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Structural Investigation of Amorphous Ni₂B by EXAFS and XRD

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Abstract. The structure and thermostability of hyperfine amorphous Ni₂B catalysts (HA-Ni₂B) have been studied by EXAFS, XPD and DSC. The samples prepared by chemical reduction have been proved to be amorphous. The grain size is between 5 nm and 20 nm. A short-range order cluster is formed. The distances of Ni-B or Ni-Ni did not alter due to the change of the conditions but the coordination number of Ni is changed. The HA-Ni₂B is only stable up to 140°C. Over 140°C, the crystal Ni and an intermediate formed. Finally the intermediate disappears but some B₂O₃ can be detected.

1. Introduction

Hyperfine amorphous catalysts have been paid attention for both of hyperfine and amorphous features. By EXAFS A. Gorrias et al. [1] studied the hyperfine amorphous Fe-Co-B alloy prepared by chemical reduction. They found a α -Fe-like cluster of Fe-Co-B and Co atoms replaced Fe atoms in α -Fe. J. Jiang [2] compared a hyperfine amorphous alloy of Fe₇₉B₂₁ with a banded quenching amorphous Fe₈₀B₂₀. The former has better isotropism and the number of B atoms about Fe atoms is larger than in the later. P.C. Maybury [3] reported that the amorphous compounds of Ni₂B and Co₂B can absorb more hydrogen than the crystal. If fresh Co-B alloy is put in water, hydrogen can be released and boric acid is formed. B. Ganem [4] reported that when amorphous Ni-B was heated to 250°C, the crystal Ni, Ni₂B or Ni₃B formed. R.C. Wade [5] found that boron disappears in the crystallization. The purpose of this paper is to study the influence of the solvents and the temperature on the structure of hyperfine amorphous Ni₂B catalysts (HA-Ni₂B) and to study the thermostability of HA-Ni₂B.

2. Experiment

2.1 Sample preparation

Drop the basic solution of KBH₄ into the solution of Ni(AC)₂ 4H₂O. The hyperfine amorphous Ni₂B alloy is formed. Three samples were prepared: (1) in anhydrous alcohol at 25°C, (2) in water at 25°C, (3) in anhydrous alcohol at 2°C.

2.2 Extended X-ray absorption fine structure (EXAFS)

The absorption data of Ni K edge were collected at the BL-10B beamline in Photon Factory, Japan. The electron energy is 2.5 GeV. The current is 300 mA. The monochromator is a channel-cut Si(311) crystal monochromator, $d = 0.163747$ nm. The data was collected from 7831 eV to 9431 eV. We registered data three times for estimating the deviation. Data was processed by the program package FXEA [6.7]. The code FEFF [8] was used to calculate the theoretical $f_j(k)$, $\lambda_j(k)$ and $\phi_j(k)$.

2.3 X-ray powder diffraction (XPD)

The XPD was carried out with a powder diffractometer D/MAX-rB manufactured by Rigaku, Japan (Cu K α radiation, 40kV, 100 mA, graphite monochromator, DS 1°, SS 1°, RS 0.15 mm).

3. Results and discussion

3.1 The structure of alloys prepared at different conditions

3.1.1 The XPD patterns of three samples showed us that there were two very diffused peaks in them, so they are amorphous.

3.1.2 Radius structure functions (RSF) of EXAFS are shown in Fig.1. The structure parameters obtained by curve fitting the filtered diagrams are listed in Table 1.

On RSF there is only one strong coordination peak (fig.1). It means that there is only short-range order and all the samples are amorphous. Comparing the σ of different coordination shells in Table 1, σ increases rapidly from 0.004 to 0.012 following the increase of bonding length. It is more evidence of short-range order.

Table 1 Structure Parameters from EXAFS

Sample	r(nm)	CN	$\sigma(\text{nm}^{-1})$	$\Delta E_0(\text{eV})$
(1)				
Ni-B	0.208(2)	2.1(3)	0.003(1)	-0.6(2)
Ni-Ni	0.218(4)	1.5(3)	0.008(1)	-0.6(2)
Ni-Ni	0.252(4)	1.0(2)	0.013(2)	-0.6(2)
(2)				
Ni-B	0.208(3)	4.0(4)	0.004(1)	-3.0(3)
Ni-Ni	0.217(3)	1.8(3)	0.008(1)	-3.0(3)
Ni-Ni	0.251(5)	1.6(3)	0.012(3)	-3.0(3)
(3)				
Ni-B	0.208(2)	4.0(4)	0.007(1)	-4.2(2)
Ni-Ni	0.218(3)	0.7(2)	0.008(2)	-4.2(2)
Ni-Ni	0.254(4)	3.8(5)	0.011(2)	-4.2(2)

Fig.1 RSF of samples (1), (2), (3)

3.1.3 From the structural parameters we got : (1) $r_{\text{Ni-B}}$ for the three samples is the same (0.208 nm). It is shorter than the sum of the atom radii of nickel and boron (0.217 nm). It means that a strong interaction exists between the nickel atom and the boron atom. (2) The nearest distance between two nickel atoms $r_{\text{Ni-Ni}}$ is 0.218 nm. It is still the same for all three samples. It is shorter than 0.250 nm and 0.230 nm which are the sum of two metal radii in metallic Ni and two covalence radii of nickel atom respectively. It also means that a very strong interaction exists between nickel atoms. We conclude that there is a cluster of Ni-B in alloy.

The second distance of Ni-Ni ($r_{\text{Ni-Ni}(2)}$) is 0.252 nm. It is close to the distance between nearest nickel atoms in metal nickel. It may mean that very fine grains of metallic nickel mix with the Ni-B cluster or it is the second Ni coordination shell in Ni-B alloy.

3.1.4 The $r_{\text{Ni-B}}$, $r_{\text{Ni-Ni}}$ and $r_{\text{Ni-Ni}(2)}$ distances for the three samples are the same in the range of experimental deviation. It means that the change of preparation conditions does not affect the interaction between Ni-B and Ni-Ni. But the coordination numbers of the three samples are different. The CNs of sample 1 are smaller than the other two. It means that the size and the structure of cluster Ni-B changes with the change of the conditions. The grain size is between 5-20 nm measured in the photo of TEM. Our data are close to the data of S.N. Ishamaev [9], P. Lanparter [10], P. Kazler [11] and J. Wang [12], but they are a little smaller. The reason may be that our grains are nanometersized, i.e. much smaller than theirs.

3.2 The thermostability and the crystallization of HA-Ni₂B

By the hyperfine and amorphous features the materials has high surface energy. It makes the structure unstable. We studied the thermostability by DSC, XPD and EXAFS.

On DSC diagram there are three exothermic peaks located at 144°C, 235°C and 341°C. It means that the catalyst is only stable below 140°C which is lower than stable temperature of quenched Ni₂B. From the phase analysis of samples which were obtained by heating the sample(1) at different temperatures (100°C, 140°C, 250°C, 350°C and 500°C), it is found that the HA-Ni₂B changed to crystal Ni and Ni₃B over 140°C. At 350°C, Ni₃B changed further. An unknown intermediate formed. When the temperature reached 500°C, Ni₃B and the intermediate disappeared. All Ni changes to crystal and part of B transfers to B₂O₃.

From EXAFS, we found that after heating the distances between Ni and B or Ni are the same as before heating while the CNs are larger than before heating. It means that the cluster of Ni-B is enlarged after heating.

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