Synthesis of Ni_3C Nano-whisker from $NiSO_4$ and Sucrose by Means of Spray Pyrolysis

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(Received December 15, 2006; CL-061472; E-mail: takita@cc.oita-u.ac.jp)

Ni particles and Ni_3C whiskers with a novel morphology, grew on the Ni–carbon composite by heat treatment at 1073 K in Ar. Ni–carbon composites were prepared by spray pyrolysis of a solution of sucrose and $NiSO_4$ in Ar at 1073 K.

Formation of Ni_3C have been reported in various situations such as alloy formation[1] and diamond synthesis,[2] and some investigations of their physical properties were reported.[3,4] Formation of Ni_3C appeared in many catalytic reactions using Ni metal such as the formation of symmetric helical carbon filaments from Ni–Cu/MgO-catalyzed 1,3-butadiene decomposition,[5] Fischer–Tropsch reaction over Ni/SiO_2,[6] production of methane from a mixture of CO and H_2 over Ni(111) surface,[7] partial oxidation of methane to synthesis gas over Ni/La_2O_3 and Ni/Al_2O_3 catalysts,[8] hydrogen treatment of Ni/SiO_2 thin films prepared from the deposition of carbon from acetylene,[9] and the hydrodehalogenation of CCl_2F_2 and $CHClF_2$ over $Ni–Al_2O_3$ catalyst supported on activated carbon.[10] However, no formation of single crystal of Ni_3C has been reported so far.

We have studied the spray pyrolysis of a solution composed of sucrose in the presence of nickel salts at 873–1173 K in an inert gas flow and reported novel methods of the synthesis of a kind of Hofmann complex, $Ni(CN)_2(NH_3)\cdot0.25H_2O$ and carbon–Ni composites with several different shapes such as spheres, broken spheres, and sheets.[11,12] Hofmann complex crystals of rectangular body were formed at 973 and 1073 K. Carbon–Ni composites are composed of amorphous carbon and mainly Ni metal. No product was obtained by the spray decomposition of Ni-free sucrose and spheres of NiO were obtained from sucrose free $Ni(NO_3)_2$ solution. Therefore, $Ni(NO_3)_2$ catalyzed the formation of $Ni(CN)_2(NH_3)\cdot0.25H_2O$ and carbon–Ni composites. Spherical Ni–carbon composite was obtained from a solution composed of $Ni(CH_3COO)_2$ and sucrose at 973–1073 K. When the concentration of $Ni(CH_3COO)_2$ was much high as 0.50 M, formation of CNT on the small composite less than 1 µm in diameter was observed at 1073 K. In case of 0.005 M $NiSO_4$, genuine spherical Ni–carbon composites were obtained at 873–973 K. The optimum temperature for CNT formation depended on the concentration of $NiSO_4$; 973 K for low $NiSO_4$ concentration (0.005 M) and 1073 K for high $NiSO_4$ concentration (0.05 M). Ni particles with 7–17 nm were well dispersed in the obtained Ni–carbon composite. In the spray pyrolysis of solutions containing sucrose and metal salts, cubic crystal of $Co_2(CN)_5(NH_3)$ was obtained from only a solution of $Co(NO_3)_2$ and sucrose at 1073 K. Amorphous carbon–Co metal composites or carbon–Fe oxide composites were obtained from solutions of sucrose and Co or Fe salts such as acetate, sulfate, and chloride. The shapes of major products were spheres that have filled or egg shell structures and particles of broken large spheres. Small particles of Co metal with 7–22 nm or Fe_3O_4 with 6–22 nm were well dispersed in the formed spheres. In this way, spray pyrolysis of sucrose and metal salts is a novel, safe, and easy method of the synthesis of carbon–metal composites. Since these composite was composed of amorphous carbon, electro conductivity seems to be small.

When post treating of these composites was carried out in Ar flow, particles of Ni metals and fibers of Ni_3C were formed on the spheres. We report these novel composites for practical utilization.

Sucrose (Wako pure chem., reagent grade) and nickel salts (Wako, Pure grade) were used. An aqueous solution containing sucrose and $NiSO_4$ was fed by a spray into a reactor made of stainless steel with 10 cm in diameter. Feed rates of the liquid and Ar as a carrier gas were 300 cm^3/h and 3 L/h, respectively. A schematic diagram of the reaction system appears elsewhere.[11] The length of an electric heater for reaction chamber was 40 cm. The product was collected by a water trap. The recovered water, containing products, was filtered, washed with pure water and dried at 343 K for one night. The sample was treated at 1073 K in an Ar flow. Then, the products were supplied to analysis by XRD, TG-DTA, and SEM and TEM observations.

The products from a solution of 0.05 M $NiSO_4$ and 0.50 M sucrose at 1073 K were composed of veritable and slightly distorted spheres of 1–15 µm in diameter. Amount of non uniform particles was very small. According to TEM observation of sphere of 400 nm in size, 6–12 nm Ni particles were well dispersed in the spheres. SEM observation showed that there are many white spots of 28–40 nm on the surface. These sizes are somewhat larger than that of Ni particles observed by

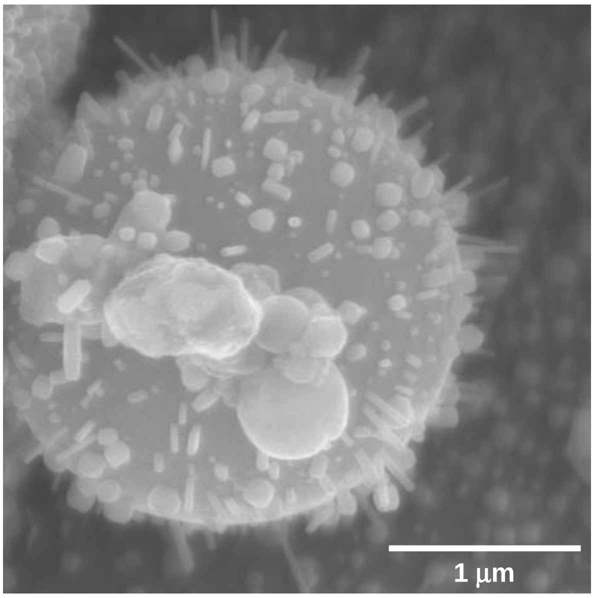

Figure 1. SEM image of the Ni–carbon composite after heat treatment at 1073 K for 3 h.

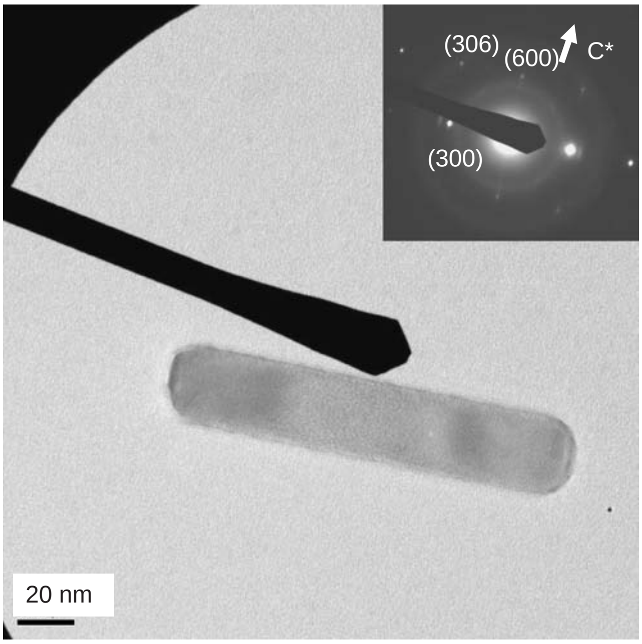

Figure 2. TEM image and electron diffraction pattern of the Ni_3C fiber.

TEM, so that it is not clear whether these spots show Ni particles or not.

Heat treatment of this sample was carried out in Ar flow at 1073 K. Many small particles of 140–180 nm in diameter and fibers of about 100 nm ϕ and less than 800 nm length were formed on the surface of the sample after heat treatment for 5 min. SEM image of the Ni–carbon composite after heat treatment for 1 h is shown in Figure 1. Both products grew up after 1 h and the size of particles was 250–400 nm and the size of fibers was 100–150 nm ϕ and 1.5 μm in length.

The sizes of the products seemed to be unchanged after heat treatment for 1 h. TEM observation revealed that particles are shaped to hexagonal prism. Both ends of fibers are round and shape is filled column because the sizes are uniform and center of the column is slightly darker than both sides. Identification of both products was carried out using electron diffraction method (Figure 2). Particle gave Debye–Scherrer rings corresponding to Ni metal and the fiber gave clear diffraction electron diffraction pattern coincided to Ni_3C crystal, so it is clear that the fiber is single crystal of Ni_3C.

Diffraction peaks due to Ni metal was obtained but no diffraction peaks due to Ni_3C was observed by XRD.

Therefore, Ni atoms in the subsurface layers of composite may be moved to surface to form Ni particles and Ni_3C fibers.

It is noteworthy that no Ni_3C whiskers grew from Ni particles; both products were present on the surface separately. In the observation by TEM, Ni_3C whiskers seem to be grown from shallow inside the composite spheres. And there are no metal particles around them. On the surface of the sample treated for 3 h, no hole from which Ni_3C whisker was withdrawn was observed. This may suggest that Ni_3C whisker grew up by root growth mechanism and growing centre may be present on the interface of Ni_3C and composite materials at shallow subsurface of composite spheres. All of the whisker particles have narrowly distributed diameters and the diameter of one Ni_3C whisker was uniform.

The formation of Ni_3C whiskers is observed not always on all spheres, so that whiskers may be formed on the Ni rich composite spheres.

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