Structural stability of hollow oxide nanoparticles at high temperatures

R Nakamura and H Nakajima
The Institute of Scientific and Industrial Research, Osaka University, 8-1 Mihogaoka, Ibaraki, Osaka 567-0047, Japan
E-mail: rnakamur@sanken.osaka-u.ac.jp

Abstract. The structural stability of hollow CuO and NiO nanoparticles, which were obtained via oxidation of Cu and Ni nanoparticles in air, was studied by transmission electron microscopy (TEM). Hollow CuO and NiO were observed to have shrunk at 473 and 623 K in annealing under $5.0 \times 10^{-5}$ Pa, respectively, where the reduction reactions from oxides to metals started. As a result of shrinking associated with reduction, hollow oxides turned into solid metal nanoparticles after annealing at higher temperatures for a long time. On the other hand, hollow oxides shrunk and collapsed through annealing in air at high temperatures. It was found that shrinking of hollow oxides during annealing in air occurs at temperature where the diffusion coefficients of slower diffusing species reach around $10^{-22}$ m$^2$s$^{-1}$. We can conclude that hollow oxide nanoparticles tend to shrink and collapse at high temperatures because hollow structures with extra surface energy are energetically unstable.

1. Introduction
The synthesis and fabrication of nano-scale controlled materials are rapidly developing fields of materials science. Particularly, hollow nanostructures have attracted much attention because their unique shape makes them applicable as delivery vehicles, fillers as well as for catalysis, and could bring about changes in physical and chemical properties [1]. Chemical reaction processes are the most common of the methods to synthesize hollow nanoparticles. However, a different principle to fabricate hollow nanoparticles based on the Kirkendall effect was demonstrated by Yin et al. [2]: the initially solid nanocrystals of cobalt turn into hollow spheres of sulfides and oxides when isolated nanocrystals of cobalt are exposed to sulfur and oxygen at relatively low temperatures near 400 K. Thereafter, it was reported by present authors that hollow Zn-[3], Al-[4], Cu-[4] and Ni-[5] oxides are formed using metal oxidation reactions. Up to now, it has been commonly recognized that the rapid outward diffusion of metal ions from the metal core to the outer oxide shell during oxidation or sulfidation is accompanied by the generation of vacancies and finally a nano-hole is formed in the oxide particles. According to several theoretical calculations [6,7], hollow nanospheres are thermodynamically unstable; they tend to shrink into solid nanospheres because a solid nanosphere has a lower surface energy than a hollow nanosphere and is therefore more energetically favorable. However, no experimental studies on structural stability of hollow nanoparticles associated with heat treatment have been performed so far. The purpose of the present study is to characterize the structural stability of hollow oxide nanoparticles during reduction and oxidation reactions at high temperatures by transmission electron microscopy (TEM).
2. Experimental procedure

Cu and Ni nanoparticles were evaporated onto an amorphous carbon mounted on a Mo grid or an amorphous Al$_2$O$_3$ film mounted on a Pt grid in an electron-beam deposition chamber (the details in [4,5]). Cu and Ni nanoparticles on the substrate were subjected to 423 K and 673 K, respectively, for 3.6 ks in air in an electric furnace and then hollow Cu$_2$O and NiO nanoparticles were obtained. The hollow Cu$_2$O and NiO nanoparticles were annealed at higher temperatures both in vacuum and in air. The isochronal annealing of the hollow Cu$_2$O and NiO from 423 to 873 K at intervals of 50 K and 1.8 or 3.6 ks in a vacuum was performed in TEM (Hitachi H-800) under $5 \times 10^{-5}$ Pa and the changes in morphology and structure of them were observed in-situ. On the other hand, the hollow oxide nanoparticles mounted on the substrate were annealed from 523 to 773 K for Cu$_2$O and from 873 to 923K for NiO for a given time in an electric furnace controlled within $\pm$0.5 K in air. Changes in morphology and crystal structure after oxidation were observed by the TEM.

3. Results and discussion

3.1. Annealing in vacuum

The change in morphology of hollow NiO during isochronal annealing from 573 to 873 K under vacuum in TEM is shown in figure 1. Hollow structures of NiO nanoparticles remain after annealing at 573 K for 1.8 ks, but it can be seen that hollow NiO nanoparticles start to shrink at 623 K for 1.8 ks. The shrinking of nano-holes in hollow NiO proceeds with increasing temperature and all the hollow nanoparticles turn into solid spheres after annealing at 873 K. We observed that the electron diffraction patterns after annealing at 573 K is the same as that before annealing, but the rings corresponding to fcc Ni appeared at 623 K where shrinking of hollow NiO started. In the case of annealing of hollow Cu$_2$O nanoparticles in vacuum, the behavior of the shrinkage was similar to that of hollow NiO; the shrinking of hollow Cu$_2$O occurred at 473 K, where the reduction reaction from Cu$_2$O to Cu started. The starting temperature for shrinking accords with that of the reduction reaction, indicating that shrinking of hollow oxide nanoparticles is closely related to the mass transport during the reduction reaction.

Figures 2 (a) and (b) show TEM images of hollow Cu$_2$O and NiO nanoparticles after annealing under $5 \times 10^{-5}$ Pa for 1.8 ks at 573 K and 773 K, respectively. As shown in figure 2 (a), a spherical particle was observed to have formed along the inner surface of hollow particles, as indicated by arrows. A similar behavior can be seen for NiO nanoparticles after annealing at 773 K for 1.8 ks in figure 2 (b). The behavior suggests strongly that the reduced metal atoms are generated at the inner surface of

![Figure 1. TEM images of hollow NiO nanoparticles during isochronal annealing for 1.8 ks in TEM: (a) before annealing, (b) 573 K, (c) 623 K and (d) 873 K.](image-url)
hollow oxide and they aggregate via surface diffusion. Formation of metal nanoparticles along the inner surface of hollow oxides during reduction of oxides to metals provides an important clue to consider the mechanism of mass transport in shrinking.

![Figure 2. A typical example of changes in morphology of hollow oxide nanoparticles during annealing under $5 \times 10^{-5}$ Pa: (a) Cu$_2$O at 573 K for 1.8 ks and (b) NiO at 773 K for 1.8 ks.](image)

According to the kinetic models of reduction of oxides [8], oxygen ions are removed from the lattice of the surface leaving behind an anion vacancy and then reduced zone are formed on the surface at the initial stage of reduction. In general, a dominant process of reduction reaction is considered to be the outward diffusion of oxygen ions via the anion vacancies generated at the surface [9]. Such mass transport results in the inward movement of the metal/reduced oxide interface. This is true of the reduction of hollow oxides; oxygen ions are removed from the outer surface to vacuum. As mentioned earlier, however, the formation of metal nanoparticles along the inner surface of hollow oxides during the reduction of Cu$_2$O to Cu (figure 2(a)) and NiO to Ni (figure 2(b)), respectively, demonstrates that the reduced Cu and Ni atoms are generated at the inner surface of hollow Cu$_2$O and NiO. The formation of metal nanoparticles at the inner surface indicates that oxygen ions diffuse from the inner surface migrate to the outer surface and that the reduced zone (i.e. Cu and Ni layers) is formed at the inner surface. After the formation of metal layers, metal atoms aggregate and make a particle in order to fill in the nano-hole. This behavior can be interpreted as the self-assembly of metal atoms which causes the extra energy of the inner surface of a hollow sphere to lower.

### 3.2. Annealing in air

Figure 3 show BFIs of hollow NiO nanoparticles after annealing in air at (a) 873 K for 36 ks and (b) 923 K for 36 ks. Although the hollow structures were maintained after oxidation at 873 K for 36 ks, almost all hollow particles collapsed into solid spheres at 923 K for 36 ks, as can be seen in figure 3(b). In the case of annealing hollow Cu$_2$O at high temperatures in air, hollow Cu$_2$O transforms into CuO at 573 K with the hollow structure being maintained. However, the shrinkage of hollow CuO was observed to begin at 673 K and completely solid CuO was formed after oxidation at 773 K.

![Figure 3. BFIs of hollow NiO nanoparticles after annealing in air (a) at 873 K for 36 ks and (b) at 923 K for 36 ks.](image)

Atkinson and Taylor reported that the activation energy and pre-exponential factor for the self-diffusion of Ni in NiO are 245 kJmol$^{-1}$ and $2.2 \times 10^{-6}$ m$^2$s$^{-1}$, respectively [10]. O’Keeffe and Moore determined those of O in NiO to be 226 kJmol$^{-1}$ and $1 \times 10^{-9}$ m$^2$s$^{-1}$, respectively [11]. At 923 K, where
hollow NiO nanoparticles completely collapse, the self-diffusion coefficient of Ni and O in NiO are estimated to be $3 \times 10^{-20}$ m$^2$s$^{-1}$ and $1.6 \times 10^{-22}$ m$^2$s$^{-1}$, respectively, based on the Arrhenius equation. On the other hand, the self-diffusion coefficients of Cu [12] and O [13] in CuO at 673 K, where hollow CuO nanoparticles shrink, are $1.3 \times 10^{-22}$ m$^2$s$^{-1}$ and $3 \times 10^{-16}$ m$^2$s$^{-1}$, respectively. It is found that the diffusion coefficients of the slower diffusing species, O in NiO and Cu in CuO, at the temperature where shrinking of hollow oxides takes place, are around $10^{-22}$ m$^2$s$^{-1}$. When $D$ is $10^{-22}$ m$^2$s$^{-1}$ and $t$ is 3.6 ks, the average diffusion distance, $(Dt)^{1/2}$, is estimated to be of the order of 0.1 to 1 nm, which is smaller than 10 to 20 nm corresponding to the radius of hollow oxide nanoparticles. It seems that, however, the calculated value can be close to several to ten nanometers, though it must be remembered that it was calculated by using the Arrhenius parameters obtained from the diffusion coefficients at high temperatures. Therefore, it is expected that atomic diffusion to fill in the nano-hole with several to ten nanometers in diameter can occur at temperatures where the diffusion coefficient is around $10^{-22}$ m$^2$s$^{-1}$. This result suggests that the idea by Gusak et al. [7] that the rate of shrinking is controlled by the slower diffusing species is valid. It should be noted that shrinking of hollow oxides by high-temperature oxidation starts at a temperature where the diffusion coefficient of the slower diffusion species reaches about $10^{-22}$ m$^2$s$^{-1}$.

4. Summary

The shrinking of hollow oxide nanoparticles occurs at a temperature, where the reduction reactions from oxides to metals start in annealing them under $5.0 \times 10^{-5}$ Pa. Hollow NiO and Cu$_2$O turn into solid Cu and Ni nanoparticles as a result of the shrinking associated with reduction. It seems that the shrinking of hollow CuO and NiO nanoparticles during annealing in air occurs at temperatures where the diffusion coefficients of slower diffusing ions in the oxides are of the order of $10^{-22}$ m$^2$s$^{-1}$. At high temperatures, where atomic diffusion is active, hollow nanoparticles tend to shrink and collapse because of their unstable structures.

5. Acknowledgement

We would like to thank Prof. H. Mori of Research Center for Ultra-High Voltage Electron Microscopy, Osaka University for our TEM experiment. This work was supported by Priority Assistance for the Formation of World Wide Renowned Centers of Research- The Global COE Program (Project: Center of Excellence for Advanced Structural and Functional Materials Design) and also by Grant-in-Aid for Scientific Research (No. 17106009) from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

References

[1] Xia Y and Halas N J 2005 MRS Bulletin 30 338
[2] Yin Y, Rioux R M, Erdonmez C K, Hughes S, Somorjai G A and Alivisatos A P 2004 Science 304 711
[3] Nakamura R, Lee J G, Tokozakura D, Mori H and Nakajima H 2007 Mater. Lett. 61 1060
[4] Nakamura R, Lee J G, Tokozakura D, Mori H and Nakajima H 2007 J. Appl. Phys. 101 074303
[5] Nakamura R, Lee J G, Mori H and Nakajima H 2008 Phil. Mag. 88 257.
[6] Tu K N and Gösele U 2005 Appl. Phys. Lett. 86 093111
[7] Gusak A M, Zaporozhets T V, Tu K N and Gösele U 2005 Phil. Mag. 85 4445
[8] Kung H H 1989 Surface Chemistry and Catalysis (New York: Elsevier)
[9] Sholz J and Langell M A 1985 Surf. Sci. 164 543
[10] Atkinson A and Taylor R I 1979 Phil. Mag. A 39 581
[11] O’Keeffe M and Moore W J 1965 J. Phys. Chem. 65 1438
[12] Tu K N, Yeh N C, Park S I and Tsuei C C 1989 Phys. Rev. B 39 304
[13] Rebane J A, Yakovlev N V, Chicherin D S, Tretyakov Y D, Leonyuk L I, Yakunin V G 1997 J. Mater. Chem. 7 2085