properties, even with alloys of nominally the same composition. It is now believed that whereas in conventional amorphous ribbons glass-formation is determined solely 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 it is the fact that these cannot readily enlarge into macroscopic crystals that results in an (almost) amorphous state. An essential feature of research into the physical properties of BMGs is therefore the determination of the possible existence and structure of any enlarged clusters or nanocrystals, as these will certainly have a major influence on the physical properties of the material. It is an investigation into the existence and volume fraction of these nanocrystals that is the basis of this application.

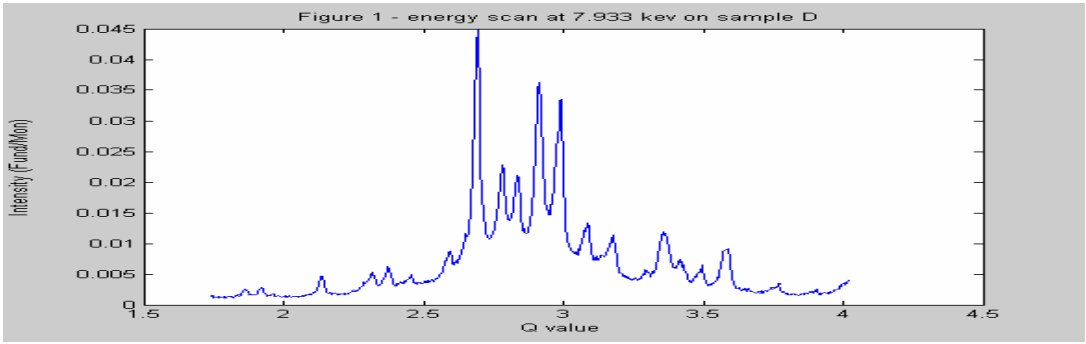
In this experiment X-ray Diffraction (XRD) data were taken from a set of amorphous ribbons in order to investigate the microcrystalline structure of the materials. Two types of experiment were performed, (1) using anomalous x-ray scattering techniques to get insight into the elemental composition of the microcrystalline phases, and (2) an annealing experiment to monitor, in a ribbon sample, the transition from the amorphous to the crystalline phase. This latter experiment used a Mar 2D detector in order to sample a large range of reciprocal space. The materials used were all of the form $Pd_{40}Ni_{(40-x)}Fe_xP_{20}$.

Experiment 1

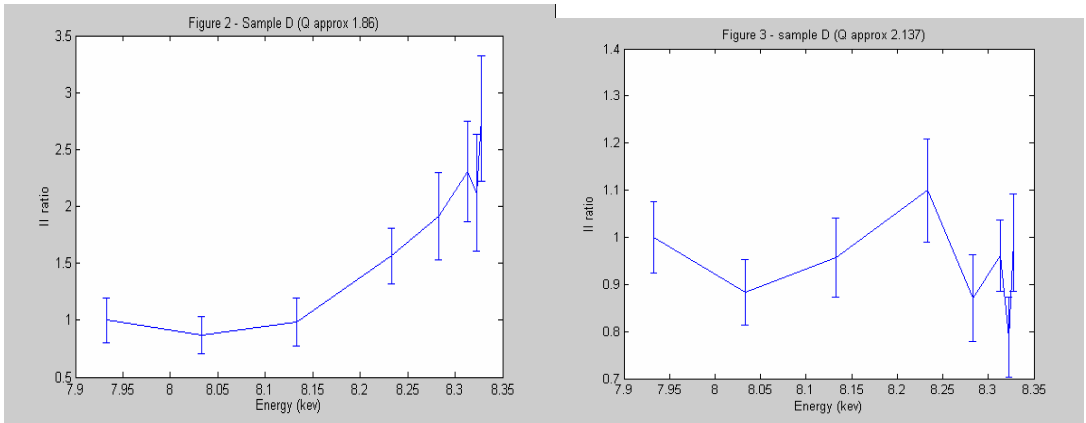
Energy scans were performed near the K edges of Ni and Fe. The idea was to see how the intensity of various crystalline peaks changed as a function of energy through the respective adsorption edge, in order to assist in the assignment of each peak to a particular crystalline phase. Two samples were studied:

Sample D - $Pd_{40}Ni_{40}P_{20}$
Sample C - $Pd_{40}Ni_{30}Fe_{10}P_{20}$

As the measurements were performed as intensity versus 2θ (scattering angle) it was first necessary to convert 2θ into Q, as this meant the peaks did not move as a function of energy. Figure 1 shows an initial scan after this conversion and with the intensity normalised:



As the above scan shows, the microstructure gives rise to many Bragg reflections. These scans were divided into smaller Q ranges and then the peaks were fitted with a Lorentzian lineshape resulting, for each peak, in data showing the integrated intensity as a function of the incident x-ray energy at both the Fe and Ni absorption edges.

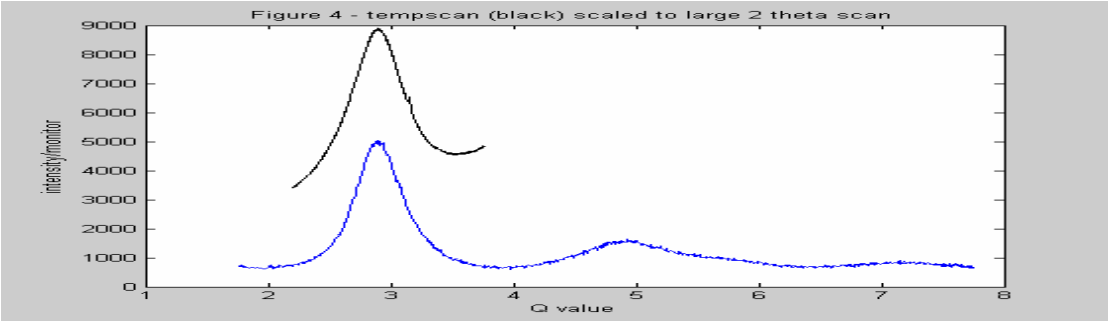


The data in figures 2 and 3 are representative of all of the results obtained and show two opposing cases for the energy dependent behaviour. Figure 3 seems significant in that, unlike figure 2, the expected dip in signal due to the absorption edge is present. This will allow differentiation of the elements responsible for

individual peaks and hence will allow the accurate indexing of the diffraction pattern. The next stage is to index the peaks to the known phases of the crystal structures and this part of the analysis is ongoing.

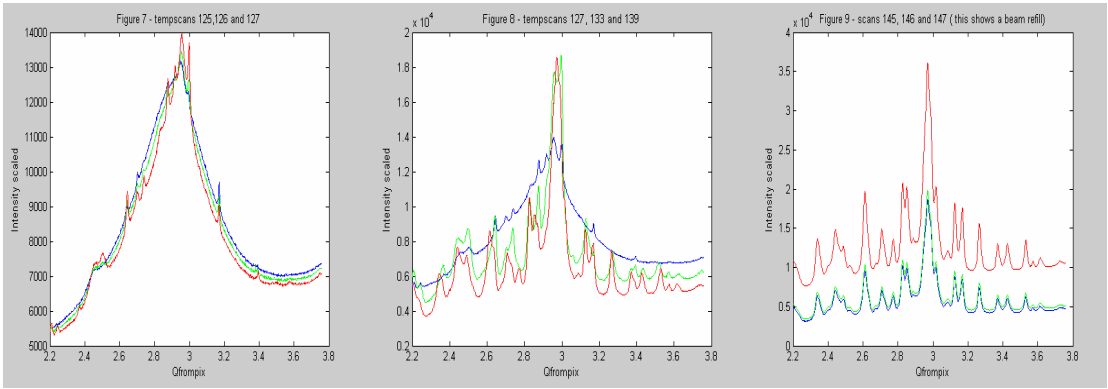
Experiment 2

In this experiment a piece of amorphous ribbon was heated until it crystallized. Data was taken using a Mar ccd camera which consists of a 2048 square pixel array. Basic trigonometric considerations allowed the assignment of a Q range to the pixel positions, which could then be superimposed onto an earlier 2θ scan. All of the images taken with the ccd camera were then integrated over the central pixel range which yielded intensity versus Q plots as a function of temperature. An image was taken every 30 seconds during the heating cycle.



From these scans it is possible to see the evolution of the crystalline phases. The Figure above shows data taken prior to the annealing where the ribbon is stll in the amorphous phase (data taken with the point detector (lower curve) is shown for comparison). The small peaks in the ccd data are due to scattering from the Be window that enclosed the sample.

The Figures below show the initial crystallisation of the sample as it was heated



The analysis of this data is ongoing. It appears that there is an intermediate crystalline phase that forms prior to the final phase that is observed. It is hoped that, using the knowledge obtained from the indexing of the phases in the first part of the experiment, it will be possible to identify the intermediate crystalline phase which may be the key to understanding the mechanism behind microcrystalline formation in the amorphous matrix.