

## Characterization of Ni-P and Fe-P by X-ray absorption spectroscopy

S. B. LALVANI, K. MONDAL, N. SATHITSUKSANOH, T. WILTOWSKI, Y. XIAO

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

Web address: <http://howard.engr.siu.edu/mech/>

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 lead to the formation of amorphous or glassy structure. In a previous study, Lalvani *et al.* [1] have studied the structure of these alloys by X-ray absorption 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 NiP) appeared to indicate a stronger transition of metal-P hybridization.

The XANES technique is superior to the ones employing X-ray photoelectron microscopy and angle-resolved XPS since the latter suffer from a number of deficiencies. They are not able to quantitatively describe the chemical composition of the passive films formed on the surface. In addition, the data obtained on the valency of species present is not clear.

One of the major problems in studying the corrosion behavior of amorphous alloys in aqueous solutions is that the passive oxide layers formed are usually very thin (typically a few nanometers), and are formed under the presence of a high electric field [2]. Generally, *ex situ* surface analysis methods are used for investigation which involve vacuum conditions and beams of electrons or ions in the absence of electric field and electrolyte which could significantly alter the passive layers. Raman spectroscopy on the other hand could be employed *in situ*, however it has certain limitations as well [3]. XANES probes electron transmissions from core levels (the 1s level for the K edge) to unoccupied levels and is thus sensitive to the valance and coordination of the absorbing atom. In addition, the height of the absorption edge is proportional to the total amount of the absorbing element present in the beam (irrespective of valence) and thus can be used to monitor dissolution of elements from thin films [4].

Fe-P and Ni-P samples were produced by electrodeposition. Electrodeposition was carried out under constant current from acidic solutions on 25 micron thick copper foil. The bath composition is given in Table I.

500 ml of electrolytic solution was used in each case. Significant agitation was provided to the bath during deposition with a magnetic stirrer. The anode and cathode were placed parallel to each other at a distance of 4 cm. The current densities and temperature conditions were:

0.05–0.23 A/cm<sup>2</sup> and 50–65 °C for Ni-P and 0.02–0.1 A/cm<sup>2</sup> and 40–50 °C for Fe-P deposition. The elemental composition of the deposits was found by atomic absorption spectroscopy. Additional experimental details are also provided elsewhere [5, 6].

The EXAFS spectrum (absorption vs. energy) and Fourier transformation (amplitude) of the signal vs. distance (Angstrom) are plotted for both, FeP and Ni-P samples in Figs 1–3. For the Fe-P sample, a peak is observed at the energy level of about 7100 eV which gradually decreases over higher energy levels. The spectrum corresponds to the Fe-K edge. XAS measurements are sensitive both to the atomic site electron states and the near shell coordination number/types. Using one shell data analysis, the bond length for Fe-P sample was estimated to be about 2–3 Å and the disorder parameter was found to be approximately 0.0066. The Fourier transformation (Fig. 2) shows one single major peak at about 2 Å which is significant in that it shows that there is no long distance order and only short distance order is possible. Hence, it is concluded that the sample is

TABLE I Bath composition for electrodeposition

A. Ni-P Bath	
NiSO <sub>4</sub> · 6H <sub>2</sub> O	150 g/l
NiCl <sub>2</sub> · 6H <sub>2</sub> O	45 g/l
H <sub>3</sub> PO <sub>4</sub> (86%)	40 g/l
H <sub>3</sub> PO <sub>3</sub>	40 g/l
B. Fe-P Bath	
FeSO <sub>4</sub> · 7H <sub>2</sub> O	200 g/l
NaH <sub>2</sub> PO <sub>4</sub> · H <sub>2</sub> O	7 g/l
Oxalic acid	0.5 g/l
Glycine	8 g/l

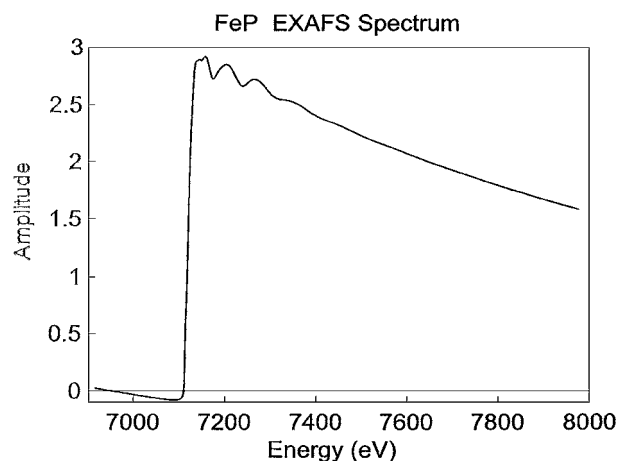


Figure 1

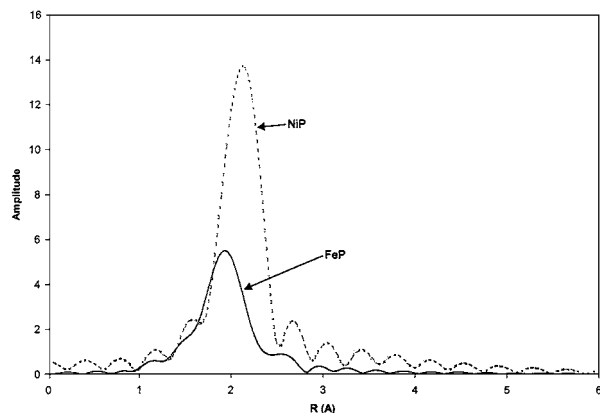


Figure 2

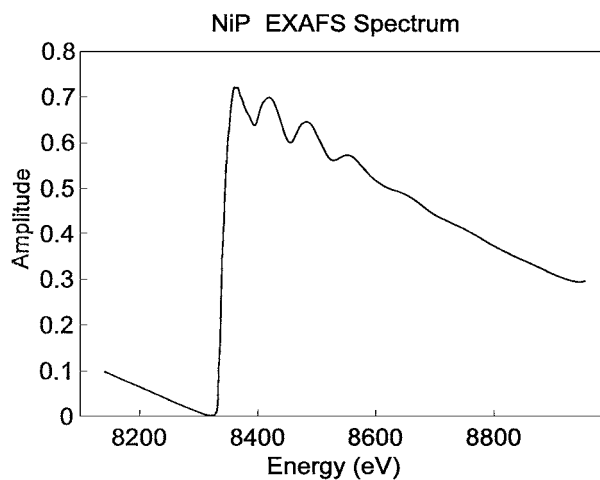


Figure 3

amorphous. The coordination number was found to be equal to 2.

For the Ni-P specimen, the best data fit was found for a two shell analysis. The Ni-K edge was observed to be

approximately equal to 8350 eV. The amplitude of the peak is lower than that seen for the Fe-P sample. The bond length was calculated to be 2.4Å and the disorder parameter was found to be approximately 0.0066. The coordination number was found to be 6. The Fourier transformation shows one single (major) peak at about 2Å which suggests that there is no long distance order. For relatively large bond lengths (>3Å), there are no major peaks and therefore only short distance order is possible. Hence, it is concluded that the specimen is not crystalline but it is amorphous. Thus, the preliminary data obtained support the use of techniques employed in this investigation for characterization of amorphous 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.

### References

1. S. B. LALVANI and M. CROFT, *J. Mater. Sci. Lett.* **18** (1999) 1281.
2. A. J. DAVENPORT, M. SANSONE, J. A. BARDWELL, A. J. ALDYKIEWICZ, M. TAUBE and C. M. VITUS, *J. Electrochem. Soc.* **141**(1) (1994) PL 6.
3. A. N. MANSOUR and C. A. MELENDRES, *ibid.* **142** (1995) 1961.
4. A. J. DAVENPORT, J. A. BARDWELL and C. M. VITUS, *ibid.* **142**(3) (1995) 721.
5. J. W. KANG, S. B. LALVANI and C. A. MELENDRES, *J. Appl. Electrochem.* **25** (1995) 376.
6. S. B. LALVANI and J. C. KANG, *J. Mater. Sci. Lett.* **11** (1992) 835.

Received 23 January  
and accepted 28 March 2001