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Vapor-grown carbon nanofibers synthesized from a Fe_2O_3–Al_2O_3 composite catalyst

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Abstract

Vapor-grown carbon nanofibers (CNFs) were synthesized from a Fe_2O_3-Al_2O_3 composite ceramic catalyst. It was revealed that the CNF constructions and structures depended on the catalyst phase. Fe_2O_3 solid solution and $FeAlO_3$ catalysts synthesized fine CNFs with diameter of 10–15 nm. These CNF structures were similar to those of MW-CNTs. Notably, the $FeAlO_3$ catalyst could synthesize aligned CNF structures. The secondary phase precipitated from $FeAlO_3$ in the specific crystal direction and this precipitation induced the cleavage fracture of $FeAlO_3$ grain during CNF synthesis. As a result, CNFs grew on the specific plane and aligned in one direction.

Keywords: Al_2O_3; Carbon; Ferrite; Catalysts; Nanocomposites; Fibres

1. Introduction

Carbon nanotubes (CNTs)[1] are expected to have unusual properties respecting electrical conductivity,[2] electrochemical property[3] and mechanical characteristics.[4] Many applications are being developed for field emission display, electrodes of secondary battery and reinforcement of materials. Most of these applications will require a fabrication method capable of producing uniform CNTs/carbon nanofibers (CNFs)[5] with well-defined and controllable properties reproducibly. In particular, field emitters would need high-density, well-ordered and aligned CNTs/CNFs. Many synthesis processes have been attempted in order to fabricate aligned CNT/CNF structure and this structure is obtained by using chemical vapor deposition[6] with catalysts embedded in zeolite[7]/mesoporous silica,[8] a hexagonal close-packed nanochemical alumina template method[9] or sol-gel methods.[10]

We have investigated the synthesis of nanocatalyst particle from metal-oxide composite ceramics by the selective reduction method.[11] It was confirmed that many catalyst particles of differing size and morphology were formed from different phases. In this study, we selected the Fe_2O_3–Al_2O_3 system that has 3 phases (Fig. 1)—Fe_2O_3 solid solution, Al_2O_3 solid solution and high-temperature phase $FeAlO_3$[12]—and investigated the influence of the phase difference on CNF structure and construction and the possibility of synthesizing aligned CNF structure.

2. Experimental

2.1. Synthesis of catalyst particles

Fe_2O_3 (Kojundo Chemical) and Al_2O_3 (AKP-53, Sumitomo Chemical) were mixed to synthesize three phases (Fe_2O_3 s.s., Al_2O_3 s.s. and $FeAlO_3$) and shaped into discs with diameters of 40 mm. These discs were sintered at 1400 °C for 10 h in air. Sintered discs were analyzed by the XRD method and synthesis of objective phases was confirmed.

These compounds were put on a SiO_2 boat and inserted in a furnace with controlled atmosphere. Catalyst particles were reduced selectively from compounds under H_2 flow (1 l/min) for 5 min or 1 h at 600 °C.

2.2. Synthesis of CNFs

After selective reduction of catalyst particles, CNFs were synthesized continuously under C_2H_4 flow (0.3 l/min) and H_2 flow (1 l/min) for 2 h at 600 °C. Synthesized CNF structure and construction were analyzed by SEM, TEM and EDS. Some CNFs

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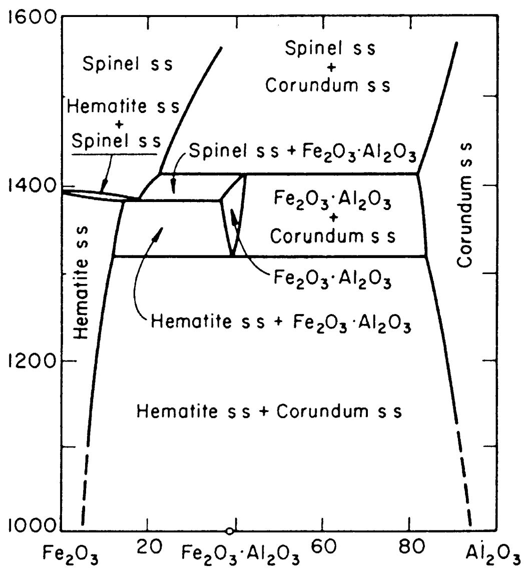


Fig. 1. Phase diagram of the Fe_2O_3–Al_2O_3 system.[12]

were observed for 18 min in order to analyze the growth process.

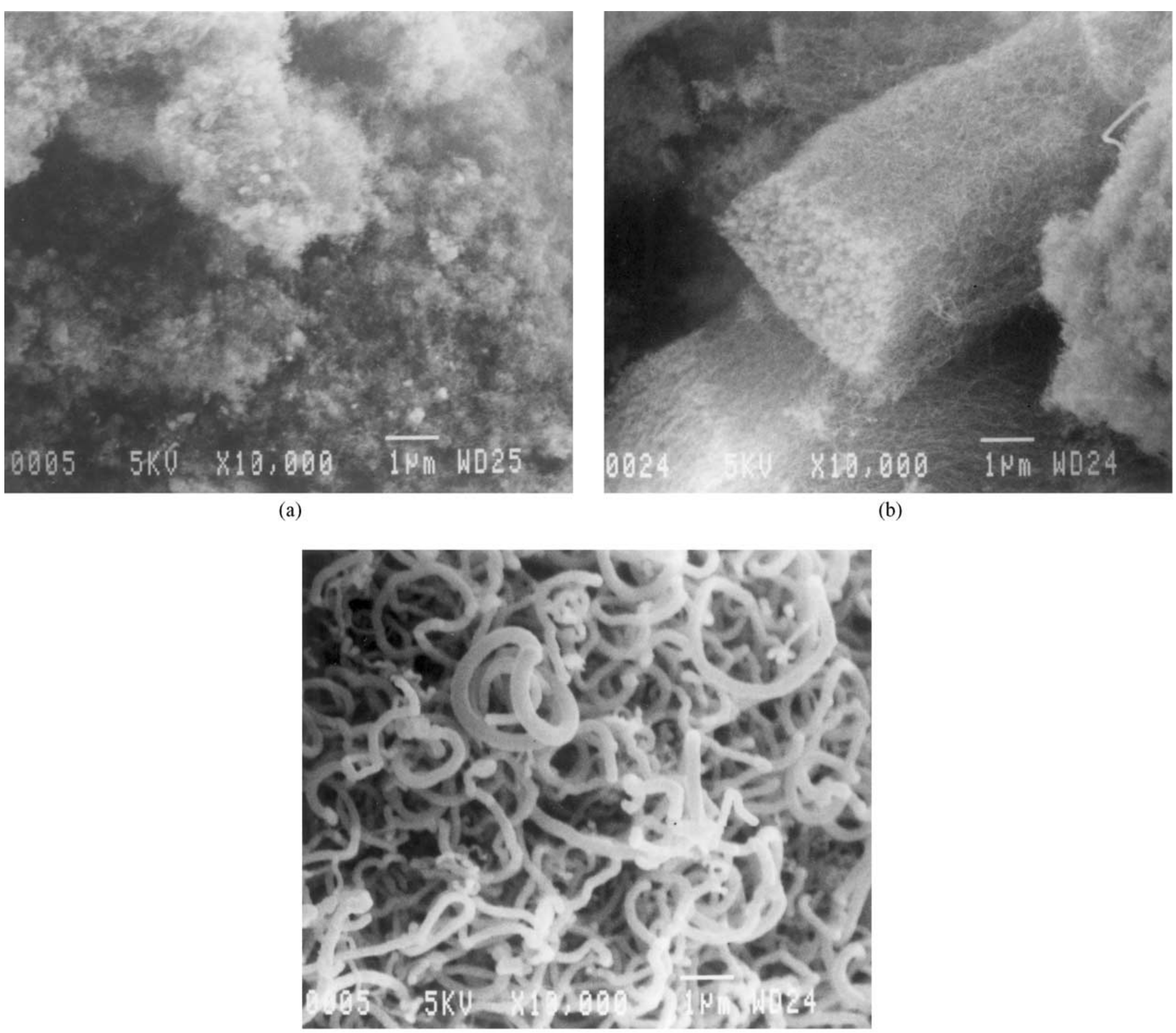
2.3. Analysis of catalyst and compound

CNFs were synthesized from three compounds. $FeAlO_3$ that synthesized a unique CNF structure was analyzed by HRTEM and EDS in order to investigate constructional and compositional change at every step.

3. Results and discussion

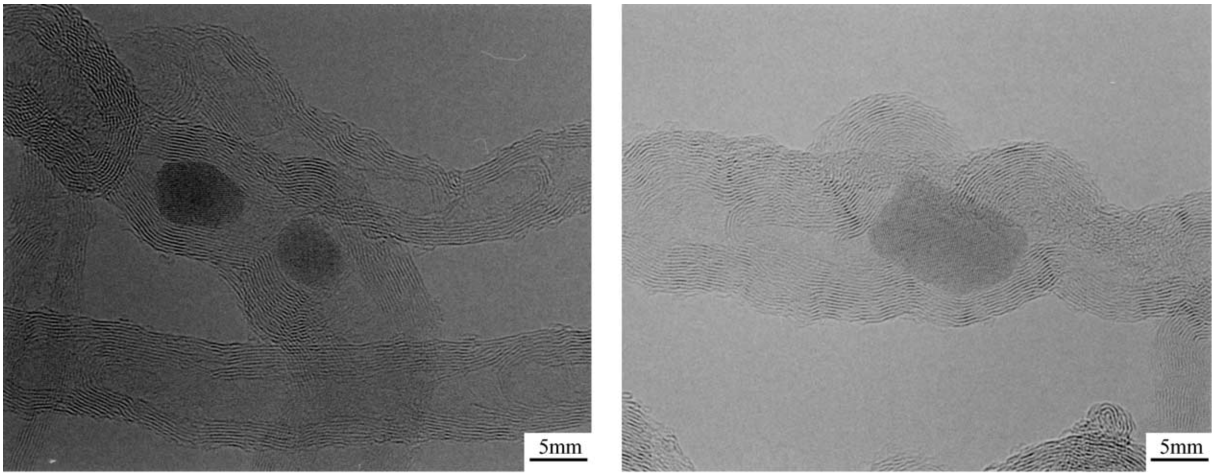
3.1. CNF structures synthesized from three phases

CNF structures synthesized from the three phases are shown in Fig. 2. Depending on the phase, different CNF constructions and structures were synthesized. From



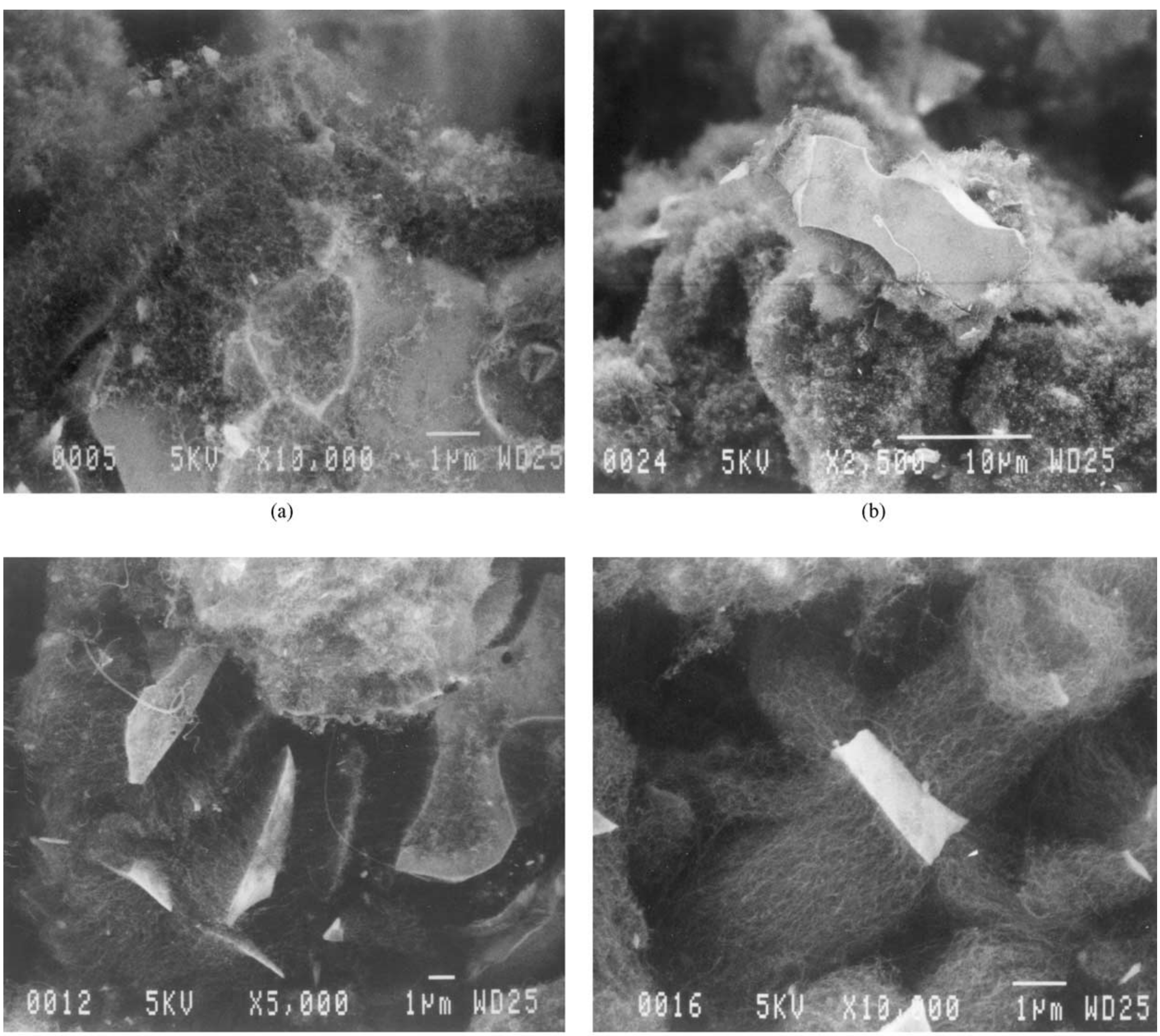
(a) (b) (c)

Fig. 2. CNF structures synthesised from three phases (a) Fe_2O_3 s.s., (b)$FeAlO_3$, (c)Al_2O_3 s.s.



(a) (b)

Fig. 3. HRTEM images of CNFs (a)Fe_2O_3 s.s., (b)$FeAlO_3$.



(a) (b)

(c) (d)

Fig. 4. CNF growth process synthesised from $FeAlO_3$ (a) 5, (b) 8, (c) 12, (d) 18 min.

Fe_2O_3 s.s. and $FeAlO_3$, CNFs with diameters of 15–20 nm were synthesized. In particular, high-density, well-ordered and aligned CNF arrays were synthesized from $FeAlO_3$. From Al_2O_3 s.s., CNFs with diameters of 200–400 nm were synthesized and their growth direction was random.

HRTEM images of CNFs synthesized from Fe_2O_3 s.s. and $FeAlO_3$ are shown in Fig. 3. Those CNF constructions were similar to multi-wall CNTs. In both images, the catalyst particles observed in the hollow were recognized to be fine Fe particles from their lattice factors and the results of composition analysis by EDS.

It is obvious that different phases synthesized different CNF constructions and structures. In particular $FeAlO_3$ synthesized uniformly aligned CNF arrays which are required for many applications. The observed catalyst particles were composed of only Fe. This means that catalyst composition does not influence the formation of aligned CNFs.

3.2. Formation process of aligned CNFs

The formation process of aligned CNFs from $FeAlO_3$ was examined. Fig. 4 shows the CNF structure for various periods of time. After 5 min from starting CNF synthesis, growth of fine CNF structure on the entire surface was observed. At this point, CNF growth direction was random and aligned CNFs were not observed. After 8 min, intergranuler fracture of $FeAlO_3$ was partially observed but aligned CNFs were not observed. After 12 min, cleavage fractures at specific planes were observed. After 18 min, formation of aligned CNFs at cleavage plane was observed.

Aligned CNFs only grew at the cleavage plane that formed after a while. Catalyst particles formed at the same time on the cleavage plane, and so crystallinity of these catalyst particles became uniform. It is assumed that catalyst uniformity caused formation of aligned CNF structure.

3.3. Structural change of $FeAlO_3$

As shown in Fig. 1, $FeAlO_3$ was stable at high temperature. The cause of cleavage fracture was investigated to ascertain whether $FeAlO_3$ was high-temperature phase or CNF growth induced this cleavage.

Fig. 5 shows TEM images of sintered $FeAlO_3$. Although many dislocations were observed in these grains, the grains were single phase. TEM observation of the structure of $FeAlO_3$ immediately after reduction revealed no change in the structure.

$FeAlO_3$ structure after aligned CNF synthesis is shown in Fig. 6. Its structure was different from that

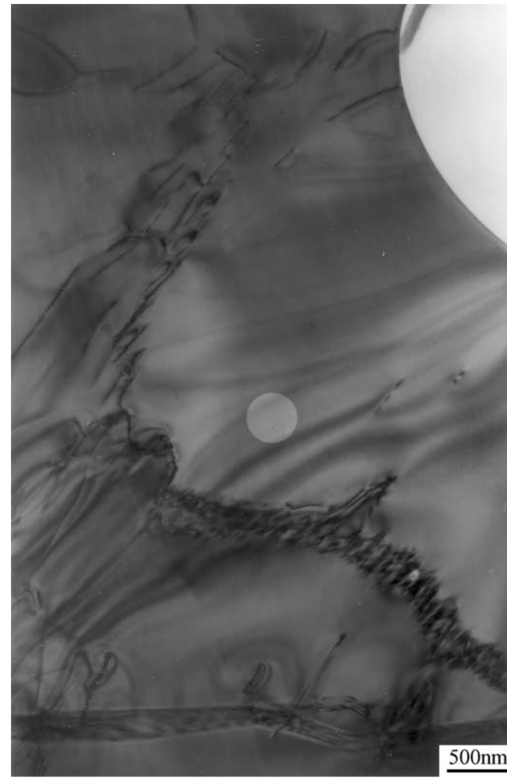


Fig. 5. TEM image of sintered $FeAlO_3$.

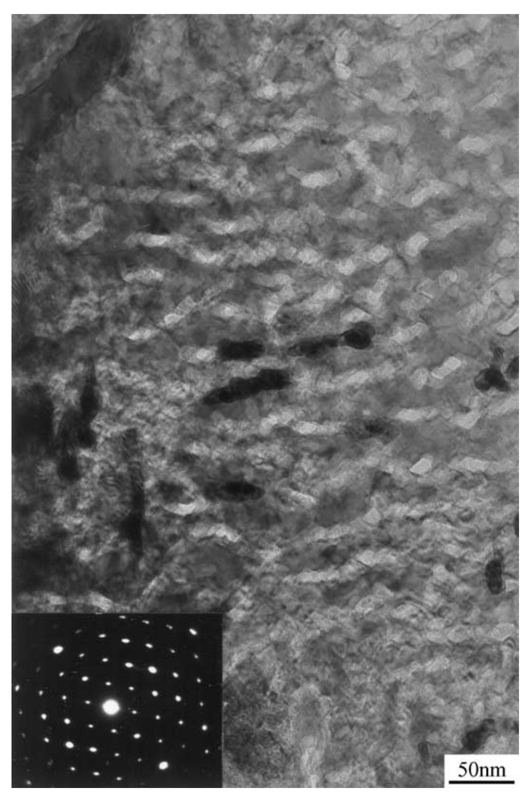


Fig. 6. TEM image and diffraction pattern of $FeAlO_3$ after synthesis of aligned CNfs.

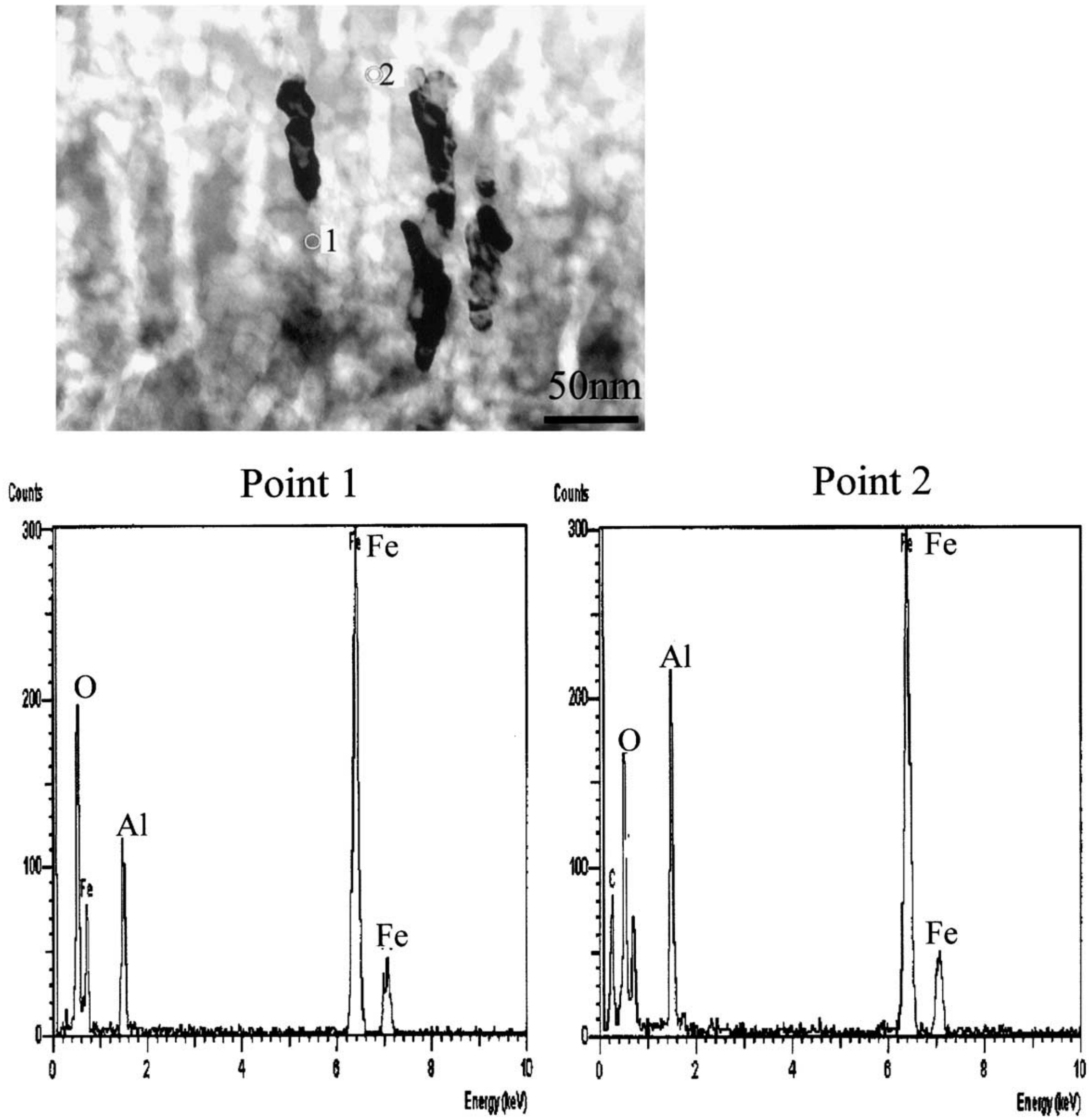


Fig. 7. TEM-EDS analysis of $FeAlO_3$ after synthesis of aligned CNFs.

shown in Fig. 5. Secondary phase precipitated in $FeAlO_3$ matrix. In this TEM observation, the diffraction pattern only indicated $FeAlO_3$. This means that secondary phase was amorphous. As shown in Fig. 7, EDS analysis revealed that secondary phase was richer in Al than was matrix. It is confirmed by HRTEM observation that secondary phase precipitated on the (111) plane of $FeAlO_3$ (Fig. 8).

It is estimated that Fe was consumed by the CNF growth and Fe in $FeAlO_3$ was exhausted. This induced the precipitation. Secondary phase was assumed Al_2O_3 and lattice image showed this phase precipitated on the (111) plane preferentially. It is assumed that this precipitation plane (111) became the cleavage plane. On the cleavage plane, catalyst particles would grow in the same time and condition, causing particle properties to become homogeneous. Consequently aligned CNF structure was formed.

4. Conclusion

We selected the Fe_2O_3–Al_2O_3 system that has three phases and investigated the influence of the phase difference on CNF structure and construction and the possibility of synthesizing aligned CNF structure.

Depending on the phase, different CNF constructions and structures were synthesized. In particular, in the case that the catalyst used is $FeAlO_3$, aligned CNF structure was synthesized. These CNFs were 15–20 nm in diameter and constructions were similar to those of multi-wall CNTs. Formation of this

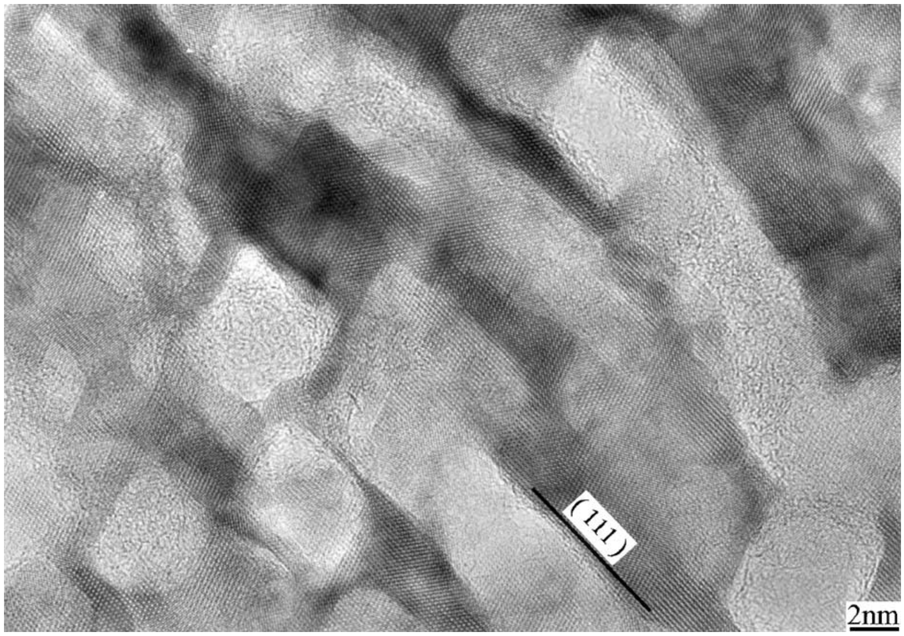


Fig. 8. Lattice image of $FeAlO_3$ after synthesis of aligned CNFs.

aligned CNF structure was attributable to the following. Because Fe was consumed in formation of catalyst particles, $FeAlO_3$ concentration became Fe poor. This induced Al_2O_3 precipitation as a secondary phase on $FeAlO_3$ (111) plane predominately. These precipitation planes became the cleavage plane. On this cleavage plane, Fe catalyst particles formed at the same time and condition, causing the catalyst particle's properties to become homogeneous and CNFs to grow in one direction. As a result, aligned CNF structure was formed.

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