



## Research paper

## Revealing the multi hydrogen bonding state within iron doped amorphous carbon

Itsuki Miyazato<sup>a</sup>, Keisuke Takahashi<sup>a,b,\*</sup><sup>a</sup> Graduate School of Engineering, Hokkaido University, N-13, W-8, Sapporo 060-8628, Japan<sup>b</sup> Center for Materials Research by Information Integration (CMI<sup>2</sup>), National Institute for Materials Science (NIMS), 1-2-1 Sengen, Tsukuba, Ibaraki 305-0047, Japan

## ARTICLE INFO

## Article history:

Received 1 October 2017

In final form 31 October 2017

Available online 2 November 2017

## Keywords:

Amorphous Carbon

Iron

Hydrogen

## ABSTRACT

Hydrogenated Fe doped amorphous carbon is synthesized via mechanically alloying. XANES analysis suggests that Fe is considered to bond with either C or H atom where the first principle calculations reveals that two types of H-C bonding is confirmed. Weak H-C bond is observed near Fe atom while strong H-C bond is seen far from Fe atom. Electronic structure discovered that weak H-C bonding is induced by Fe atoms where Fe form ionic like bond with surrounding C, resulting in the weak H-C interaction. Thus, two different types of H-C bonding is confirmed within Fe doped amorphous carbon.

© 2017 Elsevier B.V. All rights reserved.

Materials consisting of carbon and metals are well studied materials in material science as carbon forms various structures such as nanotubes, graphene, and amorphous carbon where doping metals in such materials are known to modify the physical and chemical properties [1–3]. In particular, amorphous carbon has caught much attention due to the unpredictable physical and chemical properties which are considered to be induced by the dangling bond. However, understanding the properties of amorphous carbon is challenging in general as carbon atoms are non-periodically placed [3]. Furthermore, doping the metal elements makes amorphous carbon an even more complex material as doping metals often alter the chemical and physical properties of amorphous carbon [4]. In another words, one can consider that controlling the properties of amorphous carbon can be achievable in principle if the effect of doping the metal is revealed.

The common experimental techniques to synthesize amorphous carbon is mechanical alloying, arc deposition, ion beam deposition, pulsed laser deposition, and sputtering [5–8]. It must be noted that the properties of amorphous carbon are strongly affected by how amorphous carbon is synthesized. Mechanical alloying is one way of controlling the amorphous carbon by the processing time [9,10]. In addition, metal doped amorphous carbon can be synthesized via mechanical alloying.

Reactivity of amorphous carbon is a key property as dangling bond within amorphous carbon is considered to be the origin of

the reactivity where metal doping is considered to change the reactivity of amorphous carbon. In particular, hydrogen within Fe doped amorphous carbon has demonstrated interesting behavior where it has been reported that two different hydrogen desorption temperatures are observed when hydrogenated Fe doped amorphous carbon is heated [11–14]. This raises the question whether there would be multi bonding state such as C-H and C-Fe bond or there might be unique interaction of hydrogen and Fe doped amorphous carbon. If how hydrogen behaves within Fe doped amorphous carbon is revealed, one can consider that the reactivity of metal doped amorphous carbon can be tailored. Here, Fe doped amorphous carbon is synthesized using the mechanical alloying and the role of hydrogen and iron are investigated by X-ray diffraction (XRD), X-ray absorption spectroscopy (XAS), and the first principle calculations.

100 mg of graphite powder (HIGH PURITY CHEMICALS CO LTD, Purity:99.99%, ca. 10 μm) and Fe powder (HIGH PURITY CHEMICALS CO LTD, Purity:99.9%up, M 53 μm) were mixed in the mole ratio of 1:1. This mixed powder was introduced into milling pot with 20 of ZrO<sub>2</sub> YTZ balls (φ 8 mm) under 1 MPa hydrogen (Purity:99.99999%) atmosphere, and set to planetary ball-milling apparatus (Fritsch Pulverisette P7). Subsequently, ball-milling was performed under rotation speed of 400 RPM with 15 min. pause in each 1 h in order to release friction heat. Total milling time was set to 1 h, 10 h and 80 h excluding pause time in order to find ball-milling conditions to fabricate amorphous carbon phase sample. X-ray diffraction (XRD, PANalytical, X'Pert-Pro with Cu K radiation X-ray source) is performed to acquire the structures and compositions. X-ray absorption spectroscopy (XAS) was measured via Fe-K edge energy region with transmission method at

\* Corresponding author at: Center for Materials Research by Information Integration (CMI<sup>2</sup>), National Institute for Materials Science (NIMS), 1-2-1 Sengen, Tsukuba, Ibaraki 305-0047, Japan.

E-mail address: [keisuke.takahashi@eng.hokudai.ac.jp](mailto:keisuke.takahashi@eng.hokudai.ac.jp) (K. Takahashi).

the beamline “BL14B2” in SPring-8, a synchrotron radiation facility in Japan. 0.5 mm thickness of 10 mm diameter XAS tablets were formed by pressing mixed adequate amount of samples (both hydrogenated and dehydrogenated by heat treated under 800 °C) and or X-ray transmission hexagonal boron nitride powder (h-BN, Sigma Aldrich, purity:98%,  $-1\ \mu\text{m}$ ) into template. Consequently, those formed tables were sealed by polyethylene film (thickness:0.04 mm) to avoid to expose to the air. Obtained XAS spectra was processed by “Athena”, XAS data processing and analyzing software [15] with spline range of  $k$  of 0–10.5 in order to obtain radial distribution function (RDF). All sample preparation process was performed in a glove box under Ar atmosphere in order to avoid sample oxidation.

First principle calculations using grid based projector augmented wave (GPAW) method is implemented [17]. The exchange correlation of Perdew Burke Ernzerhof (PBE) with spin polarization calculation are applied for all calculations [18] Grid spacing is set to 0.20 Å and special  $k$  point of  $4 \times 4 \times 4$  within the Brillouin-zone sampling are also applied [19]. Charge density was evaluated by Bader analysis method [20–23]. The structure of amorphous carbon is designed based on previous reports where the bulk modulus of amorphous carbon composed of 60 C atoms randomly placed within a cubic unit cell is successfully predicted [24]. Fe and H atoms are then placed into constructed amorphous carbon.

H-adsorption energy ( $E_{\text{ads}}$ ) and Fe dissociation energy ( $E_{\text{disso}}$ ) is calculated by Eqs. (1) and (2), respectively:

$$E_{\text{ads}} = E_{\text{C-Fe-H}} - E_{\text{C-Fe}} - E_{\text{H}} \quad (1)$$

$$E_{\text{disso}} = E_{\text{C-Fe}} - E_{\text{C}} - E_{\text{Fe}} \quad (2)$$

where  $E_{\text{all}}$ ,  $E_{\text{nonFe}}$  and  $E_{\text{nonH}}$  are “free energy of  $\text{C}_{\text{amorphous}} + \text{Fe} + \text{H}$  models(1–2)”, “free energy of  $\text{C}_{\text{amorphous}} + \text{H}$  models(3–4)” and “free free energy of  $\text{C}_{\text{amorphous}} + \text{Fe}$ ”, respectively. Consequently, non-Fe(3–4) and non H(5–6) models were additionally calculated to obtain  $E_{\text{nonFe}}$  and  $E_{\text{nonH}}$  to calculate  $E_{\text{ads}}$  and  $E_{\text{disso}}$ . Note that the negative energy indicate exothermic reaction.

X-ray diffraction (XRD) is performed for synthesized hydrogenated Fe doped amorphous carbon in order to characterize the structure and composition. XRD profiles for hydrogenated Fe doped amorphous carbon is shown in Fig. 1. One can see that there is strong Fe peak as well as Fe-C peaks as shown in Fig. 1 while graphite peak is not observed. Note that it has reported that  $\text{Fe}_7\text{C}_3$  is a commonly observed phase when graphite and iron are mechani-

cally milled [25,26]. This indicates that synthesized Fe doped amorphous carbon has amorphous phase with Fe-C bond.

The bonding state of hydrogenated Fe doped amorphous carbon is measured by using X-ray absorption spectroscopy (XAS). X-ray absorption near edge structure (XANES) peak of 10 and 80 h milled hydrogenated Fe doped amorphous carbon is shown in Fig. 2, respectively. One can see that the peaks are slightly different from reference Fe foil as shown in Fig. 2. In addition, it has been reported that slight different in Fe within carbon system is induced by Fe-C bond [27,28]. Therefore, XANES analysis suggest the presence of Fe-C bond in Fe doped amorphous carbon.

First principle calculations are performed to identify the bonding state of hydrogen within the Fe doped amorphous carbon. Because XRD shown in Fig. 1 indicates that hydrogenated Fe doped amorphous carbon has amorphous phase and Fe-C bond, the model of amorphous carbon is constructed by randomly placing the 60 atoms within cubic unit cell [29]. Cubic unit cell is relaxed then lattice optimization is carried out where the lattice constant of the unit cell is calculated to be 7.51 Å. Single Fe atom is then placed into constructed amorphous carbon shown in Fig. 3. Two different types of hydrogen adsorption sites is considered as shown in Fig. 3 (a) and (b) where one hydrogen atom is adsorbed near Fe atoms and another is adsorbed far from Fe atom. Here, H adsorption energy of the following 4 cases is calculated and collected in Table 1 where sites 1 and 2 are indicated in Fig. 3 while Fe dissolution energy is also calculated.

1.  $\text{C}_{\text{amorphous}} + \text{Fe} + \text{H}$  (Site 1)
2.  $\text{C}_{\text{amorphous}} + \text{Fe} + \text{H}$  (Site 2)
3.  $\text{C}_{\text{amorphous}} + \text{H}$  (Site 1)
4.  $\text{C}_{\text{amorphous}} + \text{H}$  (Site 2)

H adsorption energy in amorphous carbon without Fe atom is calculated to be  $-1.68\ \text{eV}$  and  $-2.04\ \text{eV}$  in sites 1 and 2, respectively. This high H adsorption energy suggests bonding between C and H. Doping Fe atom in amorphous carbon results in the dissolution energy of  $-1.40\ \text{eV}$  as shown in Table 1. This high binding energy indicates that Fe atom and C atoms are also strongly bonding with each other. In same fashion, H adsorption energy at sites 1 and 2 is considered where the adsorption energy is distinguishably different from amorphous carbon without Fe atom. In particular, H adsorption energy at site 1 (H near Fe) is calculated to be  $-0.97\ \text{eV}$ . This suggests the H-C bond becomes weaker upon the introduction of Fe atom. On the other hand, H adsorption energy at site 2 (H far from Fe) is calculated to be  $-5.47\ \text{eV}$ , which has good agreement

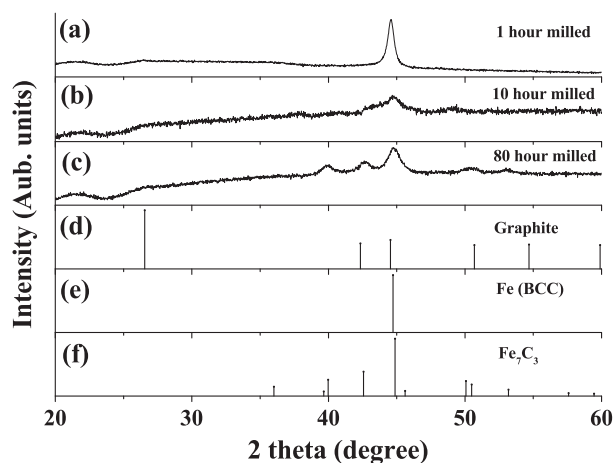


Fig. 1. XRD profiles of synthesized hydrogenated Fe doped amorphous carbon (a) 1 h milled, (b) 10 h milled, (c) 80 h milled. Referenced XRD profiles for (d) graphite [16] and (e) BCC Fe [16], and (f)  $\text{Fe}_7\text{C}_3$  [16].

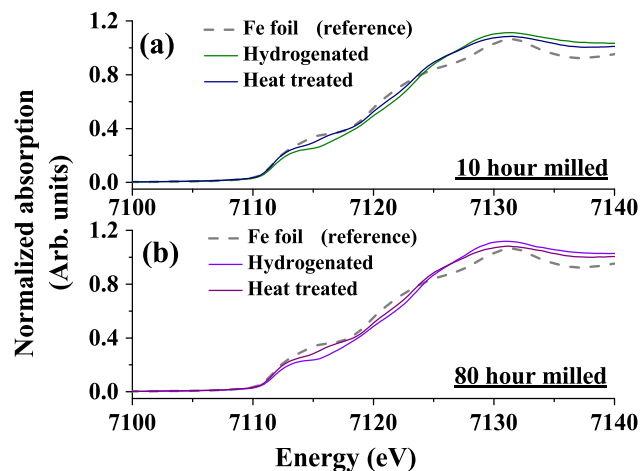


Fig. 2. XANES spectra of (a) 10 h milled, (b) 80 h milled.

Download English Version:

<https://daneshyari.com/en/article/7838524>

Download Persian Version:

<https://daneshyari.com/article/7838524>

[Daneshyari.com](https://daneshyari.com)