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Preparation of Ni particles by ultrasonic spray pyrolysis of $NiCl_2{\cdot}6H_2O$ precursor containing ammonia

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The preparation of nickel particles from nickel ammine complex was studied by ultrasonic spray pyrolysis in the presence and the absence of hydrogen. In the presence of H_2 (about 9 vol.%), nickel particles were formed at 500 °C, which is much lower than that reported. Metallic nickel, together with NiO, was obtained as a major phase at 400 °C. In the absence of H_2, metallic Ni was also obtained, but higher temperature (e.g. 900 °C) was needed. It is suggested that the addition of $NH_3{\cdot}H_2O$ and NH_4HCO_3 to $NiCl_2{\cdot}6H_2O$ precursor changes the reaction pathway of Ni formation. By careful control, spherical, solid and well-distributed Ni particles of about 0.5 μm were obtained at a residence time of 7–9 s in the aerosol reactor.

1. Introduction

There is an increasing demand for cheap and high-quality multilayer ceramic capacitors [1]. The set-up step is a high cost process since noble metal electrodes are preferably used for high temperature co-sintering of ceramic layer and internal metal electrodes. For example, metal electrode materials (e.g. metallic palladium [2, 3]) are usually estimated to account for 90% of material cost [4]. In order to decrease the electrode cost, Pd-Ag alloy (M.P. of Pd_{30}/Ag_{70} is 1220 °C) is also used. Recently, other electrode materials like Ni (M.P.1455 °C) and Cu (M.P. 1083 °C) are receiving increasing attentions because of the good electric conductivity, relatively high melting point and low cost [5, 6]. As a new kind of electrode material, metallic Ni has been prepared by liquid and gas reaction methods [7, 8]. However, the product particles with spherical morphology and non-agglomeration are not readily obtained by these methods.

Spray pyrolysis has proved itself a good method for preparing submicron metal and metal oxide powders [9–13]. Nagashima and co-workers showed ten years ago that Ni particles could be prepared by spray pyrolysis of $Ni(NO_3)_2{\cdot}6H_2O$ and $NiCl_2{\cdot}6H_2O$ in H_2-N_2 atmosphere [14, 15]. It was also illustrated that porous and hollow Ni particles were obtained below its melting point, i.e., 1600 °C. Since then, many researchers have reported Ni particle formation by spray pyrolysis. For example, similar results were obtained by Che and co-workers from $Ni(NO_3)_2{\cdot}6H_2O$ precursor in H_2-N_2 [16]. Stopic and co-workers obtained Ni particles from $NiCl_2{\cdot}6H_2O$ in H_2-N_2 atmosphere [17]. It was shown that Ni phase could only be obtained at 1000 °C or above, in which H_2 concentration was 16.5 vol.% and the residence time was about 20 s. Some hollow, slightly agglomerated Ni particles with traces of NiO were obtained at lower temperature, e.g. 900 °C. Recently, Stopic *et al.* showed that by adding a small amount of (0.1 mass%) Pd and Cu, pure Ni particles with good morphology could be formed at lower temperatures, e.g. 900 °C, from $NiCl_2{\cdot}6H_2O$ precursor [18, 19].

The complex precursors have been used for spray pyrolysis method [20–23]. Based on the common knowledge that nickel ammine complex can lose NH_3 upon heating, leaving $Ni(OH)_2$ precipitate in solution, we tried to prepare solid Ni particles at lower temperatures. The preparation of Ni particles from $NiCl_2{\cdot}6H_2O$ precursor containing ammonia and ammonium bicarbonate is studied in this paper. It shows that $NH_3{\cdot}H_2O$ and NH_4HCO_3 significantly change the pathway of Ni formation from $NiCl_2{\cdot}6H_2O$.

2. Experimental

Ni particles were prepared from $NiCl_2{\cdot}6H_2O$ precursor solution containing aqueous ammonia and ammonium bicarbonate (Kanto Chemicals, Tokyo, Japan). The concentration of $NiCl_2{\cdot}6H_2O$ solution was 0.3 mol/L for all samples. The synthesis apparatus is shown in Fig. 1. There are three heating zones at elevated temperatures, T_1 (300 °C), T_2 (600 °C) and T_3 (changeable, 600–1000 °C), unless otherwise stated. The apparatus is composed of an ultrasonic atomizer (2.5 MHz, GAPUSOL 9001, SARL RBI, France), a ceramic tubular reactor (heating length 1.0 meter, inner diameter 13 mm) and an electrostatic precipitator. In the

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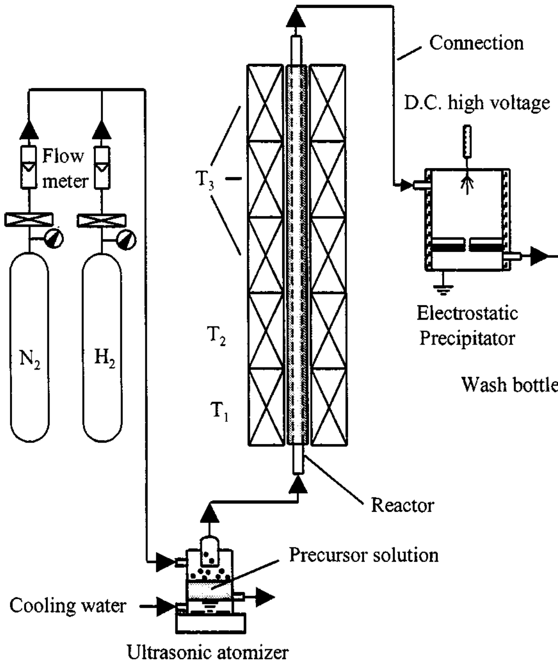

Figure 1 Schematic diagram of spray pyrolysis apparatus.

presence of H_2, the carrier gas was a mixture of H_2 and N_2, in which H_2 concentration is about 9.1 vol.% ($H_2 : N_2 = 1 : 10$). In the absence of H_2, the carrier gas is N_2. The preparation was carried out at atmospheric pressure. Under the assumption that the solution droplets move with the same speed as carrier gas in the reactor, the total residence times are 8.6–7.2 s, corresponding to T_3 temperatures of 600–1000 °C. Products were collected in an electrostatic precipitator. The precipitator and the connection part were both kept at 150 °C by tape heaters.

Particle morphology was observed using a scanning electron microscopy (JSM 5600, JEOL, Tokyo). Crystalline phases were characterized by an x-ray diffraction (XRD) equipment (Rint 2200V, Rigaku, Tokyo) with Cu K_α radiation operated at 40 kV and 20 mA. Chlorine content of Ni powder was determined by wave dispersive spectra component (WDS) attached to a SEM (JXA-8900RL WD/ED combined Microanalyser, JEOL, Tokyo) operated at 20 kV. The total dwell time was 250 s for element analysis.

3. Results and discussion

3.1. In the presence of hydrogen

Figure 2 shows the XRD patterns of the powders prepared at 400 °C and 500 °C from $NiCl_2$-$NH_3{\cdot}H_2O$-NH_4HCO_3 solution. Here, $NH_3{\cdot}H_2O$/Ni molar ratio is denoted as R. In this research, NH_4HCO_3 (NH_4HCO_3/Ni molar ratio is 2) was added to $R = 6$ solution to form stable solution because $R = 6$ is not high enough to stabilize $[Ni(NH_3)_x]^{2+}$ ($x = 0$–6, depending on the concentrations of Ni(II) and $NH_3{\cdot}H_2O$) complex ions at room temperature. The reactions were carried out at $T_1 = T_2 = 200$ °C, $T_3 = 400$ or 500 °C. It is shown in Fig. 2 that metallic nickel can be obtained at 500 °C. At 400 °C, metallic nickel is a major phase together with NiO. NH_4Cl is identified in the XRD patterns, which will be discussed in Section 3.3.

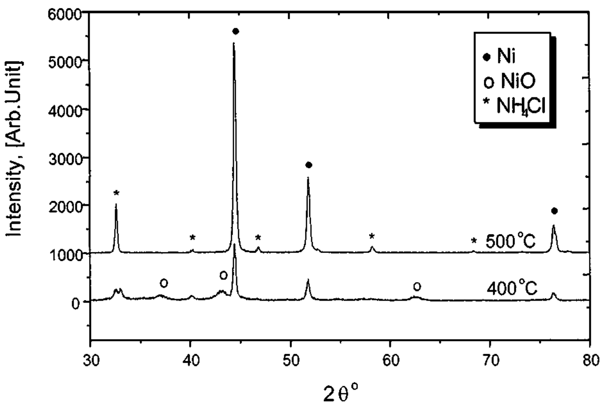

Figure 2 XRD patterns of the powders prepared at 400 and 500 °C. $NH_3{\cdot}H_2O/Ni = 6$, $NH_4HCO_3/Ni = 2$.

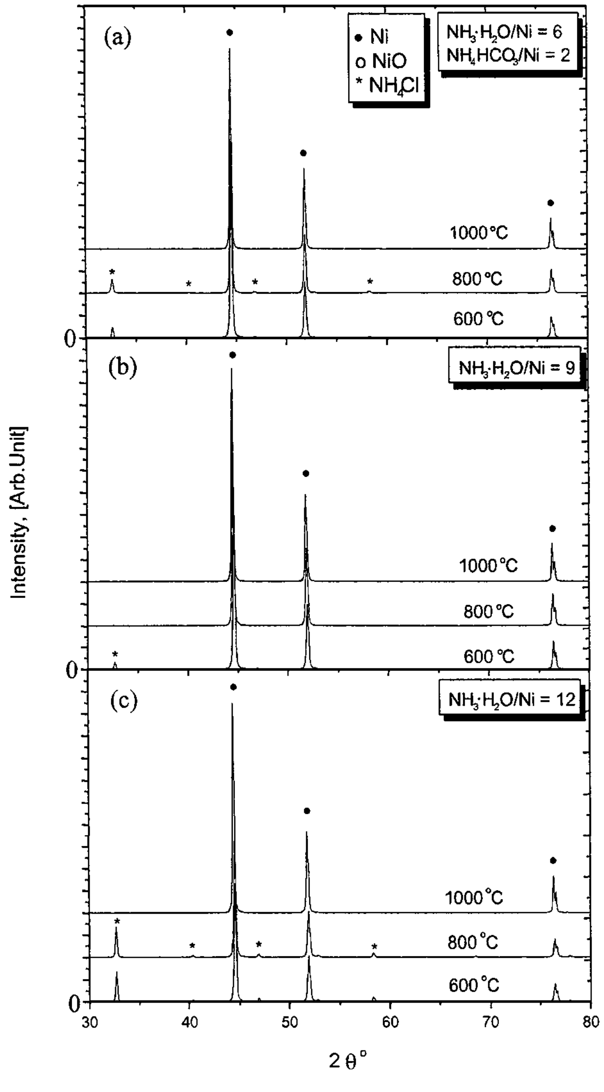

Figure 3 XRD patterns of Ni powders obtained from various R-value solutions at different temperatures.

Figure 3 shows the XRD patterns of the powders obtained from different R-value solutions at 600–1000 °C. It shows that Ni particles without NiO were obtained from all solutions at all temperatures. The Ni peaks become more intense and sharper at higher temperature, showing the better crystallinity. The $R = 9$ sample has the highest peak intensities at 600 °C and 800 °C among the three samples, while the three samples have similar peak intensities at 1000 °C.

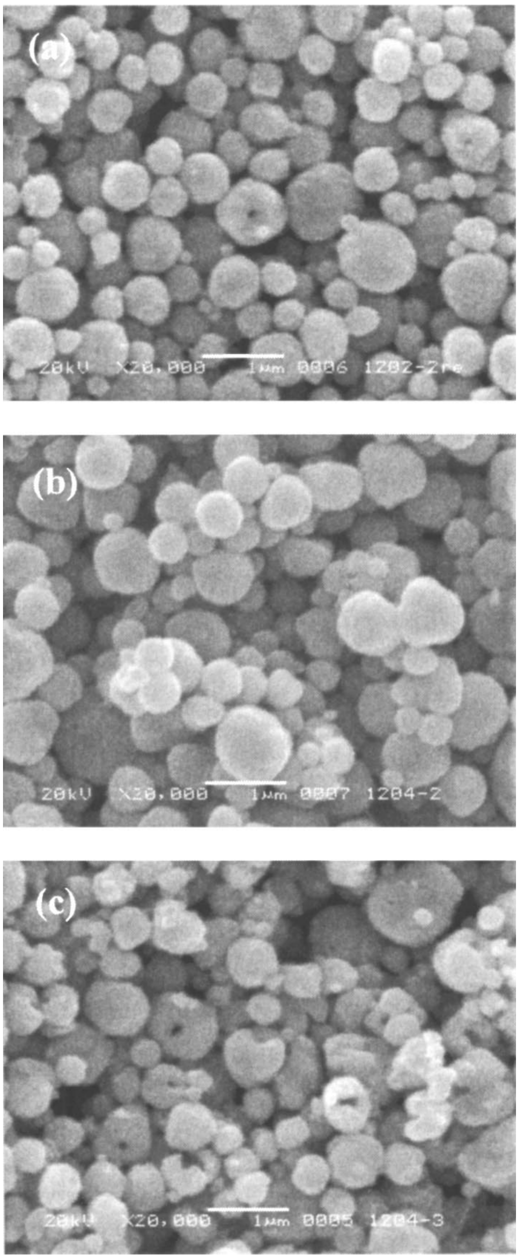

Figure 4 SEM images of the Ni powders prepared at 800 °C from different solutions. (a) $R = 6$, (b) $R = 9$, and (c) $R = 12$.

Figure 4 shows the SEM images of the powders prepared at 800 °C from different solutions. As it shows, some porous and irregular-shaped particles are observed for the $R = 12$ sample. A small amount of porous particles are also observed for the $R = 6$ sample, while the $R = 9$ sample consists of solid particles. Therefore, the particle morphologies formed at 800 °C change with the precursor solutions. This situation also holds for the samples prepared at 600 °C. However, the samples obtained at 1000 °C have similar particle morphologies, i.e., spherical, solid particles have been obtained.

Figure 5 shows SEM image of the nickel powders prepared at 1000 °C from the $R = 9$ solution containing NH_4HCO_3. As shown in this figure, the particles are solid, spherical and well-distributed with an average size of about 0.5 μm. It has been found that in addition to improving the atomizing stability of $[Ni(NH_3)_x]^{2+}$ complex, NH_4HCO_3 has other effects on products. For example, it was observed that though similar particle morphologies were formed from NH_4HCO_3 containing and non-containing solutions, the particle size was slightly better distributed in the case of adding NH_4HCO_3. However, the amount of NH_4HCO_3 should be controlled since improperly high concentration can deteriorate particle morphology.

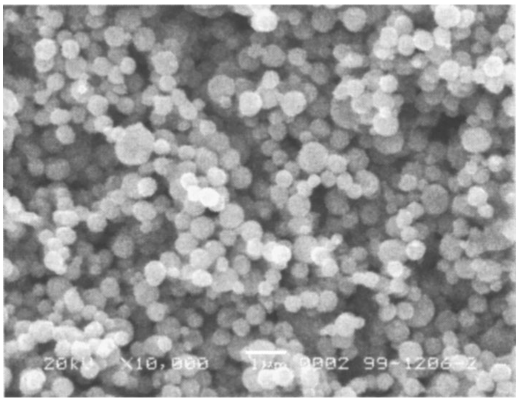

Figure 5 SEM image of the Ni particles formed at 1000 °C from $R = 9$ solution containing NH_4HCO_3 ($[NH_4HCO_3] = 0.3$ M).

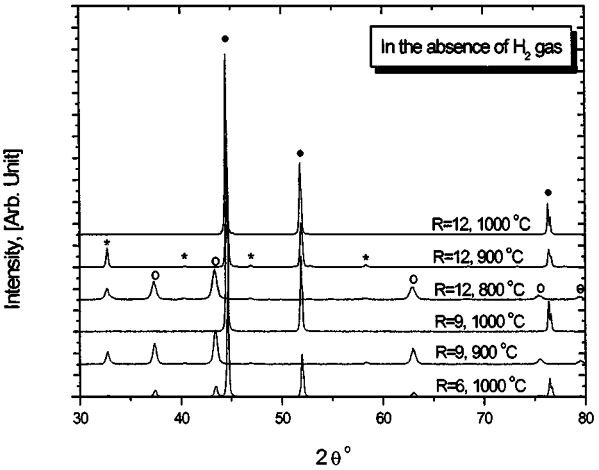

Figure 6 XRD patterns of the samples obtained from different solutions at various temperatures in the absence of hydrogen. It shows that higher R-value solution can form metallic nickel at lower temperature. (● : Ni, o : NiO, * : NH_4Cl).

As shown in Fig. 2 (also in Fig. 6), NiO, instead of $NiCl_2$, was formed as an intermediate phase from $NiCl_2$-$NH_3{\cdot}H_2O$ (NH_4HCO_3) complex solutions and then it was reduced to Ni particles by H_2. In contrast, in the case without any additives, it has been suggested that $NiCl_2$ would be directly reduced by H_2 gas as follows [17]:

$$NiCl_2 + H_2 = Ni + 2HCl$$

Therefore, it is clear that the addition of $NH_3{\cdot}H_2O$/NH_4HCO_3 changes the reaction pathway of nickel formation.

3.2. In the absence of hydrogen

Since ammonia is a kind of reductive gas, it is interesting to know whether metallic nickel can be formed in the absence of hydrogen gas. Fig. 6 shows some XRD patterns of the samples formed from different solutions

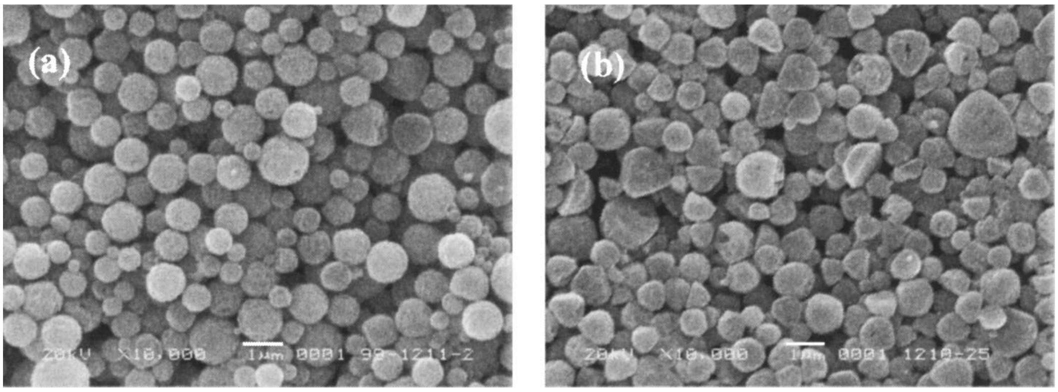

Figure 7 SEM images of NiO particles obtained at 800 °C in the absence of H_2. (a) $R = 9$, and (b) $R = 12$.

at various temperatures. For these cases, nitrogen was the carrier gas. For the $R = 6$ sample, no pure Ni was formed at 1000 °C or below, and the mixture phases of Ni and NiO were obtained at this temperature. In addition, only NiO was obtained at 900 °C. In the case of the $R = 9$ sample, phase pure Ni was obtained at 1000 °C, but only NiO phase was obtained at 900 °C. However, phase pure Ni was obtained at both 1000 °C and 900 °C from the $R = 12$ solution. The above results indicate that the formation of Ni phase is correlated with R value, or $NH_3{\cdot}H_2O$ concentration in the starting solution. Therefore, it is possible to obtain metallic nickel at lower temperature if ammonia concentration is further increased.

It was observed that the particle morphologies obtained at 1000 °C were similar to each other for the $R = 9$ and 12 samples. However, at lower temperature, e.g. 800 °C, NiO particles were obtained and have different morphologies shown in Fig. 7. It shows that the $R = 9$ sample consists of spherical and solid NiO particles. In addition to spherical and solid particles, the $R = 12$ sample also contains some irregular-shaped and porous NiO particles.

There may be two mechanisms for the intermediate NiO to be reduced to metallic Ni under present experimental conditions. One is the direct reduction of NiO by NH_3 gas. The other is associated with the possible generation of H_2 gas during spray pyrolysis because NiO is a catalyst. Clearly, more experiment is needed to study the reduction mechanism.

3.3. NH_4Cl and its removal

NH_4Cl is present in product powders formed below 1000 °C, as shown in Figs 2, 3 and 6. As well known, NH_4Cl sublimates at 340 °C and melts at 520 °C. The evolution of NH_4Cl gas (or decomposed to NH_3 and HCl gases) at above its sublimation or melting points is believed to be responsible for the formation of porous particles (e.g. Fig. 4). Upon exiting the reactor, it can condense onto the particle surface and cause agglomeration. If a particle is porous, NH_4Cl can condense not only onto the particle surface but also into the inner part. Therefore, different amounts of NH_4Cl were observed in Fig. 3. At 600 °C and 800 °C, the $R = 9$ sample has the smallest amount of NH_4Cl, among the three samples. This agrees well with its solid particle structures. At 1000 °C, no NH_4Cl is indicated for all samples due to the formation of dense particles at this high temperature.

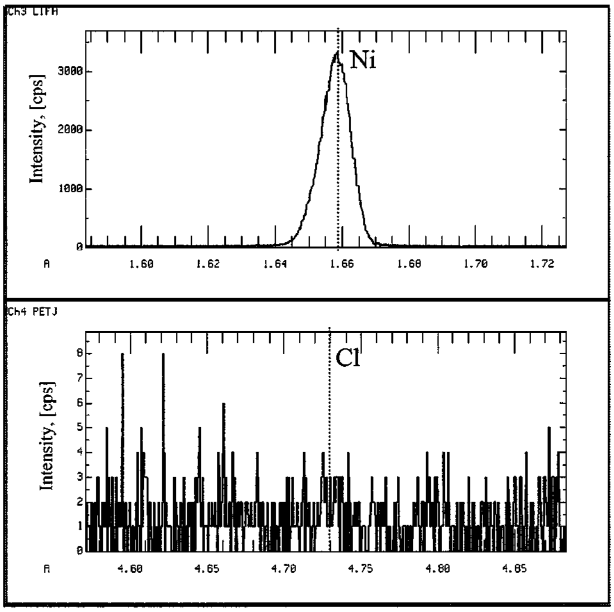

Figure 8 WDS of $R = 12$ sample after purification, showing no evidence of chlorine. The sample was prepared at 600 °C. The purification condition: 400 °C × 2 h, N_2 atmosphere.

NH_4Cl can be removed by one of the following ways:

1) Keeping the product collector at above the sublimation temperature;
2) Heating the product at above the sublimation temperature;
3) Washing the product with solvent.

Heating was carried out at 400 °C for 2 hours in a N_2 atmosphere to remove NH_4Cl. Higher temperature can be used if the improvement of crystallinity is aimed to. Fig. 8 demonstrates the wave dispersive spectra (WDS) for the $R = 12$ sample prepared at 600 °C that contains the greatest amount of NH_4Cl shown in Fig. 3. The dotted lines indicate the wavelengths of the strongest peaks for Ni (K_α 1.659 Å) and Cl (K_α 4.729 Å). As it shows, the Ni peak intensity at 1.659 Å is as high as 3300 cps, while no peak at 4.729 Å is indicated for Cl and all background is below 10 cps. Therefore, no chlorine can be detected by WDS after purification.

4. Conclusion

The preparation of metallic nickel submicron particles from $NiCl_2 \cdot 6H_2O$ precursor solution containing ammonia and ammonium bicarbonate was studied by ultrasonic spray pyrolysis. It was shown that the additives significantly changed the pathway and the mechanism of Ni formation.

(1) Nickel particles was formed at 500 °C, while Ni/NiO mixture phases were obtained at 400 °C and Ni was the major phase;

(2) $NH_3 \cdot H_2O$/Ni and NH_4HCO_3/Ni molar ratios have remarkable influences on particle morphology. By careful control, spherical, solid and well-distributed nickel particles of about 0.5 μm were formed from nickel ammine complex precursor;

(3) In the absence of hydrogen gas, Ni particles can also be obtained but at higher temperatures, e.g. 900 °C. The formation of metallic nickel is correlated with $NH_3 \cdot H_2O$ concentration. Higher concentration favors the formation of metallic Ni at lower temperature.

(4) NH_4Cl was present in the powders prepared below 1000 °C, which was an indicator of particle microstructures. It has unfavorable influence on products, but it can be removed by heating the powder in N_2.

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References

1. L. SHEPPARD, *Amer. Ceram. Soc. Bull.* **72** (1993) 45.
2. S. F. WANG, J. P. DOUGHERTY, W. HUEBNER and J. G. PEPIN, *J. Amer. Ceram. Soc.* **77** (1994) 3051.
3. F. AZOUGH, R. AL-SAFFAR and R. FREER, *J. Euro. Ceram. Soc.* **18** (1998) 751.
4. P. P. PHULE and S. H. RISBUD, *J. Mater. Sci.* **25** (1990) 1169.
5. H. HYUGA, Y. HAYASHI, T. SEKINO and K. NIIHARA, *Nanostructured Mater.* **9** (1997) 547.
6. S. SATO, Y. NAKANO, A. SATO and T. NOMURA, *J. Euro. Ceram. Soc.* **19** (1999) 1061.
7. J. YAMAMATSU and T. NOMURA, *J. Powd. Metall. Soc. Japan* **41** (1993) 1042.
8. L. BRISSONNEAU and C. VAHLAS, *Adv. Mater.* **11** (1999) 135.
9. I. W. LENGGORO, Y. C. KANG, T. KOMIYA, K. OKUYAMA and N. TOHGE, *Jpn. J. Appl. Phys.* **37** (1998) L288.
10. G. L. MESSING, S. C. ZHANG and G. V. JAYANTHI, *J. Amer. Ceram. Soc.* **76** (1993) 2707.
11. H.-F. YU and A. M. GADALLA, *J. Mater. Res.* **11** (1996) 663.
12. D. MAJUMDAR, T. T. KODAS and H. GLICKSMAN, *Adv. Mater.* **8** (1996) 1020.
13. T. C. PLUYM, Q. H. POWELL and A. S. GURAV, *J. Aerosol Sci.* **24** (1993) 383.
14. K. NAGASHIMA, M. WADA and A. KATO, *J. Mater. Res.* **5** (1990) 2828.
15. K. NAGASHIMA, T. HIMEDA and A. KATO, *J. Mater. Sci.* **26** (1991) 2477.
16. S. L. CHE, K. TAKADA, K. TAKASHIMA, O. SAKURAI, K. SHINOZAKI and N. MIZUTANI, *ibid.* **34** (1999) 1313.
17. S. STOPIC, I. ILIC and D. P. USKOKOVIC, *Int. J. Powder Metall.* **32** (1996) 59.
18. S. STOPIC, J. NEDELJKOVIC, Z. RAKOCEVIC and D. USKOKOVIC, *J. Mater. Res.* **14** (1999) 3059.
19. S. STOPIC, I. ILIC, J. NEDELIJKOVIC, Z. RAKOCEVIC, M. SUSIC and D. USKOKOVIC, “Studies in Surface Science and Catalysis,” Vol. 112 (Elsevier Science B. V., Amsterdam, 1997) p. 103.
20. C. NATARAJAN, N. FUKUNAGA and G. NOGAMI, *Thin Solid Films* **322** (1998) 6.
21. V. PETRYKIN, A. KARPOV, V. POLTAVER, S. LEE, M. KAKIHANA and YU. TRETYAKOV, *Appl. Supercond.* **5** (1997) 47.
22. N. KIEDA and G. L. MESSING, *J. Mater. Res.* **13** (1998) 1660.
23. S. WADA, A. KUBOTA, T. SUZUKI and T. NOMA, *J. Mater. Sci. Lett.* **13** (1994) 190.

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