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The oxidation behaviour of Ni nanoparticles at temperatures from 573 to 673 K and the formation process of hollow oxide particles were studied by transmission electron microscopy. In the course of oxidation, a single large void was observed at one site of the interface between inner Ni and outer NiO layer due to the vacancy clustering which occurs during the oxidation process resulting from the rapid outward diffusion of Ni ions through the NiO layer. This suggests that supersaturated vacancies generated at the interface migrate to the site over a long-range distance and aggregate at the site. Ni nanoparticles were fully oxidized to become hollow NiO, in which nano-holes in the form of vacancy clusters were located at the off-centred positions. The de-centring of the voids in hollow NiO is probably due to the large mobility of vacancies inside Ni during oxidation.

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1. Introduction

In recent years, Considerable effort has been put into the design and fabrication of nano-structured materials with functional properties. It is important to obtain nanoparticles with a specific size and morphology, taking into consideration their specific applications. Therefore, the control of the shape of nanoparticles is one of the most important objectives in the current research on nanomaterials [1]. In particular, there is an increasing interest in methods to fabricate hollow nanostructures because their unique shape gives them the potential to be used as delivery vehicle systems as well as fillers and catalysts, and could bring about changes in chemical, physical, and catalytic properties [2-4]. Various methods to fabricate hollow spheres have been developed [4-7] ,and also theoretical analyses on the stability of hollow spheres have also been carried out [8-10].

Recently, it has been reported by Yin *et al*. that when isolated nanocrystals of cobalt are exposed to sulfur or oxygen at relatively low temperatures near 400 K, the initial solid nanocrystals turn to hollow spheres of cobalt sulfides or cobalt oxides [11,12]. They concluded that the hollow spheres are formed by the mechanism analogous to the Kirkendall effect [13]; a nano-hole in the centre of a hollow particle results from the generation and aggregation of vacancies due to different mobilities of ions moving in and out of the metal particles. Their results suggest that the control of atomic diffusion and vacancy clustering is very important for the fabrication of nano-scaled hollow structures. After their work, the formation of hollow oxide nanoparticles through the oxidation of several metal nanoparticles such as Fe [14], Zn [15], Cu and Al [16] was confirmed. Up to now, it has been commonly recognized that hollow oxide nanoparticles can be formed when the growth of the oxide layer on a metal surface is dominated

by the outward diffusion of the metal ions through a thin oxide layer; metal ions diffuse much faster than oxygen ions in the oxides [16]. In order to establish the principle of the formation mechanism of hollow oxides, further experimental research on the oxidation of metal nanoparticles is required. Since the self-diffusion coefficient of Ni [17] is much higher than that of oxygen [18] in NiO, Ni nanoparticles are expected to turn into hollow oxide through an oxidation reaction. In the present work, therefore, the oxidation behaviour of Ni nanoparticles and the formation process of hollow structures are investigated by transmission electron microscopy (TEM). This work is a part of a series of systematic studies on the formation of hollow oxides using metal oxidation reactions our group is carrying out.

2. Experimental procedure

The Ni nanoparticles were prepared by electron-beam deposition in a high-vacuum chamber with a base pressure of approximately 1×10^{-5} Pa. An amorphous carbon film or an amorphous Al-oxide film on a Pt grid with ϕ 3mm for TEM observation was used as the supporting film (substrate) for the Ni nanoparticles. The distance between the Ni (99.99%) source and the substrate was set to approximately 250 mm, and a quartz thickness monitor was attached between the source and the substrate in order to control the deposition rate and average thickness. The substrate was baked at 1000 K for 300 s prior to evaporation. Ni nanoparticles were deposited onto the substrate kept at 900~950 K with a rate of 0.05-0.10 nmmin^{-1}. After deposition, the Ni nanoparticles on the substrate were exposed to air and then annealed in an electric furnace at 573 and 673 K for a given time in air. Changes in the morphology of the Ni nanoparticles associated with oxidation were observed by Hitachi H-800 type TEM operating at 200 kV. Additionally, the surface of the oxidized Ni nanoparticles was observed by

field-emission type scanning electron microcopy (FE-SEM, Hitachi S-5200) operating at 30 kV.

3. Results and discussion

Figure 1 shows bright field images of the morphology change of Ni nanoparticles (a) before and (b) after oxidation at 573 K for (b) 30, (c) 60 and (d) 120 min. The diameter of the particles before oxidation was in the range between 30 and 70 nm. At the early stage of oxidation for (b) 30 min, the Ni nanoparticles (the inner dark part) are surrounded by the oxide layers (the outer bright part) of about 5~10 nm in thickness. It can be seen that voids are formed along the interface between the Ni and oxide layer as indicated by arrows. The formation behaviour of the voids observed in figure 1 (b) is similar to that observed in the oxidation of Zn [15] and Cu [16] nanoparticles, suggesting that the outward diffusion of Ni ions through the oxide layer is the main process of Ni oxidation. However, a peculiar formation behaviour of voids is observed after long periods of oxidation in figures 1 (c) and (d). It is evident that a single large void is formed at an off-centre site of the interface between Ni and NiO.

Figure 2 (a) shows a bright field image of hollow nanoparticles formed after the oxidation of Ni nanoparticles at 673 K for 3.6 ks. The corresponding selected-area electron diffraction patterns after oxidation at 673 K are also shown in figure 2 (b), and are compared with those before oxidation, as shown in figure 2 (c). The Debye rings of fcc Ni before oxidation fully disappear and then those of NiO with NaCl structure appear in the diffraction patterns of (b). These results indicate that hollow NiO is formed via the oxidation of Ni nanoparticles. The formation mechanism of hollow NiO via the oxidation of Ni nanoparticles can be explained by the mechanism analogous to the Kirkendall effect in the Ni/NiO interface, where the outward diffusion of Ni is much faster than the inward diffusion of oxygen [19]. The rapid outward diffusion of Ni from inner Ni to outer NiO brings about supersaturated vacancies and their cluster during oxidation. This oxidation process of Ni seems to originate from the diffusion

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properties of NiO, with the self-diffusion of Ni ions [17] being much faster than that of oxygen ions [18]. Although the formation mechanism of voids in NiO particles is similar to other hollow oxides such as Co- [11,12], Zn- [15], Al- and Cu-oxides [16], hollow NiO has a peculiar morphology quite unlike theirs. As can be seen in figure 2(a), the location of the nano-holes in the hollow NiO particles deviates from the centre part of the particles and the hollow NiO doesn't have uniform shell thickness. Some hollow particles in figure 2 look as if they have the nano-holes at the centre position and uniform shell thickness. However, it means that the nano-holes are located at the top-surface side of the particles on the substrate; the direction of deviation from the centre part is nearly parallel to the incident beam and perpendicular to the substrate.

The surface structure of hollow NiO particles was investigated by FE-SEM in order to check if the nano-holes in the hollow NiO particles are closed or open to the surface. Figure 3 shows a FE-SEM image of hollow NiO nanoparticles obtained after the oxidation of Ni nanoparticles at 673 K for 60 min. The surface of the hollow NiO nanoparticles has no dimples, indicating that a nano-hole inside hollow NiO is located on the off-centred position, but is not open to the surface.

The formation mechanism of single localized voids at the Ni/NiO interface in the course of oxidation and an off-centred nano-hole in hollow NiO particles needs to be discussed in terms of the atomic movement during oxidation. The growth behaviour of the voids during the oxidation of Ni nanoparticles observed in figure 1 indicates that vacancies migrate toward a site of the interface and then become a large void at the site. With regard to the increase in internal energy, it can be assumed that formation of a single large void is more favorable rather than the multiple smaller voids when supersaturated vacancies aggregate and transform to voids since the surface energy of a single larger void is smaller than the sum of surface energies of multiple smaller voids. Thus, supersaturated vacancies seem to migrate and aggregate in order to

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suppress the increase in internal energy caused by the formation of non-equilibrium vacancies inside nanoparticles. The formation behaviour of voids during oxidation can be determined by the balance of the 'formation rate' and the 'migration rate' of vacancies. Firstly, the formation of vacancies inside Ni is closely related to the oxidation rate of Ni. The oxidation rate of Ni can be determined by the diffusion of Ni in NiO since the oxidation of Ni is dominated by the outward diffusion of Ni ions through a NiO layer. Thus, the formation of vacancies can be expressed by the diffusion of Ni ions in NiO, in other words, the formation rate of vacancies inside Ni can be described by the self-diffusion coefficient of Ni in NiO. On the other hand, the supersaturated vacancies inside Ni migrate and aggregate. Since they move in Ni, the mobility of vacancies is expressed by the self-diffusion coefficient of Ni in Ni. Therefore, the migration and clustering of supersaturated vacancies during the oxidation of Ni can be discussed by comparing the self-diffusion coefficients of Ni in NiO and that of Ni in Ni. To be more precise, the discussion should be based on a comparison between the diffusion coefficients of vacancies in Ni and NiO. Since, however, there is no data on the diffusion coefficient of vacancies, the self-diffusion data on Ni atoms in Ni [17] and NiO [20] can be used alternatively for discussion.

In figure 4, the temperature dependence of the self-diffusion coefficient of Ni in NiO [17], D_{Ni}^{NiO} is compared with that in Ni [20], D_{Ni}^{Ni}. D_{Ni}^{NiO} is one to two orders of magnitude larger than D_{Ni}^{Ni} near 600 K, the temperature at which our experiment on oxidation of Ni nanoparticles was performed. For example, D_{Ni}^{NiO} and D_{Ni}^{Ni} at 673 K are calculated using the literature data on Arrhenius parameters [17,20] to be 1×10^{-27} and 5×10^{-29} $m^2 s^{-1}$, respectively. The ratio of D_{Ni}^{NiO} to D_{Ni}^{Ni}, 20, is not so large, suggesting that the formation and migration rate of vacancies are well-balanced. In other words, vacancies, which are generated inside Ni as a result of the outward diffusion of Ni, have enough mobility to migrate toward a position over a long-range distance and aggregate inside Ni when compared to the oxidation rate. For comparison, the self-diffusion coefficient of Cu in Cu_2O [21], D_{Cu}^{Cu2O} and in Cu [22], D_{Cu}^{Cu}

are shown together in figure 4. As you can see, D_{Cu}^{Cu2O} is much larger than D_{Cu}^{Cu} around 400 K where hollow Cu_2O is formed via the oxidation of Cu nanoparticles [16]. For example, D_{Cu}^{Cu2O} at 373 K is calculated to be 2×10^{-24} m^2s^{-1}, which is nine orders of magnitude larger than D_{Cu}^{Cu} of 1×10^{-33} m^2s^{-1} at 373 K. The marked difference between D_{Cu}^{Cu2O} and D_{Cu}^{Cu} indicates that the 'formation rate' of vacancies (i.e. the oxidation rate of Cu) is much more rapid than the 'migration rate' of vacancies in Cu. Thus, the vacancies in Cu don't have sufficient mobility to migrate toward a position and aggregate there during oxidation. In other words, the vacancies aggregate uniformly at the metal-side interface as oxidation proceeds and rapidly form multiple voids at the interface. Finally, hollow oxide particles with uniform thickness are generated. In fact, we have observed the different oxidation behaviour of Cu nanoparticles from Ni nanoparticles; (i) a single large void is not observed at the Cu/Cu_2O interface in the course of oxidation of Cu nanoparticles, and (ii) the hollow Cu_2O is almost uniform in thickness and has nano-holes within them located at the centre of the particles.

The formation of vacancies, voids and a nano-hole through the oxidation of Cu and Ni nanoparticles is illustrated in figures 5 (a) and (b), respectively. Vacancies are generated along the metal-side interface as a result of the outward diffusion of metal ions at the initial stage of oxidation. As oxidation proceeds, voids are formed uniformly along the Cu/Cu_2O interface by the clustering of neighboring vacancies, while they becomes large voids at one site on the Ni/NiO interface because of the long-range diffusion of vacancies. As a result, a nano-hole is formed at the centre part of Cu_2O particles, but it is off-centre in NiO particles.

Vacancies generated in the oxidation process of Ni nanoparticles migrate to and aggregate at a site of the Ni/NiO interface since the mobility of vacancies inside Ni is large as the oxidation proceeds. This behaviour can be interpreted as the self-assembly of vacancies and this allows an energetically more stable state to be achieved.

4. Summary

The formation behaviour of voids and nano-holes during the oxidation of Ni nanoparticles was investigated by transmission electron microscopy. In the course of oxidation, a single large void was observed at a site of the interface between inner Ni and the outer NiO layer. Moreover, hollow NiO, with a nano-hole located at an off-centred position, was formed as a result of vacancy clustering during oxidation. These results can be interpreted as the localized self-assembly of vacancies, which provides for the achievement of an energetically more stable state. The vacancies in Ni have sufficient mobility to migrate toward a position and aggregate there during oxidation large because of the small ratio of self-diffusion coefficient of Ni in Ni to that in NiO. It appears that the de-centring of a vacancy-cluster in hollow NiO originates from the large mobility of vacancies inside Ni during oxidation.

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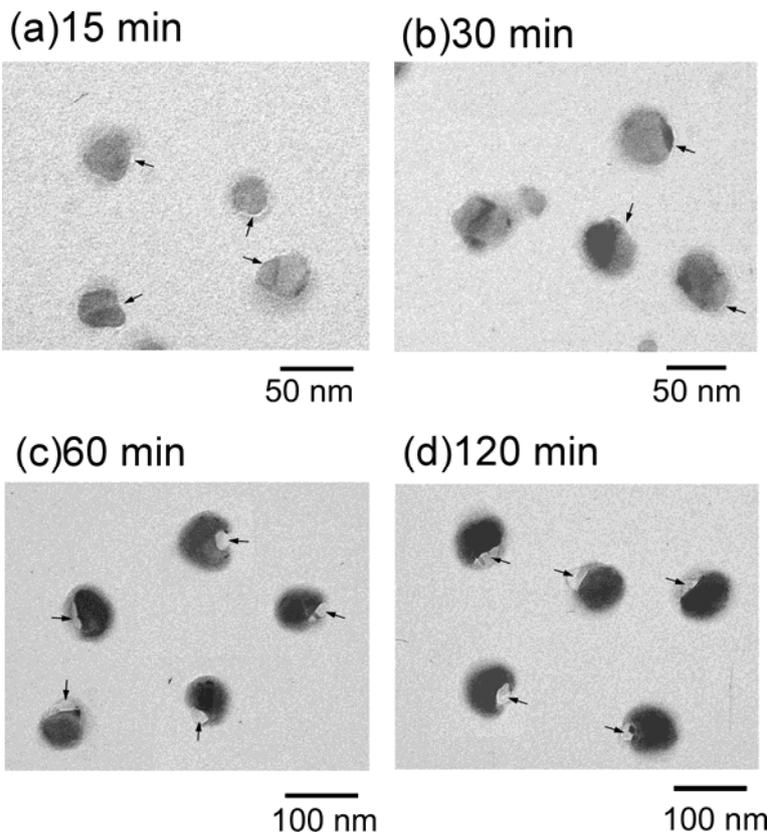[22] K. Maier, Phy. Status Solidi A **44** 567 (1977).

Figure 1   Bright field images of Ni nanoparticles (a) before and after oxidation at 573 K for (b) 30, (c) 60 and (d) 120 min. Arrows indicate the voids at the interface between Ni particles (the inner dark parts) and NiO layers (the outer bright parts).
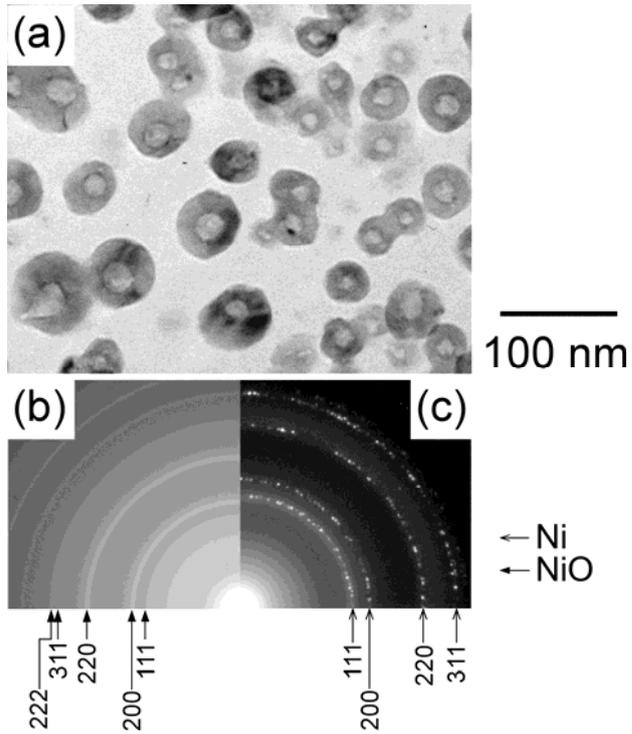
Figure 2   (a) A BFI of Ni nanoparticles oxidized at 673 K for 3.6 ks and (b) the corresponding selected-area electron diffraction patterns. For comparison, electron diffraction patterns for Ni nanoparticles before oxidation are shown in (c).
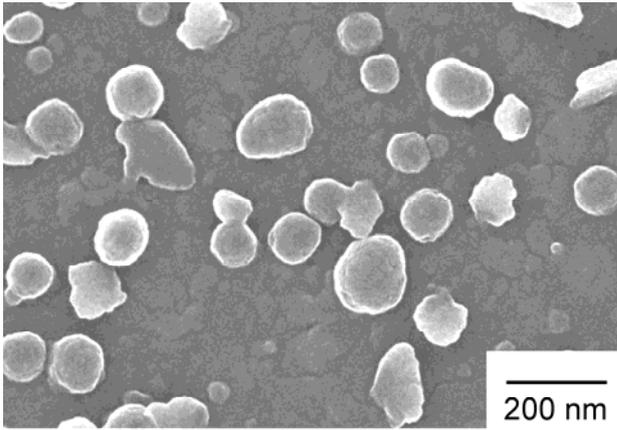
Figure 3   A scanning electron microscopy image of the surface of hollow NiO nanoparticles obtained after oxidation at 673 K for 60 min. The substrate is an amorphous Al-oxide film.
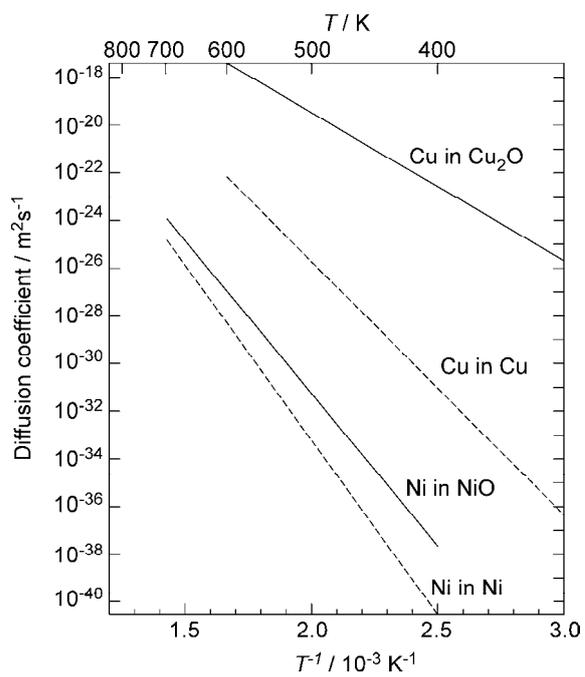
Figure 4　A comparison of self-diffusion coefficient in Ni and Cu with that of Ni ions in NiO and Cu ions in Cu_2O, respectively.
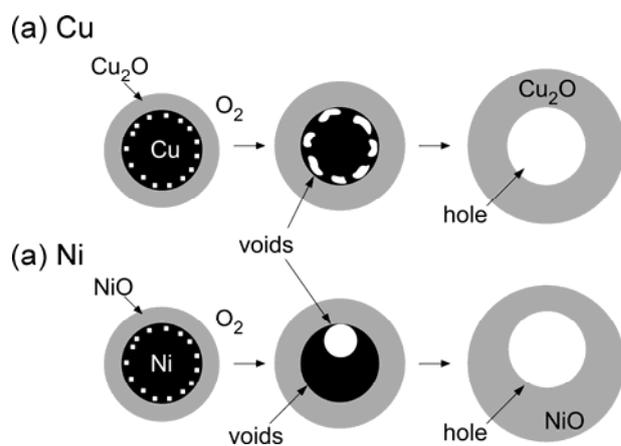
Figure 5　A schematic illustration of the formation mechanisms of vacancies, voids and a nano-hole in the course of oxidation of (a) Cu and (b) Ni nanoparticles.