SYNTHESIS AND STRUCTURAL ANALYSES OF PLATELET CARBON NANOFIBERS COMPOSED OF TWIN-FLAT FIBRILS

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Introduction

The present authors have tried to prepare the carbon nanofiber (CNF) which has a homogeneous platelet structure from CO/H2 mixed gases using Fe-Mn alloyed catalysts, since Mn is efficient controller for CNF structure. A series of CNFs were produced over iron-manganese (Fe-Mn) alloy by varying the composition of manganese to iron. The preparation (reduction and synthesis reactions) temperature was also screened to examine its influences on the structure of CNFs in terms of diameter and shape, and hexagonal alignment of the fiber.

Experimental

1. Preparation of catalysts

Iron carbonate and stoichiometically prepared iron-manganese carbonates as the precursors of the catalysts in the present study were obtained from iron nitrate(Reagent grade, Fe(NO3)3・9H2O, Wako Pure Chemical Industries, Ltd.) and manganese nitrate (Mn(NO3)2 ・xH2O, Wako Pure Chemical Industries, Ltd.) in aqueous solutions through precipitation using ammonium bicarbonate according to Best and Russell [1]. The gases used in this work, hydrogen (99.999%), carbon monoxide (99.95%), and helium (99.99995%), were obtained from Asahi Sanso Co. in Japan, respectively, and used without any further purification.

2. Preparation of carbon nanofiber

CNF was prepared from the mixed gases of carbon monoxide and hydrogen on un-supported iron and iron-manganese (Fe-Mn) catalysts (Fe/Mn = 7/3 (wt/wt), 5/5 (wt/wt), and 3/7(wt/wt)), respectively, in the temperature range of 480 – 675 oC using a conventional horizontal tube furnace. 30 mg of ground catalyst was placed in a quartz boat at the center of the reactor tube in the furnace that had a length of effective zone of 100 mm. After catalyst reduction in 20-volume % hydrogen and 80-volume % of helium (H2/He = 20/80 (v/v)%, total 200sccm) mixtures for 2h at the desired reaction temperature, helium was flush through the reactor for 0.5 h. The reactant gases of carbon monoxide and hydrogen (CO/H2 = 4/1 (vol./ vol.), total flow rate = 200 sccm) mixtures were then allowed to flow over the catalyst for 1h. The total amount of carbon deposited for a fixed period on stream was determined gravimetrically after the reactor was cooled to ambient temperature.

3. Characterization of carbon nanofibers

The crystallographic data were collected with an X-ray diffractometer (Rigaku Geigerflex II, CuKα target, Rigaku (Tokyo, Japan)) and the crystallographic parameter (d002) was calculated according to the Gakushin (JSPS) method.

Multi-point Brunauer, Emmett, and Teller (BET) surface area was made measured using a surface area analyzer (SORPTOMATIC 1990, FISONS Instrument). Prior to this measurement, the samples were degassed at 150oC for 8 hrs.

The nanostructure and morphology of CNFs were examined using a high-resolution transmission electron microscope (JEOL JEM-2100F), Stereo TEM and high-resolution scanning electron microscope (JEOL JSM 6310F). Carbon nanofibers were dispersed in n-butanol under ultrasonic radiation to observe under TEM.

Results

Figure 1 shows SEM photographs of CNFs produced for CO/H2 mixture of 1/4 over Fe-Mn (7/3) catalyst in a temperature range of 500 to 675 oC.

CNFs produced over Fe/Mn (7/3) at 500 to 540 oC showed two diameters under 100 nm and 200 - 300 nm as Fe catalyst, respectively. Produced Platelet carbon nanofibers with larger diameters and tubular ones (white arrow marked) with smaller diameters appeared mixed at 500 - 540 oC. CNFs produced at 560 - 600 oC showed platelet alignment with large diameter of 100 - 300 nm and very few tubular CNFs of small diameter. CNFs produced at 620 oC and 630 oC showed homogeneous diameters of smaller size, carrying tubular alignment. CNFs produced at 675 oC showed some aggregates with thin tubular CNFs. Many catalysts were found deactivated.

Figure 2 shows TEM photographs of CNFs produced over Fe-Mn (3/7) catalyst at 540 oC and 630 oC. Well-developed tubular alignment was confirmed with both CNFs. The difference between CNFs produced at 540 oC and at 630 oC was found in the different size of their inner diameter and wall thickness of the tube. Their inner diameters were 10 and over 15 nm, respectively, while their wall thicknesses were around 8-10 nm and their different sizes were definite around 5 nm, respectively. Detailed TEM analysis of CNF produced at 540 oC confirmed that the fiber is composed of the special twin flat type fibrils (Figure 3).

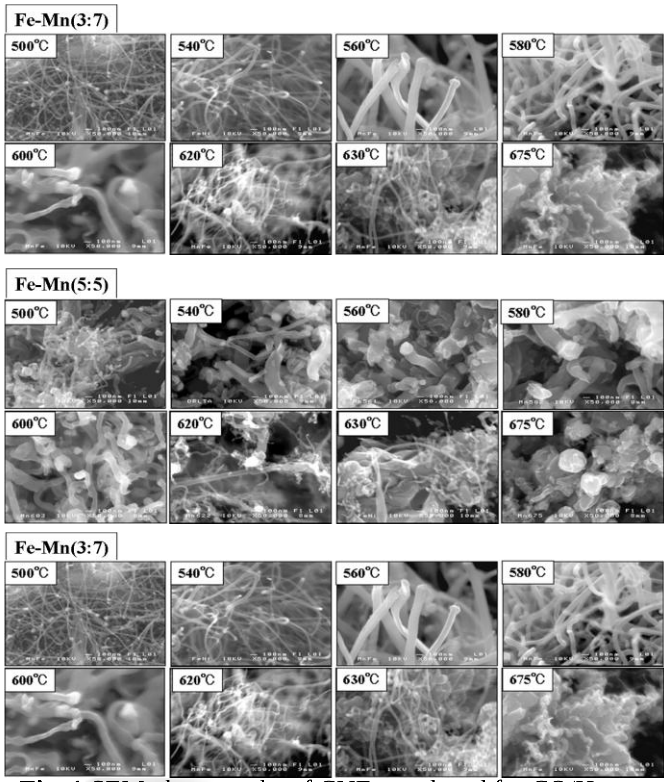

Fig. 1 SEM photographs of CNFs produced for CO/H_2 mixture of 1/4 over Fe-Mn (7/3) catalyst in a temperature range of 500 to 675 ^{o}C

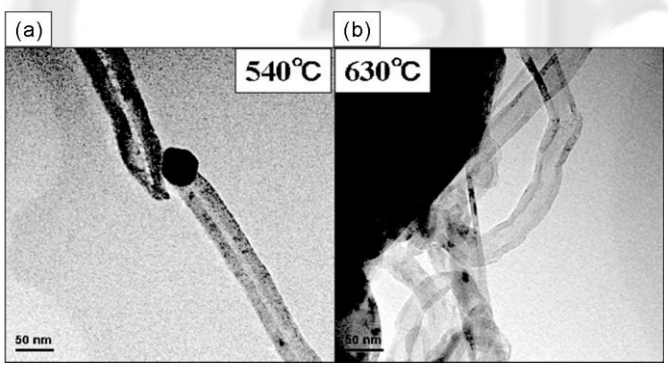

Fig. 2 TEM photographs of CNFs produced over Fe-Mn (3/7) catalyst at 540 ^{o}C and 630 ^{o}C.

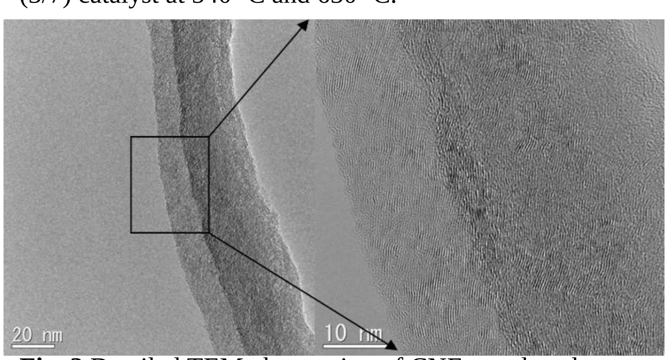

Fig. 3 Detailed TEM observation of CNFs produced over Fe-Mn (3/7) catalyst at 540 ^{o}C

Discussion

The present study confirmed that the bulk Fe-Mn catalyst was segregated into fine particles according to the temperature of reduction, conditioning and fiber growth to provide CNFs of which diameter was subjective to that of segregated particles. Such a segregation leads to the fine particles appears common to the metals and alloys as the catalyst for CNF synthesis. At the low temperature of 540 oC, Mn can contribute to segregate Fe particle to twin pieces and to produce the PCNF which is composed of twin-flat type fibrils.

The unique feature of the present particular alloy catalyst is the production of tubular type of CNF at temperature as low as 500 oC up to 675 oC, while the graphitization extent of the CNF was slightly inferior to that of CNFs prepared on Fe and Fe-Ni at a slightly higher temperature. Very uniform diameter of CNT produced at 500-540 oC over Fe-Mn (3/7) must be also noted.

Acknowledgement

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