HITACHI SCIENTIFIC INSTRUMENT TECHNICAL DATA

TEM

SHEET NO. 112

SUBJECT: HIGH RESOLUTION ELECTRON MICROSCOPY OF CARBON NANO-TUBE AT ROOM AND HIGH TEMPERATURES

INSTRUMENT: HF-2200 COLD FE TRANSMISSION ELECTRON MICROSCOPE AND DIRECT SPECIMEN HEATING SYSTEM

CONTENTS

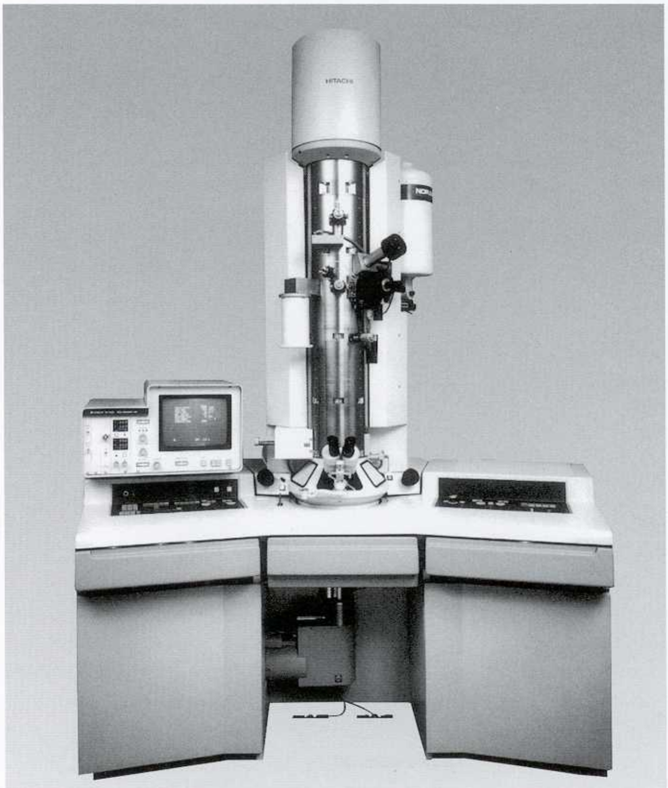

Fig. 1 A general view of the HF-2200 cold FE transmission electron microscope

1. INTRODUCTION

Carbon nano-tubes[1] were discovered in 1991. These tubes are in the form of a filament and different from normal materials in size and structure. They were assumed to have unique characteristics. Extensive research on this material has been made in various fields, specifically in terms of material characterization and manufacturing techniques[2, 3]. Practical use of carbon nano-tubes is also in progress. An electron source for a field emission display device is one of such examples[4]. An electronic device of nano-scale may be a possibility in the future.

Electron microscopes have been used for studying the structures of carbon nano-tubes. Some scum has been found on the surfaces of nano-tubes which may have adhered in the manufacturing process. We have observed carbon nano-tubes at room temperature and studied changes in the structures at various electron doses. We have also observed nano-tubes at high temperatures by heating them in the specimen chamber and studied changes in the structures, as we know that carbons and their compound materials are stable at high temperatures. We report on the details here.

2. METHOD

2.1 Instrumentation

We have used the HF-2200 cold FE transmission electron microscope. Fig. 1 shows a general view of the HF-2200. For specimen heating, we have used a direct specimen heating holder.

Fig. 2 shows the tip of the specimen holder. Fig. 3 shows the direction of Lorentz force (F) generated by the specimen heating current (I) in the magnetic lines of force (H) of the objective lens. The specimen heater expands horizontally at high temperatures. The thermal expansion of the heater, therefore, does not cause change of focus by Lorentz force. This arrangement allows stable observation without causing shift of focus nor change of magnifications during specimen heating.

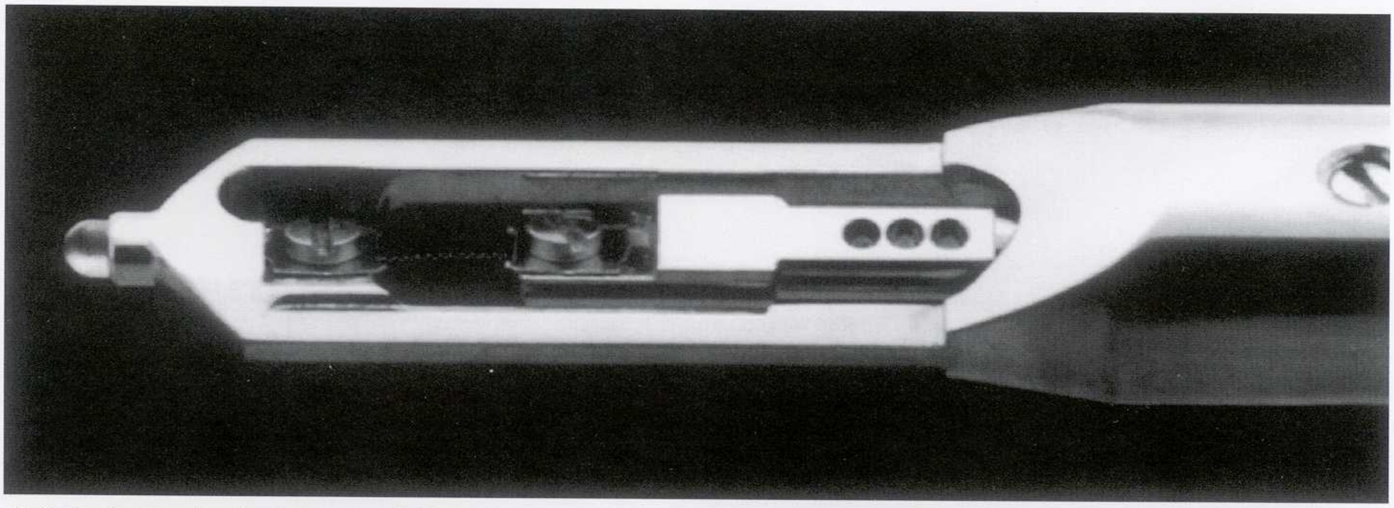

Fig. 2 The tip of the direct heating specimen holder

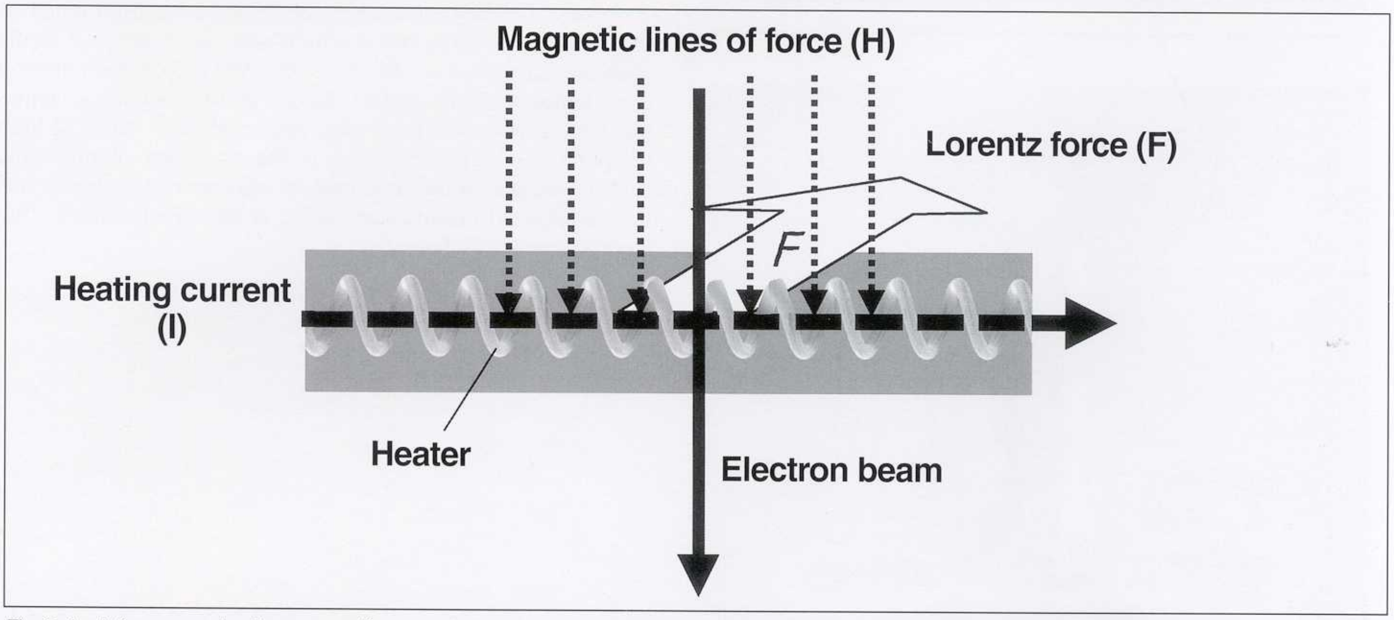

Fig. 3 A relation among heating current (I), magnetic lines of force (H) and Lorentz force (F)

2.2 Observation conditions

We have observed changes in the structures of carbon nanotubes under various electron doses at 200 kV and at room temperature. Observations were made right after the electron dose, 10 minutes after and 50 minutes after respectively.

At high temperatures, observations were made at 550°C, 1,000°C, and 650°C. After the observation at 1,000°C, the temperature was raised to 1,200°C and then lowered to 650°C. Fig. 4 shows a timetable for specimen heating. Note that microscope images were recorded at a (before heating, room temperature), b (20 minutes after heating, temperature 1,000°C), and c (140 minutes after heating, temperature 650°C) respectively. All images were recorded at a direct magnification of ×300,000.

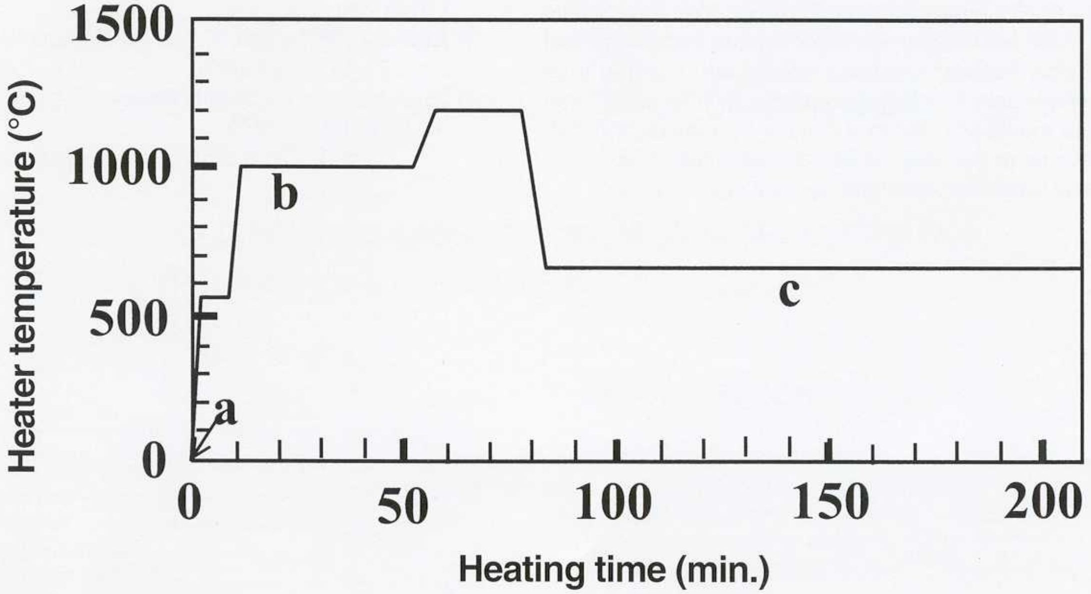

Fig. 4 A relation between heating time and heater temperature

3. OBSERVATION RESULTS

3.1 Structure changes under various electron doses at room temperature

Fig. 5 is observation results showing changes of nano-tube structures under various electron irradiation times (a: right after irradiation, b: 10 minutes after, c: 50 minutes after). The total electron dose on the specimen is about 9.5×10^5e/nm^2 for a, about 1.1×10^8e/nm^2 for b, and about 5.7×10^9e/nm^2 for c respectively.

Fig. 5a, which was recorded right after electron irradiation, tells us that the specimen is a multiwalled carbon nano-tube (MWNT). It has the structure of a number of graphite sheets uniformly overlapped. We can see some scum on the surface of nano-tube which may have adhered during the growing process. Fig. 5b, which was recorded 10 minutes after the irradiation, shows that the multiwalled structure has changed into a rounded structure including the tip of the tube. Fig. 5c, which was recorded 50 minutes after the irradiation, indicates an amorphous structure overall making the central area difficult to tell from the multiwall area. These results show that carbon nano-tubes are sensitive to electron beam irradiation and that their structures change in about 10 minutes of normal observation in the microscope.

3.2 Structure changes by heating

Fig. 6 (a ~ c) show structure changes of carbon nano-tubes by heating. The specimen was raised from room temperature to about 1,000°C and then lowered to about 660°C for observation. Fig. 6 (a) shows a TEM image recorded at room temperature (point a in Fig. 4). The total electron dose on the specimen was 7.2×10^5e/nm^2. The specimen was the same MWNT. Some scum was seen on the surface of the nano-tube. Similar scum was seen spreading on the central area. We can see that the nano-tube was covered by scum. Fig. 6 (b) is another TEM image recorded 20 minutes after heating. It was recorded at about 1,000°C while heating. The total electron dose on the specimen was 1.7×10^8e/nm^2.

Fig. 6 (c) is another TEM image recorded at about 660°C, which was achieved after reaching at about 1,200°C or 140 minutes after the heating. The total electron dose on the specimen was 1.2×10^9e/nm^2. Notice the area shown by arrow 1. As the specimen heating proceeds, a space closed by walls which was seen in Fig. 6 (a) changed like a straight line and one additional graphite sheet is formed. Notice the area shown by arrow 2. The scum disappears as the specimen heating continues and clean surfaces have been formed. Arrow 3 shows that the scum was rearranged and a sheet was formed.

Fig. 5 shows that at room temperature, crystals are decreased as electron irradiation is increased. Fig. 6, on the contrary, shows that by heating the nano-tube, scum on the surface is rearranged and forms crystals.

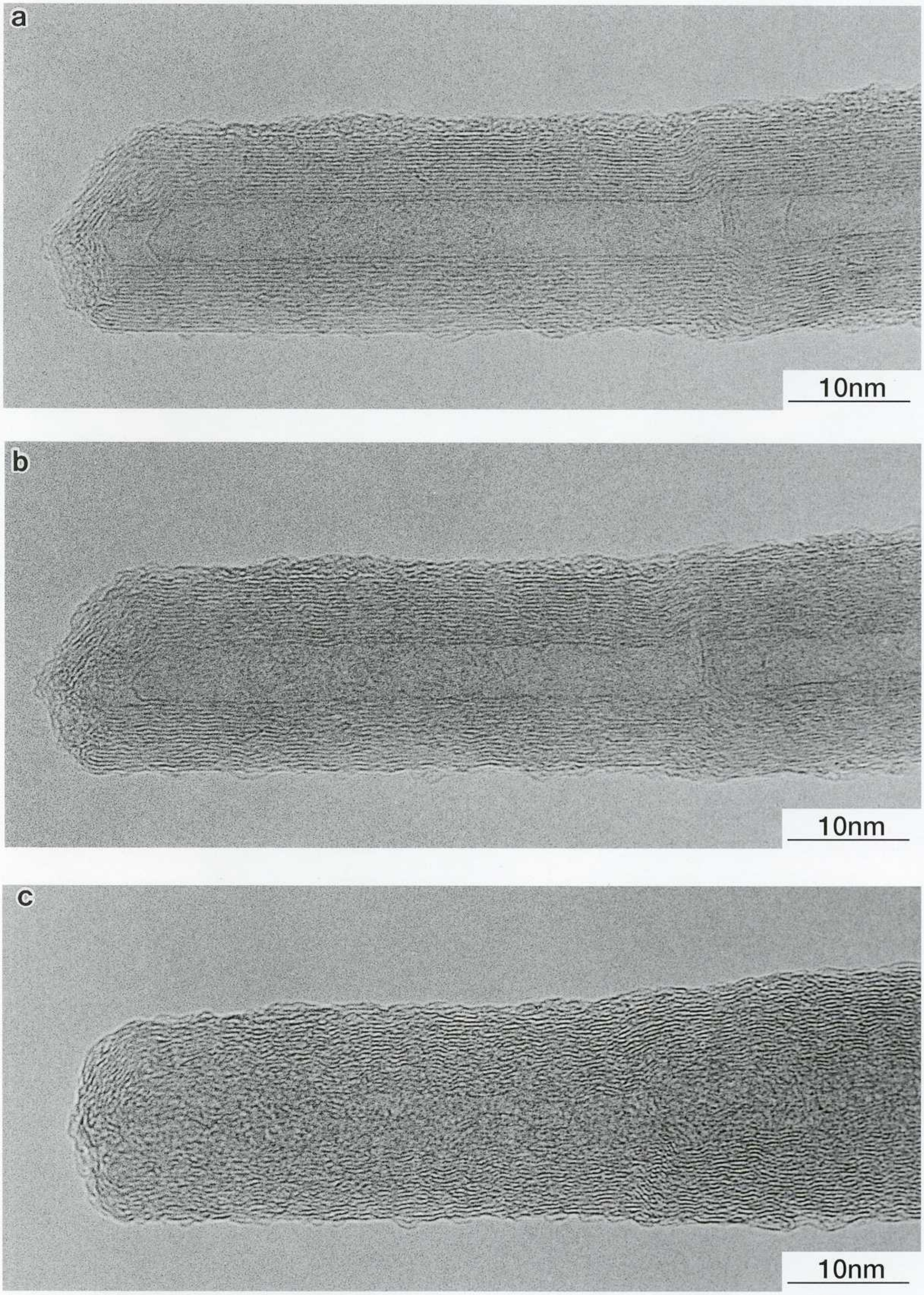

Fig. 5 Structure changes of carbon nano-tube under electron beam irradiation at room temperature
Accelerating voltage: 200 kV
Direct magnification: ×300,000

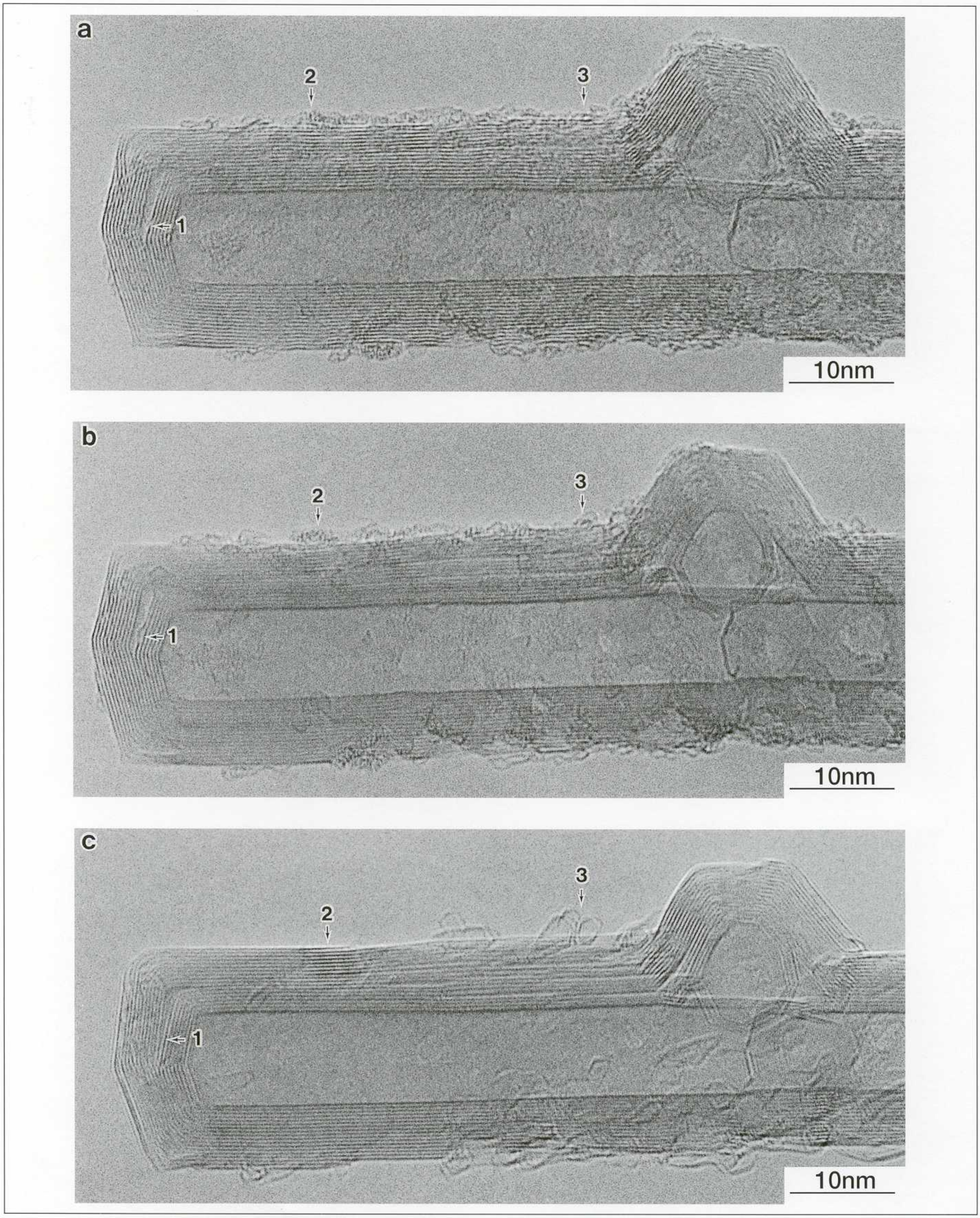

Fig. 6 Structure changes of carbon nano-tube under heating
Accelerating voltage: 200 kV
Direct magnification: ×300,000

(a) Room temperature
(b) Heater temperature: About 1,000°C
(c) Heater temperature: About 600°C

4. CLOSING

We have introduced structure changes of carbon nano-tubes by electron beam irradiation and by heating in the specimen chamber of a transmission electron microscope. We have shown that the HF-2200 cold FE transmission electron microscope and Hitachi's direct heating specimen holder allow stable high resolution observation of carbon nano-tubes which are sensitive to electron beam irradiation. We trust that our instruments will play an important role in the study of carbon nano-tubes which have many potential capabilities for future applications.

5. REFERENCES

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