Effect of Phosphorus Content on Local Structures of NiP Amorphous Alloys

Jinxiang Song, Zheng Wei, Zhiyun Pan, Zhi Xie, Shiqiang Wei

National Synchrotron Radiation Laboratory, University of Science and Technology of China, Hefei 230029, China

Abstract. XAFS technique is used to determine the atomic and electronic structures of NiP amorphous alloys with different P concentrations prepared by chemical reduction method. From the radial structural function (RSF) obtained from EXAFS, it is found that the amorphous alloys with P content less than 10 at.% still present strong peaks corresponding to high coordination shells just like crystalline Ni. This indicates the prominent existence of Ni-rich phase with the fcc-structure, which is not remarkably modified by the P atoms. As the P content is as large as 14 at.%, only the first shell peak in the RSF can be observed and the higher shell peaks disappear. Therefore the sample is totally amorphous. The XANES results show that as the P concentration is above 26 at.%, charge transfers from Ni atoms to P atoms. For P concentration lower than 20at.%, on the contrary, charge transfers from P atoms to Ni atoms, and 3d electron density of Ni atoms reaches the maximum when P concentration is about 14~20 at.%.

Keywords: NiP, EXAFS, XANES.

PACS: 61.43.Dq, 61.10.Ht

INTRODUCTION

The nano-amorphous Ni-P alloys have gained much attention because of their excellent catalytic activity, better selectivity and strong sulfur resistance for the hydrogen evolution reaction [1-5]. Compared to nano-amorphous Ni-B alloys, Ni-P alloys have higher selectivity and turnover of frequencies (TOF) despite smaller surface area [1,6], showing the potential to represent a new generation of hydrogenation catalysts. Preparing Ni-P alloys by chemical reduction method has the advantages of low cost and simple technology to be suitably applied in industry.

The content of P can remarkably change the atomic and electronic structures of the Ni-P alloys, as well as the activity of the alloys [7,8]. Alloying P can modify the catalyst structure, which results in the short range ordering and long range disordering structural characteristics [9]. XPS results show that as the P concentration is lower than 25at.%, charge transfers from P atoms to Ni atoms; and for P concentration higher than 25at.%, charge transfers from Ni atoms to P atoms[10,11]. As the content of P increases, the catalytic activity of Ni-P first increases then decreases, and reaches the maximum when P at.% is about 8~11 wt.% (14 ~ 19at.%) [12]. In order to get deeper understanding about the catalytic mechanism, the

influence of P content on the local structure of the Ni-P alloys should be studied systematically.

X-ray absorption fine structure (XAFS) can simultaneously yield the information on atomic and electronic structures, and has been recognized as a powerful tool for determining the local structure of amorphous materials [13], because of its sensitivity to the short-range order and atom species surrounding the absorbed atom. Furthermore, one can quantitatively obtain the structural parameters of one element in complex material by XAFS [14].

In this work, we will investigate the local structure of Ni-P amorphous alloys. We will use EXAFS to study the atomic structural evolution of the Ni-P alloys at different P contents, and qualitatively analyze the electronic structural properties of the samples from their XANES spectra.

EXPERIMENTAL

The $\text{Ni}_{100-x}\text{P}_x$ amorphous alloy powder was prepared with chemical reduction method. An aqueous mixture solution of 0.5 M $\text{NiCl}_2/1\text{M NaH}_2\text{PO}_2/1.5\text{M NaAc}$ was prepared by mixing an aqueous solution of NiCl_2 and NaH_2PO_2 . PH value was adapted by adding NaOH solution. Several drops of KBH_4 (2mol/l) were added into the solution to initiate the reaction. The solution was vigorously agitated by a magnetic stirrer at 40 °C. The black precipitate was filtered, washed

thoroughly with ammonia solution, distilled water and ethanol, and eventually soaked in ethanol. The atomic compositions of Ni-P powder were obtained through inductively coupled plasma spectrometry.

The X-ray-absorption spectra at Ni K-edge for the as-prepared $\text{Ni}_{100-x}\text{P}_x$ ($x=7\sim 24$) alloys were measured at the beamline of 4WB1 of Beijing Synchrotron Radiation Facility (BSRF), China. The storage ring of BSRF was operated at 2.2 GeV with a maximum current of 100 mA. The fixed-exit Si(111) flat double crystals were used as monochromator. XAFS data were analyzed by USTCXAFS 2.0 data analysis package compiled by Zhong and Wei [15] according to the standard procedures.

RESULTS

The Ni K-edge EXAFS oscillation function $k^3\chi(k)$ spectra of $\text{Ni}_{100-x}\text{P}_x$ alloys with different P concentrations are shown in Figure 1, and that of Ni foil is included for comparison. It can be clearly seen that the oscillation amplitude of EXAFS for NiP samples gradually decreases while the content of P increases. Except for the difference in amplitude, the absorption spectra of Ni_{92}P_8 and $\text{Ni}_{90}\text{P}_{10}$ are similar to that of Ni foil. However, the spectra of $\text{Ni}_{86}\text{P}_{14}$, $\text{Ni}_{80}\text{P}_{20}$ and $\text{Ni}_{74}\text{P}_{26}$ are very different from that of Ni foil, and only signal of a single frequency can be observed.

FIGURE 1. The Ni K-edge EXAFS oscillation function $k^3\chi(k)$ of $\text{Ni}_{100-x}\text{P}_x$ alloys with different P concentrations and Ni foil.

After Fourier transforming the EXAFS functions in Figure 1, we get the radial structural functions (RSFs) of $\text{Ni}_{100-x}\text{P}_x$ alloys with different P concentrations and Ni foil, as shown in Figure 2. The sample Ni_{92}P_8 and $\text{Ni}_{90}\text{P}_{10}$ present the strong third and fourth nearest neighbor peaks similar to that of Ni foil in their RSFs, which indicates that when P content is below 10 at.%, $\text{Ni}_{100-x}\text{P}_x$ alloys still have medium range order, and keep the fcc structure just like Ni foil. For $\text{Ni}_{74}\text{P}_{26}$, $\text{Ni}_{80}\text{P}_{20}$ and $\text{Ni}_{86}\text{P}_{14}$ samples, only the first shell peak is observed, which means that the samples just have short range order and are totally amorphous.

FIGURE 2. The radial structural functions of $\text{Ni}_{100-x}\text{P}_x$ alloys with different P concentrations and Ni foil.

In order to obtain the quantitative structural parameters of the Ni-P alloys, we fitted the first shell EXAFS peak in the inversely Fourier transformed k -space by including the Ni-P and Ni-Ni coordination. The theoretical back-scattering amplitude $|F(k, \pi)|$ and phase shift $\delta(k)$ functions of both coordination pairs were calculated by FEFF7 code [16]. Table 1 summarizes the structural parameters.

TABLE 1. The coordination parameters of the $\text{Ni}_{100-x}\text{P}_x$ alloys obtained from curve fitting of EXAFS.

Sample	Pair	$R(\text{\AA})$	N	$\sigma_t^2(\text{\AA}^2)$	$\sigma_s(\text{\AA})$
Ni foil	Ni-Ni	2.47	12.0	0.0064	
Ni_{92}P_8	Ni-P	2.28	0.2	0.0049	~ 0
	Ni-Ni	2.49	11.8	0.0064	0.06
$\text{Ni}_{90}\text{P}_{10}$	Ni-P	2.28	0.5	0.0049	~ 0
	Ni-Ni	2.52	11.6	0.0064	0.09
$\text{Ni}_{86}\text{P}_{14}$	Ni-P	2.27	1.8	0.0049	0.05
	Ni-Ni	2.60	10.1	0.0064	0.17
$\text{Ni}_{80}\text{P}_{20}$	Ni-P	2.27	2.6	0.0049	0.07
	Ni-Ni	2.67	9.7	0.0064	0.25
$\text{Ni}_{74}\text{P}_{26}$	Ni-P	2.27	3.0	0.0049	0.09
	Ni-Ni	2.69	9.5	0.0064	0.27

As shown in Table 1, the Ni-Ni coordination numbers of Ni_{92}P_8 (11.8) and $\text{Ni}_{90}\text{P}_{10}$ (11.6) samples are close to that of Ni foil (12.0). Combined the RSF results, we consider that there exists Ni-rich phase in the Ni-P alloy with P concentration lower than 10 at.% where Ni atoms keep the fcc structure like Ni foil. Since their Ni-P coordination numbers are no more than 0.5, we further did single shell fitting to the EXAFS curves including only Ni-Ni coordination for these two samples, finding almost no difference between the results of single shell fitting and double shell fitting. It indicates that P atoms do not enter the lattice of Ni-rich phase, but may concentrate near the

boundary of the Ni-rich phase. This is consistent with Hentschel *et al.*'s investigation on the Ni-P sample with P content of 3.6 at.% [19,20]. In addition, we also notice that the intensity of the first shell peak decreases more acutely than that of the high coordination shell peaks in the RSFs with the P concentration increasing from 8 to 10 at.%. It indicates that the size of Ni-rich phase may be larger if P content is lower [17,18].

With the P concentration increasing from 14 to 20 and 26 at.%, the structural disorder σ_s of Ni-Ni coordination increases from 0.17 to 0.25 and 0.27, two or three times larger than that of low P concentration samples. Such a large disorder confirms that the Ni-P alloys with high P concentration are totally amorphous. The coordination number of Ni-P coordination also increases from 1.8 to 3.0 following the increasing of P concentration from 14 to 26 at.%, different from the small value of Ni₉₂P₈ and Ni₉₀P₁₀. At the same time, the coordination number of Ni-Ni decreases from 10.1 to 9.5 on the contrary. This indicates that the P atoms have entered the lattice of Ni atoms and occupied part of Ni atoms. Since the structural disorder σ_s of Ni-P coordination is less than 0.1, we consider the P atoms disperse relatively uniformly.

FIGURE 3. The Ni *K*-edge XANES spectra of Ni_{100-x}P_x alloys with different P concentrations and Ni foil.

Figure 3 shows the normalized Ni *K*-edge XANES spectra of Ni_{100-x}P_x alloys and Ni foil. The main peak of *K*-edge is mainly due to 1s → 3d dipolar transitions, while the pre-edge is mainly due to 1s → 3d quadrupole transitions. White line peak appears only in the near edge of Ni₇₄P₂₆ sample, indicating that the charge transfer from Ni atoms to P atoms occurs when the P concentration is above 25 at.% and for the low-P samples the charge transfers from P atoms to Ni atoms. This accords with XPS results [10,11].

The 1s → 3d transition is dipole forbidden, 3d orbit must hybrid with 4p orbit to realize the transition. The intensities of the pre-edge can reflect the ratio of unoccupied 3d orbit. As the P content increase, the intensities of the pre-edge first decrease then increase, and reach the minimum when P at.% is about 14~20,

which means that 3d electron density of Ni atoms reaches the maximum at this time.

CONCLUSIONS

We have studied the atomic and electronic structures of Ni-P amorphous alloys with different P concentrations. It is found that Ni-rich phase exist in the Ni-P alloys with P content less than 10 at.%, in which Ni atoms keep the same fcc structure as in Ni foil. P atoms do not enter the Ni-rich phase, but concentrate near the boundary of the Ni-rich phase. The size of the Ni-rich phase increases while P content decreases. The Ni-P alloys with P concentration larger than 14 at.% are totally amorphous where the local structure of Ni atoms has been remarkably modified by P. The P atoms are uniformly dispersed into Ni atoms, and no Ni-rich phase exists.

For the Ni-P alloys with P concentration above 25at.%, charge transfers from Ni atoms to P atoms. As the P content increase, 3d electron density of Ni atoms first increases then decreases, and reaches the maximum when P content is about 14~20 at.%.

ACKNOWLEDGEMENTS

We would like to thank the Beijing Synchrotron Radiation Facility of China for the beam time of the XAFS measurements. This project was supported by the National Natural Science Foundation of China (Grant No. 20303014).

REFERENCES

1. S.P. Lee, and Y.W. Chen, *Ind. Eng. Chem. Res.* **38**, 2548 (1999)
2. H. Li, Y. Xu, *Mater. Lett.* **51**, 101 (2001)
3. S.P. Lee, Y.W. Chen, *J. Mol. Catal. A: Chem.* **152**, 213 (2000)
4. X. Yu, H. Li, J.F. Deng, *Appl. Catal. A: Gen.* **199**, 191 (2000)
5. A. Molnar, G.V. Smith, M. Bartok, *Adv. Catal.* **36**, 329 (1989)
6. H. Li, H.X. Li, W.L. Dai, W. Wang, Z. Fang and J.F. Deng, *Appl. Surf. Sci.* **152**, 25 (1999)
7. T. Burchardt, T. Valand, T. O. Saetre (Eds.), Kluwer Academic, Dordrecht, pp. 191-196 (1998)
8. T. Burchardt, *Int. J. Hydrogen Technol.* **25**, 627 (2000)
9. A. Molnar, G. V. Smith, M. Bartok, *Adv. Catal.* **36**, 329 (1989)
10. Y. Okamoto, Y. Nitta, T. Imanaka, *J. Chem Soc, Faraday Trans* **175**, 2027 (1979)
11. H. Li, W. Wang, H. Li and J. Deng, *J. Catal.* **194**, 211 (2000)
12. T. Burchardt, *Int. J. Hydrogen Technol.* **25**, 627 (2000)
13. E. D. Crozier, *Physica B* **209**, 330 (1995)
14. B. R. Shen, S. Q. Wei, K. N. Fan, and J. F. Deng, *Appl. Phys. A: Mater. Sci. Processing A* **65**, 295 (1997)

- 15 W.J. Zhong and S.Q. Wei, *J. Univ. Sci. Tech. China* **31**, 328(2001)
16. J.J. Rehr, S.I. Zabinsky and R.C. Albers, *Phys. Rev. Lett.* **38**, 3397(1992)
17. Y. Gao, Z.J. Zheng, M. Zhu and C.P. Luo, *Mat. Sci. Eng. A* **381**, 98 (2004)
18. T. Burchardt, V. Hansen and T. Valand, *Electrochim. Acta* **46**, 2761 (2001)
19. H. Xie and B. Zhang, *J. Mater. Process. Tech.* **124**, 8 (2002)
20. T. Hentschel et al., *Acta Mater.* **48**, 933 (2000)