
Hidehiro Kudo*1, Ken Unno*2, Atsunori Kamegawa, Hitoshi Takamura and Masuo Okada

Department of Materials Science, Graduate School of Engineering, Tohoku University, Sendai 980-8579, Japan

Vapor grown carbon nano-fibers (VGCFs) were synthesized by using Fe ingots, Fe powders, nanocrystalline Fe91Zr7B2 and Fe75Si15B10 alloy catalysts with fine bcc-Fe grains (∼20 nm). The Fe particles worked as catalysts were formed by fracturing original Fe ingots, Fe powders, and nanocrystalline alloys before the formation of VGCFs. TEM and HREM observations indicated that VGCFs’ structures turned out to be platelet type grown from Fe powders and Fe91Zr7B2, and the tubular type grown from nanocrystalline Fe75Si15B10 alloy. In addition to these structures, VGCFs grown from Fe ingots exhibited herringbone and coil type structures. Diameter of VGCFs prepared from nanocrystalline Fe75Si15B10 alloy was smaller than that of grown from Fe91Zr7B2 alloy. This could be originated from the difference of fracturing process between nanocrystalline Fe91Zr7B2 and Fe75Si15B10 alloys. Protium absorbing properties of VGCFs were evaluated by a Siverts-type apparatus and electrochemical method. It turned out that VGCFs had little protium absorbing capacity.

(Received October 19, 2001; Accepted December 3, 2001)

Keywords: vapor grown carbon nano-fiber, iron-based catalysis, protium absorbing material

1. Introduction

Protium absorbing alloys are the key materials for hydrogen energy system. On the other hand, it is important to develop carbon materials as protium absorbing materials instead of alloys because carbon is abundant and lighter than alloys. It was reported that activated carbon with porous structure could absorb 5 mass%H under 5 MPa hydrogen.1) But activated carbon exhibits protium absorbing at low temperatures such as liquid nitrogen temperature, because the absorbing mechanism will be physical adsorption. It was reported in 1997 that Single-Walled Carbon NanoTube (SWCNT) had about 10 mass%H of protium absorbing property.2) Specially Vapor Grown Carbon nano-Fibers (VGCFs) have been paid attention to be used for protium absorbing materials, in addition, it was reported in 1998 that herringbone type VGCFs absorbed protium about 67 mass%H at room temperature.3) However, detailed methods to prepare VGCFs are not known, and almost few works to confirm their results are reported.

VGCFs can be prepared by catalytic decomposition of hydrocarbons or CO gas passing through over heated metal particles including Fe, Co, Ni, and their alloys. The different crystal structure of VGCFs will be formed by varying the composition of catalysts and reactant gas, temperature, and other experimental conditions.4,5) In addition, diameter of the fibers is determined by the size of catalyst particles.6) So, the synthesis of VGCFs requires the nanoscale-size catalysts. Thus, a coprecipitation technique followed by reduction of metal carbonates, by which fine metal or alloy catalysts with a diameter of less than 100 nm can be obtained, is usually employed to prepare the catalysts.7) Instead of the conventional coprecipitation technique, we select Fe–Zr–B and Fe–Si–B alloy systems as novel catalysts where nanoscale α-Fe particles are formed.8–10) These alloys are well known to precipitate nanoscale bcc-Fe crystal grains with a diameter of 15–20 nm in amorphous phase by annealing alloys. In this study, bcc-Fe grains work as novel catalysts for the growth of VGCFs synthesis, are expected.

Thus, the purpose of this study is to prepare the VGCFs by using nanocrystalline Fe–Zr–B and Fe–Si–B alloys, Fe ingots, and Fe powders as novel catalysts, and to clarify the experimental conditions to form various VGCFs and their protium absorbing properties.

2. Experimental Procedures

Nanocrystalline Fe–Zr–B and Fe–Si–B alloys were prepared by a melt-spinning technique, following by annealing. The raw materials for the studied alloys were Fe (purity, 99.9 mass%), Zr (99.6 mass%), Si (99.5 mass%), and crystalline B (99.5 mass%). The ingots of Fe, Fe91Zr7B2, and Fe75Si15B10 were prepared by arc-melting method in Ar atmosphere. To obtain melt-spin ribbons, Fe91Zr7B2 and Fe75Si15B10 ingots were then melted and injected onto a Cu roller rotating at a roll speed of 42 m/s in Ar atmosphere. The X-ray diffraction pattern indicated that the obtained ribbons consisted of an amorphous phase without any crystalline phase. To precipitate nanocrystalline bcc grains, the as-quenched ribbon samples with the size of a cross section of about 8 × 0.02 mm2 were then annealed at 773 K (Fe75Si15B10) or 873 K (Fe91Zr7B2) for 5 min in Ar. The grain size of bcc-Fe after the heat treatment was found to be about 20 nm from Sherrer’s equation using the half width of (110)bcc diffraction. The annealed ribbon samples were finally ground into powders with the size of less than 45 μm. The size of Fe powders (99.6 mass%) is below 3 mm.

The nanocrystalline Fe91Zr7B2 and Fe75Si15B10 alloy powders, Fe ingots, and Fe powders were placed onto a Pt boat, and introduced into a reactor tube equipped with an infrared lamp. First of all, to activate the catalytic function of the catalysts, the catalyst powders were annealed under H2 atmosphere at 623 K for 30 min. Then, temperature was increased up to 773 K or 873 K, and the reactant gas of 80%CO–20%H2 was introduced into the reactor tube. The gas-flow rate of
50 cm³/min was fixed through this study.

The morphology of the VGCFs were observed by field-emission-type scanning electron microscopy (FE-SEM, Philips XL-30FE), transmission electron microscopy (TEM, JEOL JEM-2000EX and HITACHI H-800), and high-resolution electron microscopy (HREM, Philips CM200FEG).

After metal-catalysts in VGCFs were removed by soaking in 2 kmol/m³ HNO₃, the VGCFs was annealed at 873 K in Ar. Then VGCFs were evacuated for 1 h to remove absorbing gas molecular, protium absorbing properties of the VGCFs were measured by a Siverts-type apparatus.

After charging of that current density was 100 mA/g for 4 h, electrochemical PCT properties of VGCFs were also measured at 298 K in 6 kmol/m³ KOH electrolyte. Measuring current density was 10 mA/g. Samples were prepared by mixing with Ni powder (99.9 mass%, diameter is 2–3 mm), and were pressed into the pellet electrodes of 0.10 g VGCFs and 0.90 g Ni powder. The voltages were refered to a Hg/HgO/OH⁻ reference electrode.

3. Results and Discussion

3.1 Synthesis of VGCFs on Fe ingot catalysts

The deposition of carbon on the Fe ingots was confirmed by naked-eye after the 80%CO–20%H₂ mixture gas was introduced in reactor tube at 873 K for 5 h. Figure 1 shows transmission electron micrographs (TEM) of the VGCFs which has (a) herringbone and (b) coil type structures grown from Fe ingot catalysts. In Fig. 1(a), the shape of catalytic Fe particle with dark contrast is facet. It indicates that the VGCF has herringbone type structure.

Similar morphology of VGCF was also reported by Chambers et al. In Fig. 1(b), it is observed the VGCF which has coil type structure. In addition, from the TEM observation, tubular and twist type VGCFs were observed. Fiber diameters of VGCFs grown from Fe ingots were around 50–400 nm. It should be mentioned that catalytic Fe particle observed in Fig. 1(a) must be formed by fracturing the Fe ingots.

3.2 Synthesis of VGCFs on Fe powder catalysts

VGCFs were prepared by using the Fe powders under 80%CO–20%H₂ mixture gas at 873 K for 1 h. Figure 2 shows (a) a TEM of the VGCF grown on Fe powder and (b) a corresponding lattice image of the VGCF taken by high-resolution electron microscopy (HREM). It can be seen that the diameter of the VGCF is about 250 nm which grown from the lower right of catalyst particle with dark contrast to upper left in the Fig. 2(a). From the corresponding lattice image shown in Fig. 2(b), the VGCF consists of graphite plates that are stacked perpendicular to the fiber axis. Thus, it is considered that the structure of this VGCF is platelet type, which was also reported by Chambers et al. In addition, from scanning...
electron microscopy, it was observed that fiber diameter was around 100 to 500 nm. It should be mentioned that the size of catalytic Fe was below 500 nm, then that the observed Fe particles in Fig. 2(a) was formed by fracturing the original Fe powders.

Comparing to the case of using Fe ingots, structure of VGCFs grown from Fe powders is only platelet type. It indicates that changing catalyst form from bulk to powder causes the changing structure of VGCFs.

3.3 Synthesis of VGCFs on nanocrystalline Fe$_{91}$Zr$_7$B$_2$ alloy powder catalysts

VGCFs were prepared by using nanocrystalline Fe$_{91}$Zr$_7$B$_2$ alloy powders under 80%CO–20%H$_2$ mixture gas at 873 K for 15 min. Figure 3 shows (a) a TEM of the VGCF and (b) a corresponding lattice image of the VGCF. Amongst the VGCFs that can be seen in Fig. 3(a), the fiber is grown from the lower right of catalytic Fe with a width of about 160 nm to the upper left. From the corresponding lattice image, the VGCF consists of graphite platelets that were stacked perpendicular to the fiber axis. Thus, it is considered that the structure of this VGCF is platelet type. The fiber diameter is around 50–200 nm. The size of the VGCF is larger than that of Fe grain (~20 nm) in nanocrystalline Fe$_{91}$Zr$_7$B$_2$ alloys. This means that the catalytic Fe agglomerates seemed to be formed by fracturing original Fe$_{91}$Zr$_7$B$_2$ alloy powders as polycrystalline Fe particles. The detailed mechanism is discussed elsewhere.$^{11}$

3.4 Synthesis of VGCFs on nanocrystalline Fe$_{75}$Si$_{15}$B$_{10}$ alloy powder catalysts

VGCFs were prepared using nanocrystalline Fe$_{75}$Si$_{15}$B$_{10}$ alloy powders under 80%CO–20%H$_2$ mixture at 773 K for 1 h. Figure 4 shows (a) a micrograph of the VGCF grown on nanocrystalline Fe$_{75}$Si$_{15}$B$_{10}$ alloy powders, and (b) a corresponding lattice image of the VGCF taken by HREM. It is observed that fiber diameter is around 40 nm in Fig. 4(a). Judging form the lattice image, the graphite sheets seems to be stacked parallel to the fiber axis at the edge of the fiber. This suggests that the VGCF has a tubular type structure, which was also reported by Chambers et al.$^3$

In the case of Fe$_{75}$Si$_{15}$B$_{10}$ alloy, the diameter of catalytic Fe grains is about 20 nm, which almost corresponds with the size of α-Fe in the alloy. This suggests that the Fe catalyst is formed by fracturing the nano-sized Fe phase each in the alloys.

On the other hand, the diameter of VGCFs grown on nanocrystalline Fe$_{75}$Si$_{15}$B$_{10}$ alloy is smaller than that of VGCFs grown on Fe$_{91}$Zr$_7$B$_2$ alloy catalyst. It is well known that the diameter of VGCFs is governed by the size of catalyst particles.$^{4,5,11}$ The size of catalyst particles fracturing

---

Fig. 3 (a) TEM images of VGCF grown from nanocrystalline Fe$_{91}$Zr$_7$B$_2$ alloy powder at 873 K for 15 min and (b) corresponding lattice image of the VGCF taken by HREM selected area in (a).

Fig. 4 (a) HREM micrograph of VGCF grown on nanocrystalline Fe$_{75}$Si$_{15}$B$_{10}$ alloy powder at 773 K for 1 h and (b) corresponding lattice image of the VGCF taken by HREM selected area in (a).
form nanocrystalline Fe\(_{75}\)Si\(_{15}\)B\(_{10}\) alloy is also smaller than that of Fe\(_{91}\)Zr\(_{7}\)B\(_{2}\). One of the reasons seems to be the difference of brittleness between catalytic alloy powders. It is considered that since nanocrystalline Fe\(_{75}\)Si\(_{15}\)B\(_{10}\) alloy is more fragile than Fe\(_{91}\)Zr\(_{7}\)B\(_{2}\) alloy catalysts, catalytic Fe grains of nanocrystalline Fe\(_{75}\)Si\(_{15}\)B\(_{10}\) alloy will tend to fracture easily comparing to Fe\(_{91}\)Zr\(_{7}\)B\(_{2}\) alloy. Thus, fine catalytic Fe grains seem to be formed from nano-sized \(\alpha\)-Fe phase in the Fe\(_{75}\)Si\(_{15}\)B\(_{10}\) alloy. The difference of fracturing and fiber growing process between Fe\(_{91}\)Zr\(_{7}\)B\(_{2}\) and Fe\(_{75}\)Si\(_{15}\)B\(_{10}\) alloy is schematically illustrated in Fig. 5. The growth process includes two stages, i.e., “the separation of catalyst particles” and “fiber growth” as follows:

1. The catalyst particles containing fine bcc-Fe grains are partially separated from alloy powders through interactions with reactant gas.
2. The primitive VGCFs start growing from the catalyst particles.
3. The VGCFs with catalyst particle are detached from the catalyst powder.
4. \(\rightarrow\) (5) Each VGCFs continues to grow.

Each step in the process mentioned above can occur simultaneously, even through the repetition of the first three steps, i.e., the separation of catalyst particles; (1)-(2)-(3)-(1)-... would be terminated as the original alloy powders disappeared.\(^{11}\)

3.5 Protium absorbing properties of VGCFs

In this study, protium absorbing properties of VGCFs were measured by a Siverts-yype apparatus and a new sample cell was designed for this measurement. In this sample cell, it is possible to anneal the VGCFs at 873 K in Ar to remove absorbing gas molecular before measuring protium absorbing properties. In addition, the quality of this sample cell was confirmed, such that error was under 0.1 mass%H using MmNi\(_5\) alloy.

Figure 6 shows equilibrium pressure-composition isotherms of VGCFs grown on Fe powders, nanocrystalline Fe\(_{91}\)Zr\(_{7}\)B\(_{2}\) and Fe\(_{75}\)Si\(_{15}\)B\(_{10}\) alloy powder catalysts at 298 K. It can be seen that the maximum protium content of VGCFs was only 0.13 mass%, which is very small value compared to the reported value.\(^{3}\) The plateau region such as observed in protium absorbing alloys was not observed.

Figure 7 shows the change in protium concentration as a

Fig. 6 Pressure-Composition isotherms (absorbing process) of VGCFs grown on Fe powder, nanocrystalline Fe$_{91}$Zr$_7$B$_2$ and Fe$_{75}$Si$_{15}$B$_{10}$ alloy powder catalysts at 298 K.

Fig. 7 Change in protium concentration of VGCFs under hydrogen atmosphere (10 MPa) as a function of time.

function of time in the presence of VGCFs at 298 K. It was also observed that there was little change of protium concentration with reaction time. Thus, it is considered the absorbing reaction is rapidly occurred.

Figure 8 shows Pressure-Composition isotherm of VGCFs grown on Fe powders at 873 K for 5 h obtained by using an electrochemical method at 298 K. VGCFs can absorb protium electrochemically about 0.13 mass%H at equilibrium hydrogen pressure about 0.12 MPa, but plateau region as protium absorbing alloys is not observed. This value is also very small comparing to the reported value. In comparing the measurement results by a Siverts-type apparatus, equilibrium hydrogen pressure of gas-solid reaction is over 80 times higher than that of electrochemical reaction. So, the protium absorbing mechanisms of these reactions seem to differ from each other. The further consideration is required for clarifying the mechanism of absorbing the hydrogen.

4. Conclusion

The VGCFs were prepared by using nanocrystalline Fe$_{91}$Zr$_7$B$_2$ and Fe$_{75}$Si$_{15}$B$_{10}$ powders as novel catalysts. The Fe ingots and powders were used as the catalysts for the comparison. From TEM and HREM observations, it was found that the structures of VGCFs grown from nanocrystalline Fe$_{91}$Zr$_7$B$_2$ alloy were platelet, and the tubular type for nanocrystalline Fe$_{75}$Si$_{15}$B$_{10}$ alloy. Specially, VGCFs grown from Fe$_{75}$Si$_{15}$B$_{10}$ alloy had fine diameter of 40 nm. But the VGCFs grown from Fe ingots showed the various type such as platelet, tubular, herringbone and coil, but ones from Fe powders were platelet type. It indicated that the shape, size, and mechanical properties of the catalysts alter the structure of VGCFs. The diameter of VGCFs was governed by the size of catalyst particle that was attributed to the differences of fracturing process depending on the brittleness of catalyst alloy.

The protium content of VGCFs was about 0.13 mass%H, measured by a Siverts-type apparatus at 298 K. The maximum protium content of VGCFs was also 0.13 mass%H, which was measured electrochemically. The equilibrium hydrogen pressure of gas-solid reaction was over 80 times higher than that of electrochemical reaction.

Acknowledgments

This work was partially supported by Grant-in-Aid for Scientific Research on Priority Area A of “New Protium
Function” from the Ministry of Education, Culture, Sports, Science and Technology.

REFERENCES