

A Time-Resolved X-Ray Scattering Experiment For The Study Of Phase Transitions And Crystallization Processes In Metallic Alloys

J. F. Pelletier ^a, M. Sutton ^a, Z. Altounian ^a, S. Saini ^b, L. B. Lurio ^c,
A. R. Sandy ^c, D. Lumma ^c, M. A. Borthwick ^c, P. Falus ^c,
S. G. J. Mochrie ^c, G. B. Stephenson ^d

^a *Centre for the Physics of Materials, McGill University, Montréal, Québec, H3A 2T8, Canada*

^b *Department of Materials Science and Engineering and* ^c *Center for Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139-4307*

^d *Materials Science Division, Argonne National Laboratory, Argonne, IL 60439*

Abstract. An experimental setup to perform high-resolution time-resolved X-ray scattering has been commissioned on the side station of beamline 8-ID at the Advanced Photon Source. A Peltier-cooled diode detector array covering an angle range of 20 degrees is mounted on a 4-circle goniometer and is used to temporally resolve X-ray scattering patterns with a resolution up to 10 ms. Metallic ribbon samples can be quickly heated and cooled from temperatures up to 500 °C inside a furnace with controllable atmosphere and equipped with a beryllium window. A description of the setup is presented along with actual results showing time-resolved phase transitions and crystallization processes in AlYNi metallic alloys. These results demonstrate the power of this technique to investigate complex crystallization processes as well as the versatility of this time-resolved X-ray scattering spectrometer.

INTRODUCTION

Many of the new advanced materials depend on sophisticated annealing sequences, often involving phase transitions, to control their microstructure and thus optimize their physical properties. As well, the kinetics of materials as they undergo a phase transition leads to many interesting tests of current theories of non-equilibrium statistical mechanics. The ability to make *in situ* X-ray diffraction measurements in a time resolved manner is one of the most direct ways of experimentally studying these systems. In this article we discussed a spectrometer setup to make time-resolved powder diffraction measurements using an undulator beamline at the Advanced Photon Source (APS). It is similar in design to an earlier spectrometer on beamline X20 at the National Synchrotron Light Source (1-4).

SPECTROMETER CHARACTERISTICS

A spectrometer optimized for time resolved X-ray diffraction has been commissioned on the side station of the MIT-McGill-IBM insertion device beamline

(8-ID) at the APS. The main characteristics of this beamline have already been described elsewhere (5). The spectrometer is located on a side station of 8-ID and for this experiment uses X-rays coming off a diamond (111) monochromator at 7.66 keV having a bandwidth $\Delta\lambda/\lambda=6.2\times 10^{-5}$. Two sets of slits, located 1.3 m apart between the monochromator and the spectrometer's sample chamber, are used to adjust the beam size and two ion chambers monitor the X-ray intensity reaching the sample. For the experiment described here, the X-ray beam had dimensions of $0.6 \times 0.9 \text{ mm}^2$ and a flux of $\sim 5 \times 10^{12}$ photons per second for a storage ring current of 100 mA.

The main component of the spectrometer consists of a vertical scattering θ - 2θ goniometer with $\pm 20^\circ$ tilt stages on which a furnace is mounted. One particular setup can be seen in Figure 1, which shows a front view of the spectrometer with a linear photo-diode array detector (PSD) mounted on the 2θ arm. This detector, which is described in more details in Ref. (1), is made up of 1024 25- μm pixels which can be electronically grouped to trade off resolution for faster readout time. It can be used for acquiring powder diffraction measurements as fast as every 5 ms over a range of approximately $2\theta \pm 10^\circ$ for 2θ values between 20° and 100° . The setup also allows switching from this detector to a point detector in order to measure high-resolution conventional θ - 2θ powder diffraction patterns. A sample chamber equipped with a 10-mm wide Be window covering approximately 200° in 2θ is mounted on the tilt stages attached to the θ circle of the goniometer. The current sample chamber is equipped with a number of feedthroughs (for high-current, voltage, thermocouple, positioning, and vacuum) and can accept different types of samples and heating devices. One such specialized geometry allows rapid heating and quenching of samples made of metallic ribbons by passing an electrical current through the sample. The samples can be heated either in vacuum or helium gas where the thermal time constants are below 1 second. Sample temperature is monitored with an infrared

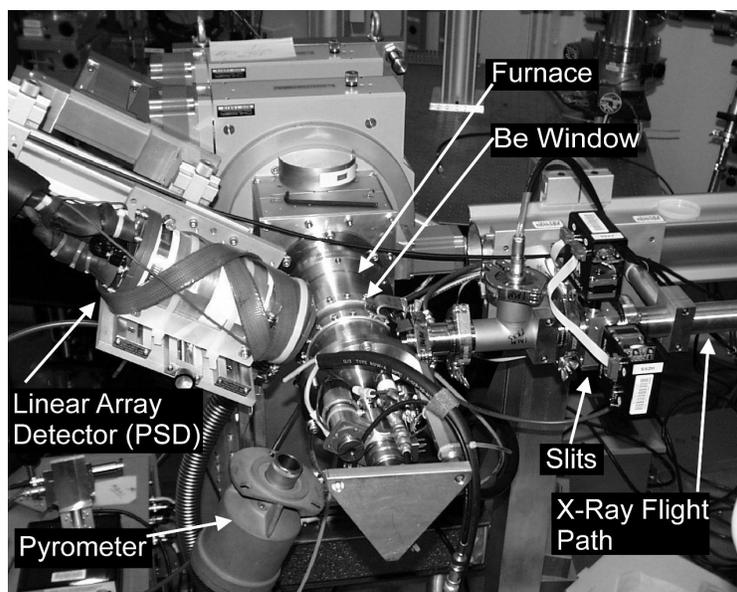


FIGURE 1. Photograph of an experimental setup installed on the monochromatic X-ray beam in 8-ID-E at the Advanced Photon Source. Key elements are indicated with arrows.

pyrometer, looking at the sample through a quartz view port, or with fast thermocouples.

INVESTIGATION OF AL-Y-NI METALLIC GLASSES

The discovery of high specific strength Al-Y-Ni metallic glasses (6) has spurred interest in their development and study. Several papers have been devoted to studying the crystallization (7-10) behavior of these metallic glasses to better understand microstructure evolution. Upon heating, these materials undergo different sequences of phase transitions, which strongly depends on the stoichiometry, annealing rates and annealing times. *In-situ* time resolved X-ray scattering provides an ideal tool to study this type of problems as one can quickly explore large regions of this phase space.

The alloys we studied had a composition of $\text{Al}_{85}\text{Y}_{10}\text{Ni}_5$ and were prepared by arc melting and melt-spinning to produce uniform ribbons 2 mm wide and $\sim 50 \mu\text{m}$ thick. The ribbons were heated in an atmosphere of flowing He to temperatures ranging between 190 and 220 °C at a rate of $\sim 2 \text{ }^\circ\text{C/s}$.

Time Resolved X-ray Scattering

An example of a raw image as obtained from the PSD is presented in Fig. 2 (a) and shows the temporal evolution of the X-ray scattering for a sample of $\text{Al}_{85}\text{Y}_{10}\text{Ni}_5$ being heated by a linear temperature ramp. It shows the transformation from the initial amorphous state of the metallic glass into three subsequent crystal phases. Figure 2 (a) shows a false-color contour plot of the X-ray scattering intensity while Fig. 2 (b) shows diffraction patterns taken from the PSD image at different intervals. The two main peaks at $q=2.69$ and 3.10 \AA^{-1} are the Al (111) and (200) peaks respectively. The

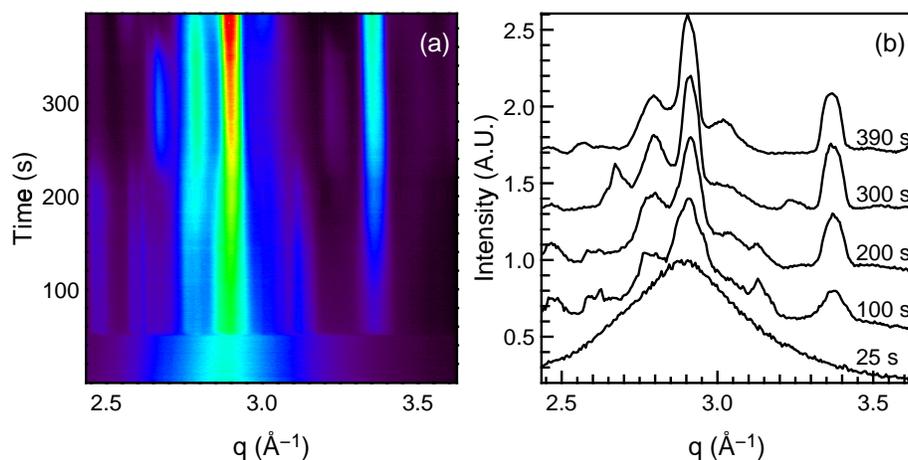


FIGURE 2. Temporal evolution of the X-ray scattering for a sample of $\text{Al}_{85}\text{Y}_{10}\text{Ni}_5$ being heated by a linear temperature ramp showing three distinct phase transitions. (a) false-color contour plot of the X-ray scattering intensity where intensity increases with lighter tones, (b) selected diffraction patterns taken at different times.

first transformation from amorphous to crystalline is clearly visible as an abrupt transition at about 50 s. The following two transformations are also easily seen at ≈ 230 s and ≈ 380 s respectively where a diffraction peak at $q=2.67 \text{ \AA}^{-1}$ appears and subsequently disappears.

High-Resolution Powder Diffraction

The crystallization sequence for this composition is relatively complicated. To investigate these transitions further we have carefully followed the crystallization history of one sample and quenched it as soon as a transition was observed. By following the crystallization with the time-resolved detector we could insure that no transition had been missed nor had any further transformation occurred on cooling. The linear detector array used to obtain the time-resolved scattering patterns was then temporarily replaced with a sensitive point detector in order to measure a conventional $\theta-2\theta$ powder diffraction pattern between 20° and 100° of 2θ . In total, we have observed that this sample goes through five different stages before reaching its final product. Figure 3 presents high-resolution powder diffraction patterns obtained for each crystallization stage. Careful analysis of these patterns has confirmed that the second stage is mostly Al_4Y with some unknown residual phase from the first stage.

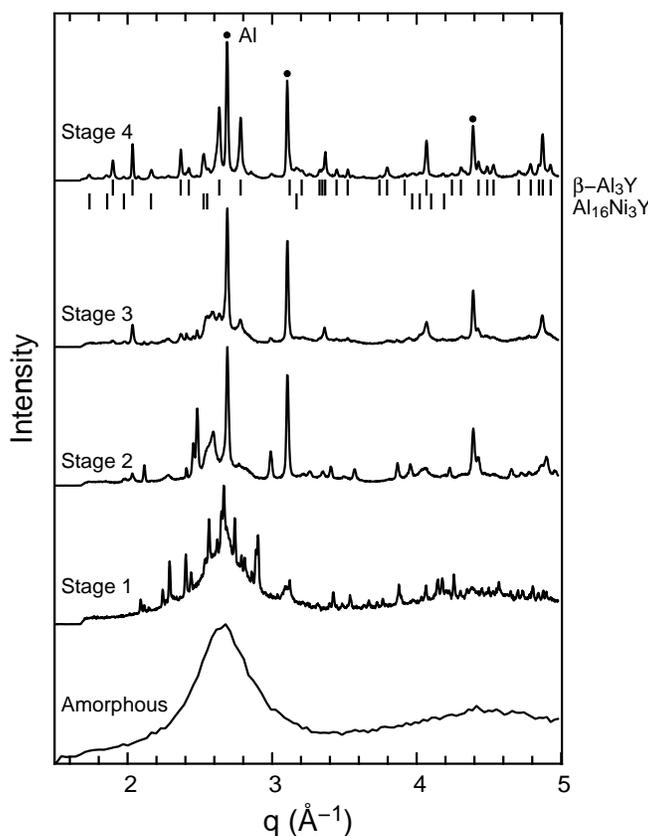


FIGURE 3. High-resolution powder scattering patterns showing the four phase transition steps observed for $\text{Al}_{85}\text{Y}_{10}\text{Ni}_5$.

The third stage is a mixture of Al_4Y , $\beta\text{-Al}_3\text{Y}$ and $\text{Al}_{16}\text{Ni}_3\text{Y}$ phases. The final crystallization products are $\beta\text{-Al}_3\text{Y}$ and $\text{Al}_{16}\text{Ni}_3\text{Y}$ as shown at stage 4 in Fig. 3. However, the combination of high-resolution diffraction patterns with dynamic measurements of the formation of the first stage has revealed it is more complicated than expected. Different hypotheses have been studied but we can not conclude on its structure at this time. Further analysis is currently underway.

CONCLUSION

We have described a recently commissioned spectrometer on beamline 8-ID at the Advanced Photon Source which is dedicated to time-resolved X-ray scattering. This spectrometer has been used to investigate the crystallization processes in $\text{Al}_{85}\text{Y}_{10}\text{Ni}_5$ metallic glasses and has proven to be the ideal tool to study the complex sequences of phase transition observed for this particular kind of Al-rich alloy. We have presented interesting new results that will improve our understanding of these glasses.

ACKNOWLEDGMENTS

Beamline 8-ID was developed with support from the NSF Instrumentation for Materials Research Program (DMR 9312543), from the DOE Facilities Initiative Program (DE-FG02-96ER45593), and from NSERC. Use of the Advanced Photon Source was supported by the U.S. Department of Energy, Basic Energy Sciences, Office of Science, under Contract No. W-31-109-Eng-38. We thank Harold Gibson for his valuable technical assistance.

REFERENCES

1. G.B. Stephenson, *Nucl. Instrum. Methods Phys. Res.* **A266**, 447 (1988).
2. G.B. Stephenson, K.F. Ludwig Jr., J.L. Jordan-Sweet, S. Brauer, J. Mainville, Y.S. Yang, and M. Sutton, *Rev. Sci. Instrum.* **60**, 1537 (1989).
3. S. Brauer, J.O. Ström-Olsen, M. Sutton, Y.S. Yang, A. Zaluska, G.B. Stephenson, and U. Köster, *Phys. Rev. B* **45**, 7704 (1992).
4. S. Brauer, H.E. Fisher, J.O. Ström-Olsen, M. Sutton, A. Zaluska, and G.B. Stephenson, *Phys. Rev. B* **47**, 11757 (1993).
5. A.R. Sandy, L.B. Lurio, S.G.J. Mochrie, A. Malik, G.B. Stephenson, J.F. Pelletier, and M. Sutton, *J. Synchrotron Rad.* **6**, 1174 (1999).
6. A. Inoue, K. Ohtera, A.-P. Tsai, and T. Masumoto, *Jpn. J. Appl. Phys.* **27**, L479 (1988).
7. M. Calin, and U. Köster, *Mater. Sci. Forum* **269-272**, 749 (1998).
8. V. Kwong, Y.C. Koo, S.J. Thorpe, and K.T. Aust, *Acta Metall.* **39**, 1563 (1991).
9. J. Latuch, H. Matyja, and V.I. Fadeeva, *Mater. Sci. Eng.* **A179/A180**, 506 (1994).
10. R. Sabet-Sharghi, Z. Altounian, and W.B. Muir, *J. Appl. Phys.* **75**, 4438 (1994).