

## X-ray absorption spectroscopic analysis of amorphous Cr-P obtained via electrodeposition

K. MONDAL, N. SATHITSUKSANOH

*Mechanical Engineering and Energy Processes, Southern Illinois University, Carbondale, IL 62901-6603, USA*

M. CROFT

*Department of Physics and Astronomy, Rutgers University, Piscataway, NJ 08855, USA*

S. B. LALVANI\*

*Mechanical Engineering and Energy Processes, Southern Illinois University, Carbondale, IL 62901-6603, USA*

*E-mail: lalvani@engr.siu.edu*

Amorphous alloys are non-crystalline solids which have no long range order but contain short range order of a few atomic distances. Due to the lack of long range order and hence the absence of grain boundaries, amorphous alloys have unusual physical properties. For example, they have excellent corrosion resistance. The presence of metalloids such as P and C leads to the formation of amorphous or glassy structure. Amorphous alloys are produced by a number of techniques, such as rapid melt quenching, high energy to— or neutron— bombardment and electrodeposition. Researchers have suggested that corrosion resistance of amorphous alloys can be attributed to the presence of metalloids such as P as in the case of Fe-P, Ni-P, Ni-Cr-P, Fe-Ni-Cr-P alloys. Virtanen [1] studied the passive films on amorphous alloys of Fe-Cr-B-C using X-ray photoelectron spectroscopy (XPS). In a previous study, Lalvani *et al.* [2] have studied the structure of these alloys by X-ray absorption near edge spectroscopy (XANES). The energy level used in these structures was quite low (less than 2200 eV) which enabled the investigation of P K-edge. Their research indicated both a metalloid-P character in amorphous Ni-P and the transfer of charge from the Ni to the P-p orbitals in this material. They also showed that scratching of the sample leads to a  $p^{5+}$ -oxidized feature. The Fe-P sample (relative to the Ni-P) appeared to indicate a stronger transition metal-P hybridization. In a recent study, Lalvani *et al.* [3] characterized amorphous Ni-P and Fe-P using the extended X-ray absorption fine structure (EXAFS) analysis at the metal K-edge and estimated the coordination numbers, bond lengths and structural disorder parameter values. Their investigations showed the existence of short range order in both samples with major peaks of the Fourier transformed spectrum at about 2 Å. The estimated bond lengths were about 2–3 Å. EXAFS analysis of the electrodeposited Cr-P amorphous alloy at the Cr K edge and P K-edge is presented in this letter.

Cr-P samples were produced by electrodeposition using a bath consisting of 180 g/L  $\text{Cr}_2(\text{SO}_4)_3$ , 30 g/L

sodium hypophosphite, 100 g/L ammonium sulfate, 10 g/L ammonium bromide, 0.1 g/L glycine and 50 g/L boric acid at a temperature of 50 °C and a current density of 0.22 A/cm<sup>2</sup>. The pH of the solutions was kept at 1.25. The substrate used was a 25 μm thick copper foil. Significant agitation was provided during electrodeposition with a magnetic stirrer. The anode and cathode were placed parallel to each other at a distance of 4 cm and separated by a Nafion™ membrane. The elemental composition of the deposits was found by atomic absorption spectroscopy.

The EXAFS spectra (absorption vs. energy) are plotted for both the Cr and P K-edge (Figs 1 and 2). In Fig. 1, major peaks are observed at energy levels of about 6008 and 6069 eV. The spectrum corresponds to the Cr-K edge. The P K-edge (Fig. 2) was observed at 2149 eV followed by peaks at 2154, 2157 and 2162 eV.

The raw EXAFS spectrum is converted from the energy space into the momentum space ( $k$ ) using Planck's relation [4] and the spectrum is amplified by  $k^2$ . The spectroscopic process that gives rise to the scattering between each Cr (absorber) atom in the sample and nearby elements is called backscattering. Although the scattering process affects all atoms, the scattering between the absorber atom and the neighboring atoms within a radius of 7 Å to the absorbing atom typically affect the EXAFS spectrum. The interaction between the multiple absorber-backscatterer pairs of atoms appears in the EXAFS spectrum as a superimposition of sinusoidal oscillations that can be separated in angstrom space using the Fourier transformation. The Fourier transformation (Fig. 3) of the EXAFS spectrum at the Cr-K edge shows one single major peak at about 1.9 Å which is significant in that it strongly implies that there is no long distance order and only short distance order is possible.

A non-linear least squares fitting routine was used to compare the sample spectrum with a spectrum generated using the computer code FEFF 7 [5]. The bond lengths for Cr-Cr and Cr-P were

\* Author to whom all correspondence should be addressed.

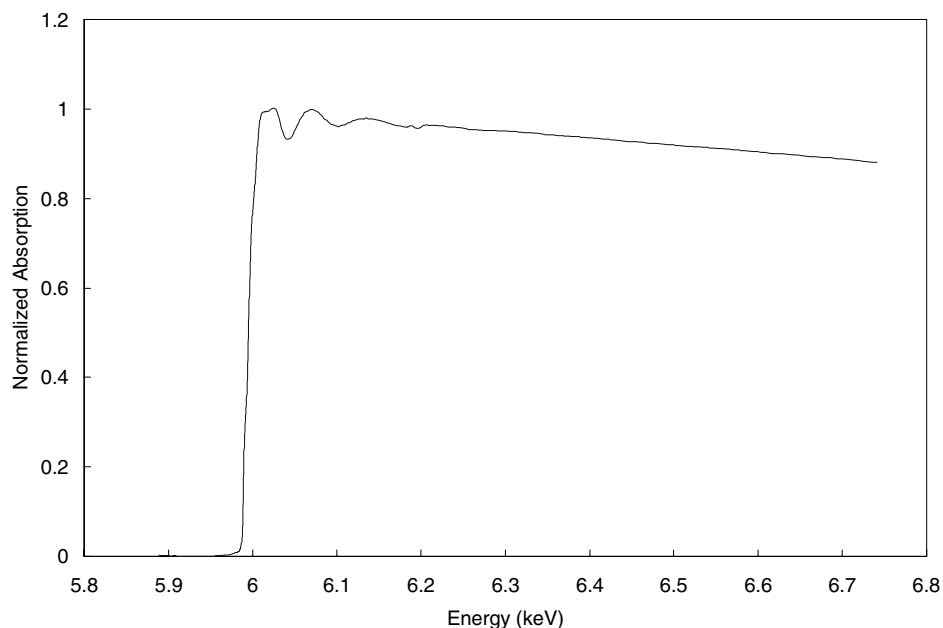


Figure 1 EXAFS spectrum for Cr-P sample at the Cr K-edge.

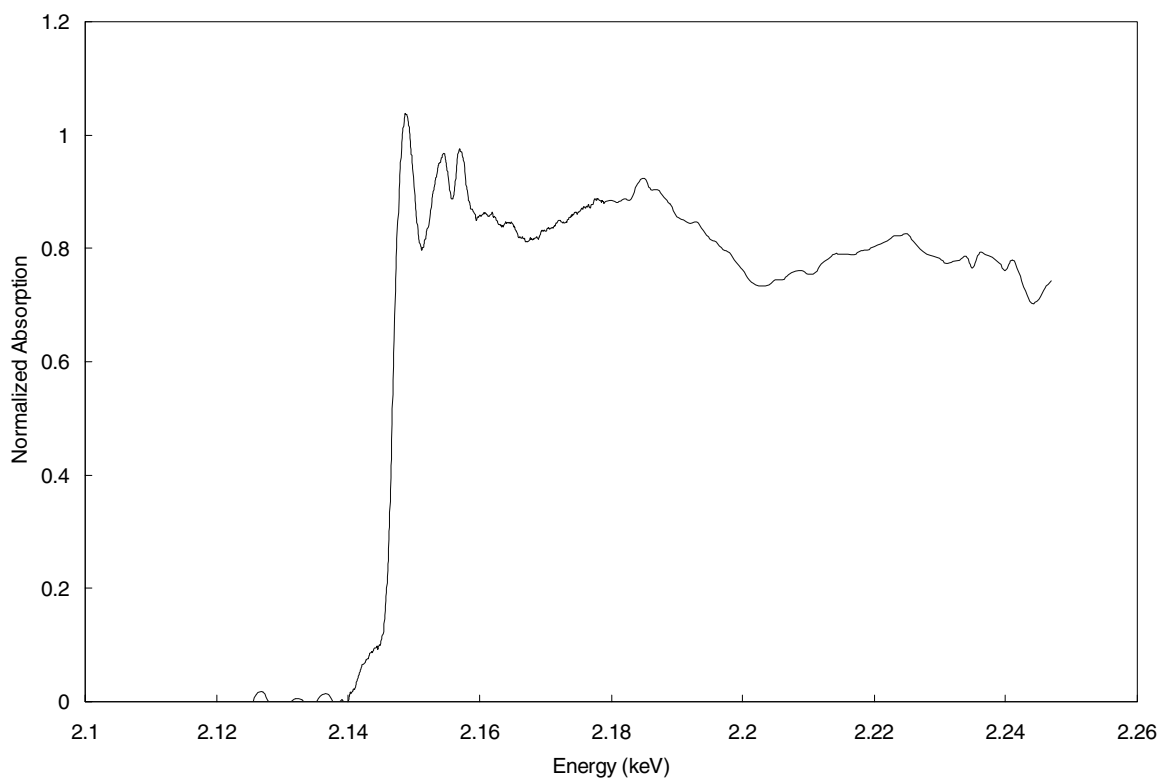


Figure 2 EXAFS spectrum for Cr-P sample at the P K-edge.

estimated to be about  $2.342 \pm 0.00018 \text{ \AA}$  and  $2.467 \pm 0.00015 \text{ \AA}$ , respectively and the disorder parameters were found to be approximately 0.011 and 0.012, respectively. The coordination numbers for the Cr-Cr and Cr-P pairs were found to equal 9.5 and 4.09, respectively.

The Fourier transform of the EXAFS spectrum for the phosphorus K-edge is shown in Fig. 4. Using the same analysis method as described above, the following parameters were determined. The bond length was calcu-

lated to be  $2.762 \pm 0.000085 \text{ \AA}$  and the disorder parameter was found to be approximately  $0.008 \pm 0.000034$ . The coordination number was found to be 3.03. The Fourier transformation shows one single (major) peak at about  $2.9 \text{ \AA}$  indicating that there is no long distance order. For relatively large bond lengths ( $>3 \text{ \AA}$ ), there are no major peaks therefore only short distance order is possible. Hence, it is concluded that the specimen is not crystalline but amorphous. Thus, the preliminary data obtained support the use of techniques employed

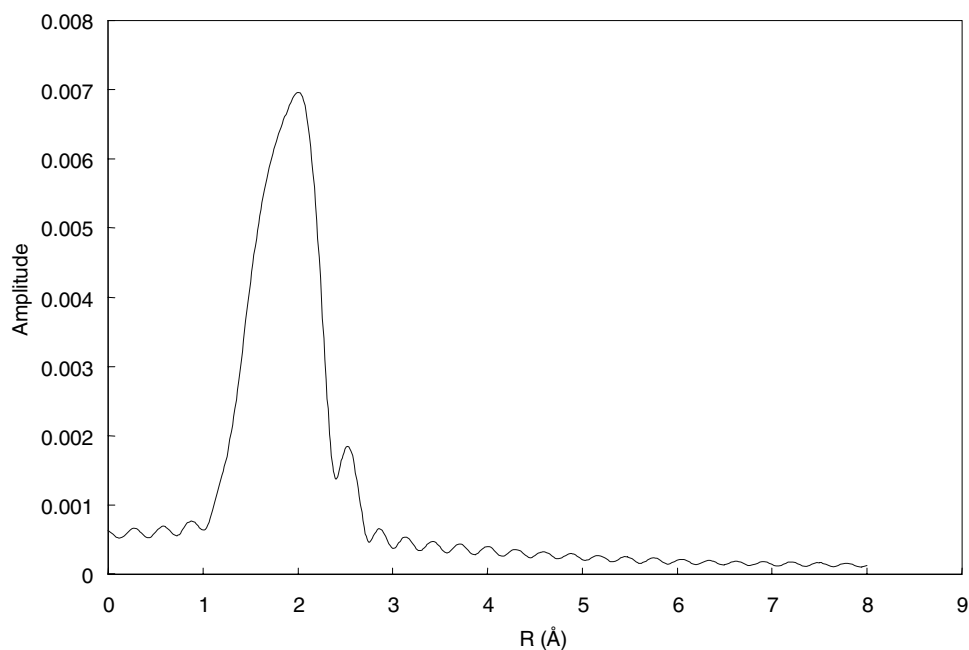


Figure 3 Fourier transform of EXAFS spectrum of Cr-P at the Cr K-edge.

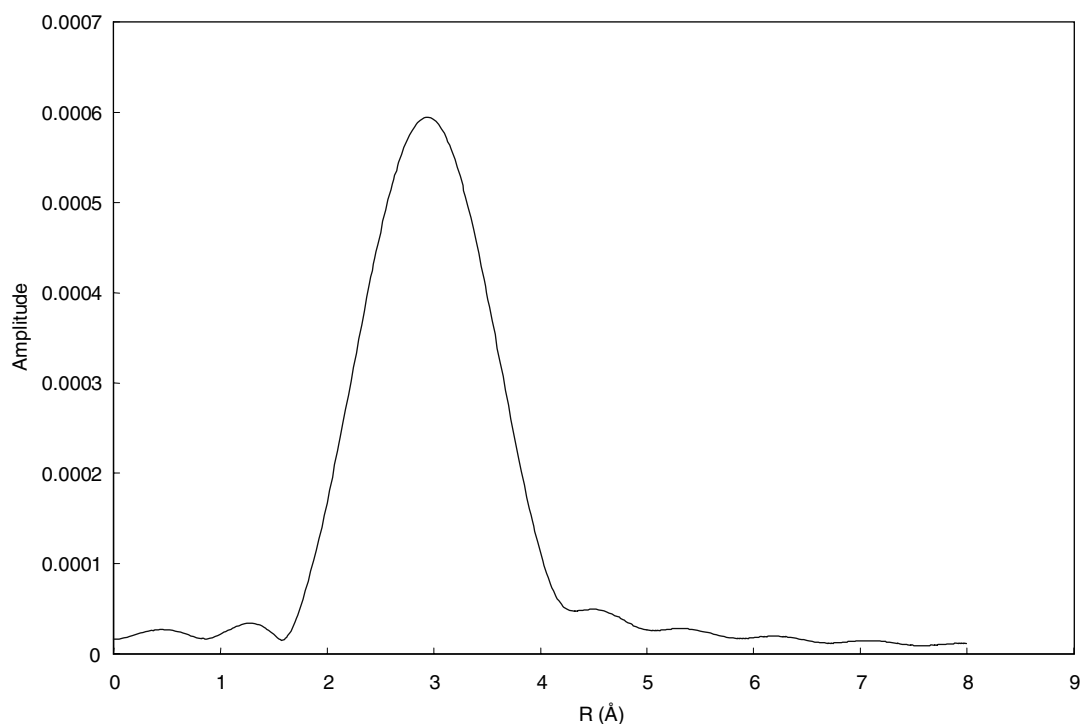


Figure 4 Fourier transform of EXAFS spectrum of Cr-P at the P K-edge.

in this investigation for characterization of amorphous metal-metalloid alloys.

### Acknowledgments

Support for this research was funded through Southern Illinois University, Carbondale provided by CARS, Argonne National Labs and Materials Technology Center of SIU-Carbondale and National Synchrotron Light Source at Brookhaven National Laboratories.

### References

1. S. VIRTANEN, E. M. MOSER and M. Bohni, *Corrosion Science* **36** (1994) 3373.

2. S. B. LALVANI and M. CROFT, *J. Mater. Sci. Lett.* **18** (1999) 1281.
3. S. B. LALVANI, K. MONDAL, N. SATHITSUKSANOH, T. WILTOWSKI and Y. XIAO, *ibid.* **20** (2001) 1097.
4. D. E. SAYERS and B. A. BUNKER, in "X-ray Absorption: Principles, Applications and Techniques of EXAFS, SEXAFS and XANES," edited by D. C. Koningsberger and R. Prin (John Wiley and Sons, New York, USA, 1988).
5. A. L. ANKUDINOV and J. J. REHR, *Phys. Rev. B* **56** (1997) R1712.

Received 26 September 2002  
and accepted 21 January 2003