J MATER SCI **41** (2006) 3033–3039

The coating of nickel compounds with copper compounds

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Uniform fine particles of nickel basic carbonate were synthesized by heating, aqueous solution containing 0.08 mol dm^{-3} nickel sulfate and 0.8 mol dm^{-3} urea, at 85°C for various periods of time. These particles were then coated with copper compound by heating them in aqueous dispersion, containing urea and copper nitrate, at 85°C. The coating material was found to be amorphous and was composed of $Cu_2(OH)_2CO_3$. The coating mixture, when heated under similar conditions in the absence of the dispersed cores, produced greenish dispersion of the precipitated particles [coating precursor solids]. The later were also amorphous in nature and had the same chemical composition [$Cu_2(OH)_2CO_3$] as that of the coating material of the coated particles. Air-dried core, coated, and coating precursor materials were calcined at 700°C for 1 h at the heating rate of 5°C min^{-1} in the air atmosphere, which converted them into NiO, $NiO_{[core]}/CuO_{[coating]}$, and CuO, respectively. Scanning electron microscopic examination showed no sintering occurred in all these solids during the calcinations process and the particles retained their identities to a significant extent.

1. Introduction

Synthesis of inorganic fine powders, composed of bare or coated particles of uniform morphological features and chemical compositions is the research domain of a number research groups in different parts of the world [1–6]. In fact, inorganic powders are widely used in a number of hi tech applications, such as fuel cells [7], advanced ceramics [8], gas sensors [9], photocatalyst [10], etc. In all these applications, particle shape, size, chemical composition, and the uniformity there in play a vital role in tailoring the properties of the powders, as well as powder based gadgets to the desired level. In this regard, we have established recipes for various types of powders, composed of bare and coated systems of uniform fine particles [11–19].

In continuation of the same efforts, attempts have been made in this study to establish optimum conditions for the synthesis of uniformly dispersed coated particles, comprised of core and coating materials of nickel and copper compounds, respectively. It is mentioned that such composite system of fine powders has never been reported before. We hope that the obtained materials would be proved novel precursors for the fabrication of high temperature gas sensors, since compounds of nickel [NiO] and copper [CuO] have separately been employed elsewhere [20, 21] as the basic materials for making thick film gas sensors.

This study reports the synthesis of nickel basic carbonate particles and their coating with basic copper carbonate by means of urea based homogeneous precipitation method. In the absence of the core particles, the optimized coating mixture generates spherical particles of amorphous basic copper carbonate precipitates, designate as coating precursors. On calcination at the elevated temperatures, the core, coated, and coating precursor particles convert into nickel oxide, copper oxide$_{(coating)}$/nickel oxide$_{(core)}$, and copper oxide, respectively.

2. Experimental procedures

2.1. Material

Merck reagent grade Nickel (II) sulfate, copper (II) nitrate, and urea were used as the starting chemicals for the synthesis of the reported materials. Stock and other required solutions of these chemicals were made with doubly distilled water, using all Pyrex glass vessels. The glass vessels were initially cleaned with dilute nitric acid,

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DOI: 10.1007/s10853-006-6772-8

then thoroughly rinsed with copious amount of doubly distilled water, and then dried in a drying oven. All the solutions were filtered through 0.1 μm pore size membrane filter before use. The working and stock solutions were never used longer than 4 days.

2.2. Synthesis of nickel compound [core particles]

In this case, 500 cm^3 of aqueous solution, containing 0.08 mol dm^{-3} nickel sulfate and 0.8 mol dm^{-3} urea, was prepared at room temperature. This solution [reactant mixture] was then transferred to a 600 cm^3 double-walled Pyrex glass reactor, pre-heated at 85°C by hot circulating water. The reactor was closed at the top by means of a perforated lid and the reactant mixture was aged up to 5 h. During aging period, the initially clear homogeneous solution converted into dispersion of the precipitated particles, which settled down at the bottom of the reactor, leaving clear supernatant solution above. In some cases, the clear supernatants were heated under similar conditions after separating them from the settled solids. In all the experiments, the precipitated solids were isolated from the liquid phase by vacuum filtration through 0.1 μm pore size membrane filter, and then washed extensively with doubly distilled water. The obtained wet material was either dispersed in distilled water and stored in the form of dispersion in a tightly stoppered Pyrex glass vessel, or dried in air and stored in a desiccator in the form of dry powder.

2.3. Synthesis of copper/nickel compound [coated particles]

Various amounts (0.2–0.8 g dm^{-3}) of the originally wet core particles of the nickel compound were ultrasonically dispersed in aqueous solutions, containing varying quantities of urea [0.2–1.0 mol dm^{-3}] and copper nitrate [0.002–0.02 mol dm^{-3}]. In all cases, the resulting dispersions were stirred by means of a magnetic stirrer for 6 h in a glass stoppered titration flask at room temperature. Later on, all the dispersions were individually transferred to a double-walled Pyrex glass vessel [reactor], described in section 2.2. The content of the reactor was aged at 85°C for 10–120 min with constant stirring. At the end of this treatment, temperature of the reactor was immediately brought down to room temperature by means of cold circulating water. This dispersion was then filtered through a 0.1 μm pore size membrane filter in order to separate solids from the liquid phase. The solids retained on the membrane filter were extensively washed with doubly distilled water, dried in air, and then stored in desiccator.

2.4. Heat treatment

Air-dried powders of the core and coated particles were heated at 700°C in the tube furnace, equipped with a programmable controller. Heating was performed in air atmosphere for 1 h at the heating rate of 5°C min^{-1}. After this treatment, the furnace was turned off and the heat-treated samples were cooled down to room temperature inside the furnace.

2.5. Characterization

Shape and size of the core and coated particles were evaluated by scanning electron microscopy [SEM; JEOL, JSM-6300]. For this study, the powder samples were mounted on standard stubs, which were then coated with a thin conducting layer of gold in a sputtering machine. During microscopic examination, the SEM was operated at 15 keV.

The coated solids were subjected to energy-dispersive x-ray analysis [EDX, Noran Voyager x-ray microanalysis system] for the qualitative evaluation of their metal content. Similarly, wet chemical methods, as described in our earlier paper [16], were employed for determination of quantitative composition of the coated particles.

Crystallinity of the selected air-dried and heat-treated powder samples was evaluated on a Siemens D500, x-ray diffractometer, with CuK$_\alpha$ radiations. The diffractometer was operated at 40 kV and 20 mA during the measurements. Continuous scanning was carried out on these samples in the 2θ range from 5–80°.

The desired powder samples were also analyzed by thermogravimetry, using the Perkin Elmer 7, TGA machine. In this analysis, the sample was heated at the rate of 10°C min^{-1} in nitrogen ambient, maintained in the sample compartment by continuous flow of nitrogen.

3. Results and discussion

3.1. Core particles of nickel compound

A transparent aqueous solution, containing nickel nitrate and urea was used as the precursor solution for the preparation of core particles of nickel compound. This solution was subjected to aging at 85°C for the periods up to 5 h. It was noted that visual turbidity started to appear in this solution after ~45 min, obviously due to the formation of tiny precipitated particles in the aging mixture. The turbidity increased with the passage of time and after 90 min of aging, the precipitated solids settled down at the bottom and leaving transparent supernatant solution at the top. On continuous heating of the same reactant mixture, turbidity re-appeared in the supernatant solution after 105 min of the total aging period, which increased with time. Once again, the precipitated solids settled down at the bottom within 30 min of the inception of the appearance of the second turbidity and leaving a transparent supernatant at the top. The same mixture was kept hot at 85°C for further 5 h, but the supernatant solution stayed transparent during the course of aging.

Following the above-mentioned results, it was of interest to see the difference, if any, in the properties of the two solids, obtained in the same reactant mixture in two consecutive precipitation steps. For this purpose, a separate experiment was performed in which aging of the above-mentioned reactant mixture was terminated after 90 min and the settled solid and clear supernatant were separated from each other. The solid was dried in air after extensive washing with distilled water and designated as S1. Similarly, the supernatant solution was aged at 85°C, which produced precipitated solids within nearly 45 min. The latter were separated from their mother liquor, washed, air-dried, and designated as S2.

In order to account for the conversion of the transparent reactant solution into dispersion of the precipitated solids, it is firmly believed that on heating the initial solution mixture, dissolved urea started to liberate hydroxyl and carbonate ions in the bulk of the solution, which resulted in the formation precipitated particles of nickel compound. It is worth mentioning that urea has widely been used by the researchers as the thermally activated precipitant for producing uniform fine particles of inorganic compounds of various morphological features and chemical compositions with high degree of success [4, 5, 11–18, 22–24].

The appearance of first and second turbidity in the reactant mixture during the aging period at 85°C pointed to two consecutive nucleations [primary and secondary], which took place at the interval of nearly 15 min. Scanning electron micrographs of S1 [Fig. 1A], and S2 [Fig. 1B] revealed that both samples were composed of particles with nearly identical features and size distributions.

We believe that due to rather long time interval between the primary and secondary nucleation, the primary particles got sufficient time to grow to full grown particles and thus settled down at the bottom of the reaction vessel. Though the supernatant of these particles was relatively weak in the reactants content, yet nucleation took place in it and lead to full-grown precipitated particles.

It must be noted that multiple nucleation ended with polydispersed system of particles of cadmium compound, produced by urea based homogeneous precipitation process, reported in our earlier study [18]. This aspect of urea based homogeneous precipitation process is further being investigated in our laboratory for different systems.

X-ray diffractometric [XRD, Figs 2A, and B] studies indicated that the solids depicted in Fig. 1A-B were crystalline and composed of $NiCO_3 \cdot Ni(OH)_2 \cdot H_2O$. This showed that the primary particles appeared in both the primary and secondary nucleation process emerged as crystalline entities having identical crystal structures, which was maintained during the course of their growth. Composition of these solids, as identified by XRD, matched very well with that determined by the chemical methods. It is reported here that only the particles shown in Fig. 1A were employed for further study.

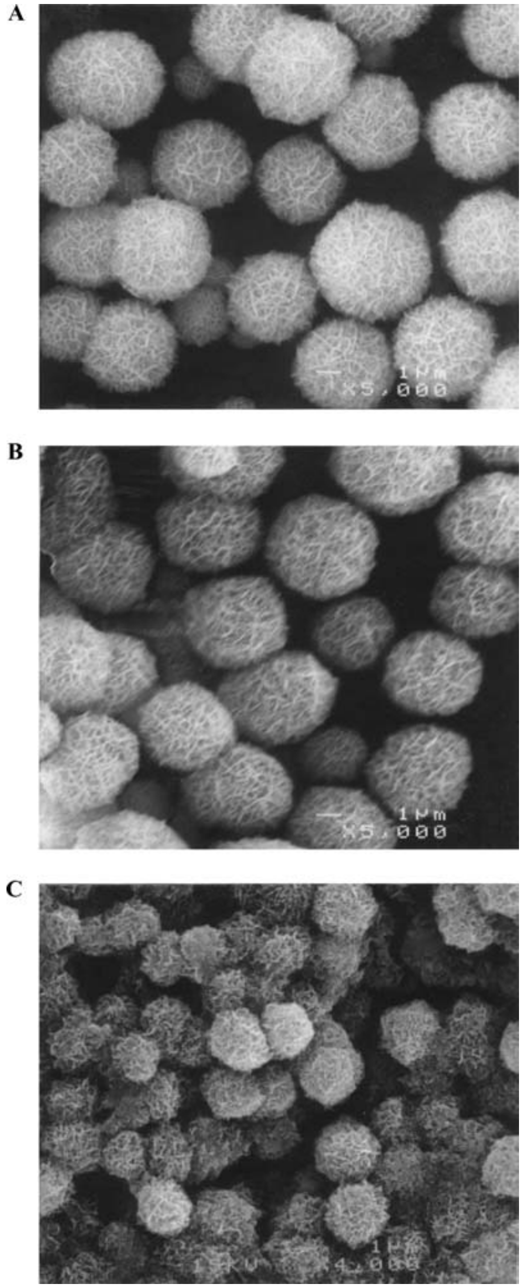

Figure 1 Scanning electron micrographs (SEM) of the particles obtained, when (A) aqueous solution, containing 0.08 mol dm^{-3} $NiSO_4$ and 0.8 mol dm^{-3} urea was heated for 90 min at 85°C; (B) supernatant of the precipitated particles obtained in A was heated at 85°C for 45 min; (C) the particles shown in A were calcined at 700°C for 1 h at the heating rate of 5°C min^{-1}.

The particles shown in Fig. 1A were heated in the thremogravimetric analyzer [TGA] from 30–700°C at the heating rate of 5°C. It was observed that weight of the sample decreased as a result of the heat treatment. The weight loss of the sample was recorded as a function of temperature and is given in Fig. 3A. As is clear from the plot in this figure that the solid lost its thermally decomposable components mostly in the temperature range of 350–400°C. The weight loss verses temperature trace becomes almost parallel with the temperature axes in the temperature range of 400–700°C, indicating negligible changes in weight as a result of heat treatment in this temperature range. The total weight loss observed as a result of heating at 700°C was found to be ∼40%. The sample was recovered from the machine at the end of the experiment, and found it black in color.

Another heat treatment experiment was performed in which a weighed powder sample of

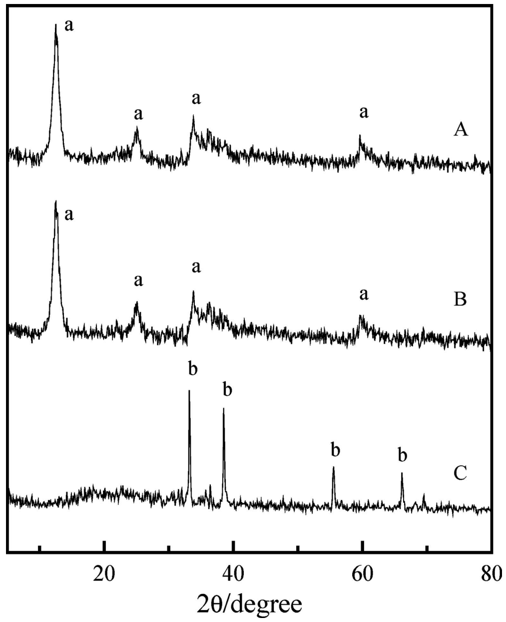

Figure 2 X-ray diffraction (XRD) patterns of the particles shown Fig. 1A (A); Fig. 1B (B); and Fig. 1C(C). Symbols: a, $NiCO_3 \cdot Ni(OH)_2 \cdot H_2O$; b, NiO.

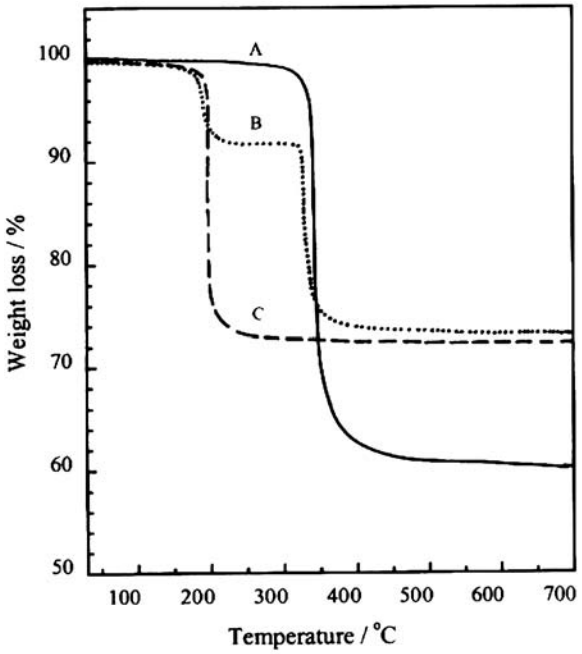

Figure 3 Thermogravimetric analysis (TGA) curves for the particles shown in Fig. 1A: (A); Fig. 4A (B); and Fig. 5A (C).

$NiCO_3 \cdot Ni(OH)_2 \cdot H_2O$ was heated in a tube furnace at 700°C for 1 h at the heating rate of 5°C min^{-1} in air atmosphere. This sample lost ∼39% of its weight as a result of the heat treatment. The observed weight loss agreed very well with the weight loss registered in the TGA experiment. The heated powder was analyzed by x-ray diffractometry and was found to be NiO [XRD, Fig. 2C]. The transformation of $NiCO_3 \cdot Ni(OH)_2 \cdot H_2O$ to NiO was believed to take place according to the following reaction:

$$NiCO_3 \cdot Ni(OH)_2 \cdot H_2O \xrightarrow[34.9\%]{700^\circ C} 2NiO + CO_2 + 2H_2O \quad (1)$$

The weight loss indicated in Eq. (1) is based on the given chemical composition of this solid, which was less than the experimentally determined weight loss of ∼39%. This difference in the weight loss could be due to the decomposition of impurities [possibly, cynate and sulfate ions] associated with this solid during the precipitation process (12).

Scanning electron microscopy demonstrated [SEM, Fig. 1C] that particles of the heated powders [NiO] retained their morphological features to a significant extent. Slight damage to the original features of the particles is obviously due to the loss of material during the calcinations process.

3.2. Coated particles

Dispersion of the $NiCO_3 \cdot Ni(OH)_2 \cdot H_2O$ particles [Fig. 1A] in aqueous solutions, containing copper nitrate and urea in specific ratio, when heated at 85°C for 1 h, converted into dispersions of the coated particles. The precipitation of the coating material on the dispersed cores was outcomes of the thermal decomposition of urea, which increased pH of the medium and generated carbonate ions in the coating mixture. Under such circumstances, copper ions in the same ambient could not maintain their ionic states and precipitated out on the surface of the dispersed core particles, most probably in the form of copper basic carbonate. It was noted from the scanning electron microscopic observations of different batches of the solids, obtained in the coating experiments, that the coating reaction was dependent upon the reaction conditions, i.e., amount of copper nitrate, urea, and dispersed cores in the coating mixture, as well as aging period at the given temperature. As such, extensive variations in the applied experimental parameters were performed for achieving the optimum conditions under which uniformly coated particles could be produced.

Fig. 4A exemplifies the coated particles with maximum loading of the coating material, as obtained under the described experimental conditions. Increase in the solid/solution ratio in the same coating mixture lead to a corresponding decrease in the % gain in weight of the dispersed core particles, resulted from the precipitated shells.

Similarly, the solids shown in Fig. 5A were produced, when the coating mixture, described in the legend of Fig. 4A, was heated at 85°C for 1 h in the absence on the dispersed cores. Yield of these particles corresponded well with the increase in weight [∼30 wt%] of the core particles during their conversion to coated solids [Fig. 4A]. This observation leads to the fact that the dispersed cores had negligible effect on the precipitation process of the shell material. However, the presence of the dispersed cores did affect the growth of the precipitated copper

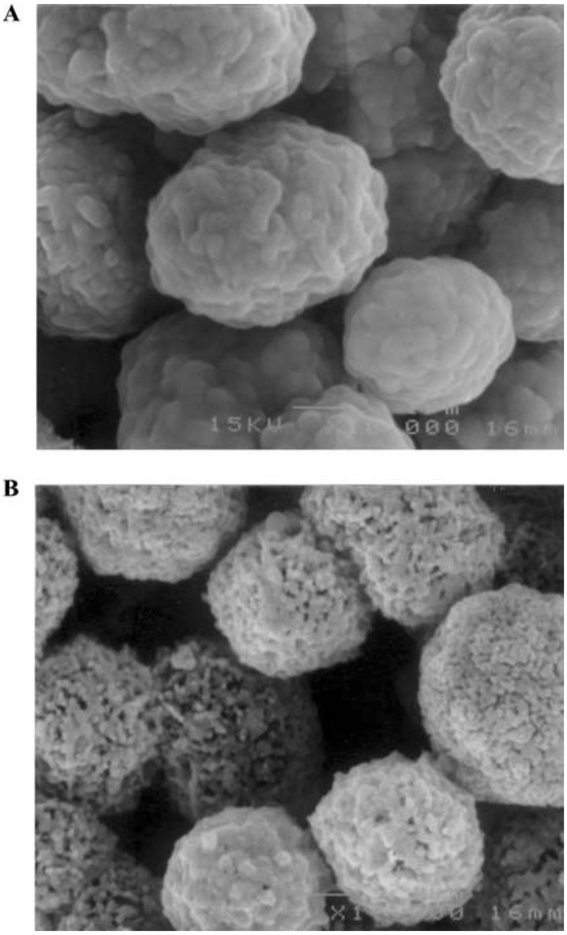

Figure 4 Scanning electron micrographs (SEM) of the coated particles obtained, when (A) an aqueous dispersion, 0.5 g dm^{-3} in $NiCO_3 \cdot Ni(OH)_2 \cdot H_2O$ cores, 0.008 mol dm^{-3} in $Cu(NO_3)_2$, and 0.5 mol dm^{-3} urea was aged for 25 min at 85°C; (B) particles shown in A were calcined at 700°C for 1 h at the rate of 5°C min^{-1}.

compound, since the latter precipitated out in spherical morphology [Fig. 5A] in the absence of the core particles.

It was also observed that the shell material of the coated particles got dissolved and leaving bare cores, when pH of the dispersion of the former particles was adjusted to values <4.0 and >10.5 and allowed to stay for 1 h with constant stirring. Nearly 100% dissolution of the shell material was achieved in this process, as confirmed from the chemical analysis of the filtrate of the same dispersion and weight of the dried residue [core]. Energy-dipersive x-ray analysis showed no traces of copper in the latter solid. Similarly, its XRD pattern was identical with that of the bare $NiCO_3 \cdot Ni(OH)_2 \cdot H_2O$ particles. All these finding pointed to the absence of chemical interaction between the shell and core materials during and after the completion of the coating process.

The coated particles, shown in Fig. 4A, were analyzed by x-ray diffractometry. The XRD pattern obtained [Fig. 6A] was almost the same, as obtained [Fig. 2A] for the core [$NiCO_3 \cdot Ni(OH)_2 \cdot H_2O$] particles. This demonstrated amorphous nature of the shell material. It was also

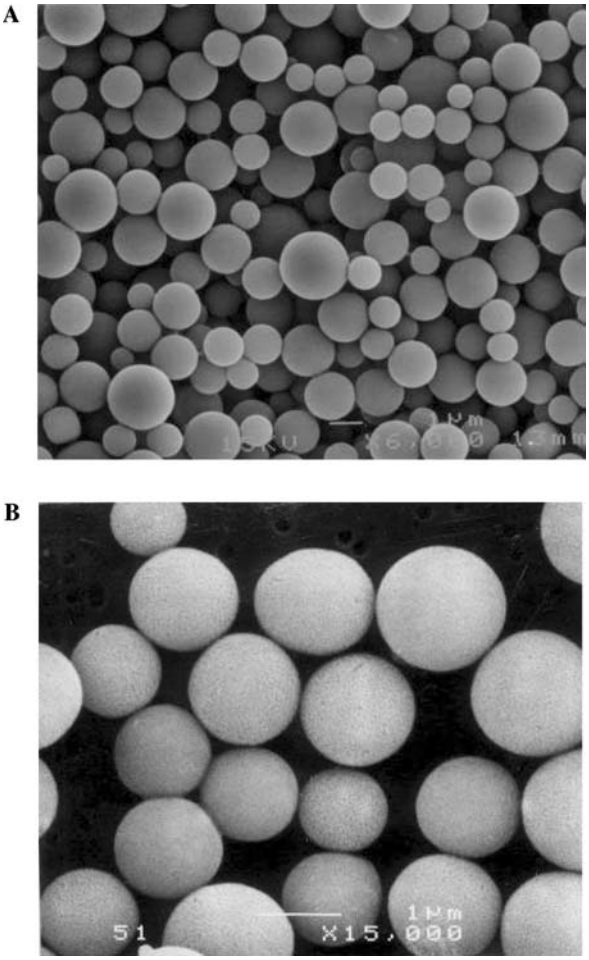

Figure 5 Scanning electron micrographs (SEM) of the particles obtained, when (A) aqueous solution, containing 0.008 mol dm^{-3} $Cu(NO_3)_2$ and 0.5 mol dm^{-3} urea was heated for 30 min at 85°C; (B) particles shown in A were calcined at 700°C for 1 h at the rate of 5°C min^{-1}.

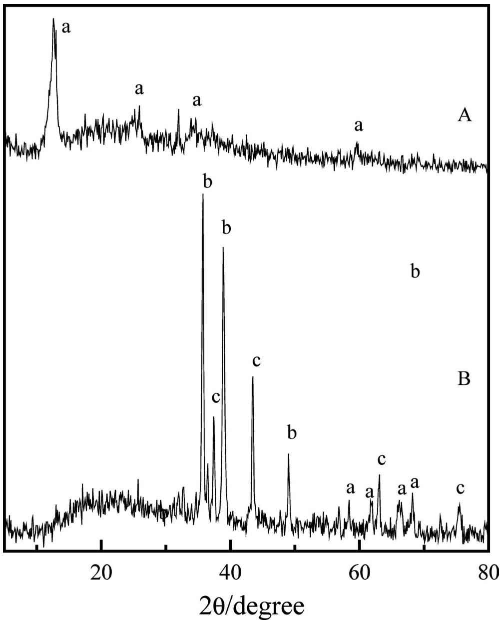

Figure 6 X-ray diffraction (XRD) patterns of the coated particles, shown in Fig. 4A (A); and Fig. 4B (B). Symbols: a, $NiCO_3 \cdot Ni(OH)_2 \cdot H_2O$; b, CuO; c, NiO.

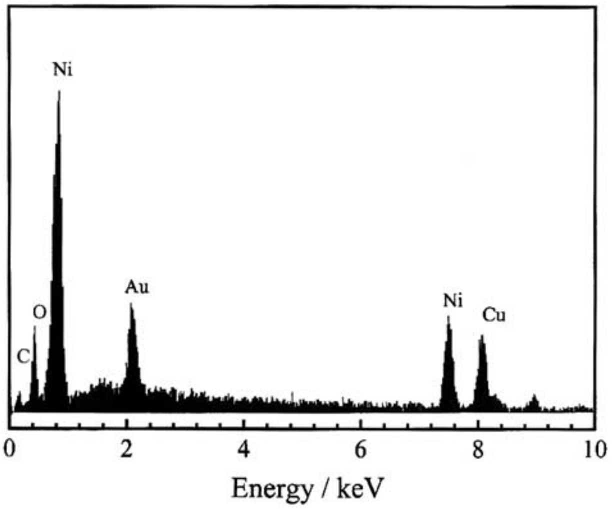

Figure 7 Energy-dispersive x-ray analysis (EDX) pattern of the particles displayed in Fig. 4A.

noted that particles [Fig. 5A] produced in the coating mixture in the absence of dispersed cores were found to be amorphous, which further substantiated the fact that the presence of the dispersed cores in the coating mixture had negligible effect on the chemistry of the precipitation process.

Energy-dispersive x-ray analysis [Fig. 7] showed that the coated particles, shown in Fig. 4A, contained copper and nickel. These metals were obviously resided in matrices of the shell and cores materials, respectively. Wet chemical analysis showed that shell material of the coated particles was composed of $Cu_2(OH)_2CO_3$.

The coated particles, shown in Fig. 4A were also subjected to thermogravimetric analysis [TGA]. The TGA trace obtained for this solid in the temperature range of 30–700°C is given in Fig. 3B. As is evident from this figure, the coated solid lost its noticeable weights at two different temperatures. The first weight loss occurred at 220°C, whereas the second weight loss took place at around 350°C. These weight changes at two different temperatures were due to the presence of two different types of materials [coating and core materials] in the coated solids. This was further substantiated by the TGA experiments performed independently with the cores [TGA trace, Fig. 3A] and coating precursors [TGA trace, Fig. 3C] particles, which indicated weight losses at ∼220, and 350°C, respectively. Thus the latter experiments confirmed the fact that the weight losses in the coated solid at 220 and 350°C [TGA trace, Fig. 3B] were due to the core and coating material, respectively. Furthermore, the TGA trace of the coated solids gave no indication of any reaction between the core and coating material during the course of heating and transformed independently into other phases.

In order to identify the thermally generated phases in the coated solids, the as-prepared coated particles [Fig. 4A] were calcined at 700°C under the controlled condition of heating in the air atmosphere, and then analyzed by the powder x-ray diffractometry. The XRD pattern of the calcined solid is shown in Fig. 6B. This figure pointed to the presence of only two phases, i.e. NiO, and CuO in this solid, which obviously emerged from the core [$NiCO_3 \cdot Ni(OH)_2 \cdot H_2O$], and coating [$Cu_2(OH)_2CO_3$] materials, existed in the original solid.

SEM of the calcined coated particles is shown in Fig. 4B. Inspection of the figure revealed that coating got damaged during the calcination process, while the cores retained their morphological features to a significant extent.

It was interesting to note that on calcinations under similar conditions, the coating precursor particles [Fig. 5A] transformed into CuO particles with very small change in surface features of the particles. This observation revealed that in the present case, the copper basic carbonate material was thermally more fragile in the coating than as independent particles.

4. Conclusions

Light green particles of $NiCO_3 \cdot Ni(OH)_2 \cdot H_2O$ precipitated out in aqueous solution mixture of urea and nickel sulfate, when it was heated at 85°C. Two distinct stages were noted during the precipitation process, caused by the inception of primary and secondary nucleation at the interval of about 15 min. The solids resulted in both the precipitation stages were isolated independently from the mother liquors, which were found to be identical in morphological features, chemical compositions, and crystalline nature. They transformed into NiO particles without sintering and any significant change in particle morphology, when calcined at 700°C at the heating rate of 5°C min^{-1}.

The as-prepared $NiCO_3 \cdot Ni(OH)_2 \cdot H_2O$ particles were coated with $Cu_2(OH)_2CO_3$. For this purpose, aqueous dispersion, containing the optimized amounts of the urea, copper nitrate, and the core particles, was heated at 85°C for 1 h. The coating material got dissolved and left behind the core particles, when pH of the dispersion of the coated particles was adjusted to values <4.0 and >10.5 and allowed to stay for 1 h with constant stirring. This showed the absence of chemical bonds between the core and coating materials. Dry powder of the coated particles transformed into composite solids, composed NiO and CuO. Obviously, NiO, and CuO were the calcination products of the core and coating materials, respectively. This further indicated that the core and coating materials stayed mutually inert during the heat treatment.

Acknowledgement

We are thankful to Dr. Egon Matijević, Victor K. LaMer Professor of Colloid and Surface Science, Center For Advanced Materials Processing, Clarkson University, Potsdam, New York 13699, USA, for providing all sorts of facilities for the characterization of the powder samples.

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*Received 11 April
and accepted 6 September 2005*