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One-step fabrication of Cu–Al_2O_3 nanocomposite via solution combustion synthesis route

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ABSTRACT

Solution combustion synthesis (SCS) is a well-known method for production of different metal oxides and composite materials such as metal matrix composites. To the best of our knowledge, producing of metal matrix composite needs an extra reduction step after combustion synthesis. In the current research, the authors introduced a novel method to eliminate the reduction step and showed that Cu matrix composite could be produced just in one-step. For this purpose, $Cu(NO_3)_2{\cdot}3H_2O$ and Al $(NO_3)_3{\cdot}9H_2O$ were used as oxidizers and urea as fuel, and one-step combustion synthesis was performed in the presence of graphite. The structure and morphology of the products were studied by XRD, SEM and TEM techniques, respectively. XRD patterns proved that the presence of graphite could prevent formation of copper oxides. SEM and TEM micrographs showed that Cu matrix reinforced with nano-sized alumina could be achieved in one-step through SCS method.

1. Introduction

Copper has been extensively used because of its high heat and electrical conductivity. However, pure copper has not very well mechanical properties like tensile and yield strength. There are several methods to improve the properties, such as its alloying with other elements. However, in this way, electrical and thermal properties of copper decrease, significantly. Copper could also be strengthened by incorporating fine particles of a second phase like metallic or oxide one, causing only a relatively small loss in conductivity. Among oxide phases, addition alumina to copper matrix is very common. This is because it is cheap with stable properties even up to high temperatures [1–4].

In order to fabricate copper matrix composite and especially copper–alumina nanocomposites several methods exist such as, high energy ball milling and self propagation high temperature synthesis (SHS). But, these methods have weakness points. For example, fabrication of Cu–Al_2O_3 nanocomposites using ball milling process takes about 8 h [5]. In the SHS method, copper oxide and aluminum are used as raw materials for fabrication of Cu–Al_2O_3 nanocomposite. Mixing condition and compaction pressure are two important factors in the SHS method [6–8].

Solution-combustion is an attractive approach to synthesis oxide and even nanoparticles and it is sourced from SHS techniques. The main benefits of SCS are low ignition temperature and better homogeneity of final products. The most outstanding specification of SCS is the utilizing of the released heat from the chemical reactions as a source of energy. It means, it dose not need an extra external energy source. SCS has some distinctive features as follows: (a) the primary materials (nitrate and fuel) dissolute and distribute in water in molecular level. It means they do not need long distance diffusion, (b) high combustion temperature ensures the production of powders with crystalline structure and (c) sintering of produced powders can be prevented by gases exhaustion during SCS [9–11].

If SCS is utilized for production of oxide components, synthesis will be occurred just in one-step. But in the case of metal matrix composites, especially copper composite it needs some extra steps like reduction process. It is worth noting that the reduction step is carried out in a reducing atmosphere, such as hydrogen. Based on literature survey done by the authors, in the previous works SCS was used for fabrication of Cu–alumina composite if and only if the process was followed by reduction step. In fact during SCS, copper oxide and alumina fabricated and then the material reduced in hydrogen atmosphere [1,2,4,9].

In this investigation, a novel attitude based on SCS method was introduced for production of Cu–alumina nanocomposite just in one-step. For this purpose, an auxiliary material was used in order to perform in situ reduction step.

2. Materials and methods

Copper nitrate (Cu $(NO_3)_2{\cdot}3H_2O > 99.5\%$), aluminium nitrate (Al $(NO_3)_2{\cdot}9H_2O > 99.5\%$) as oxidizer and urea ($(NH_2)2CO > 98.5\%$) as fuel were used to produce Cu–25 wt% Al_2O_3 nanocomposite. In fact, graphite as an auxiliary material was mixed with nitrates and urea before adding water to them.

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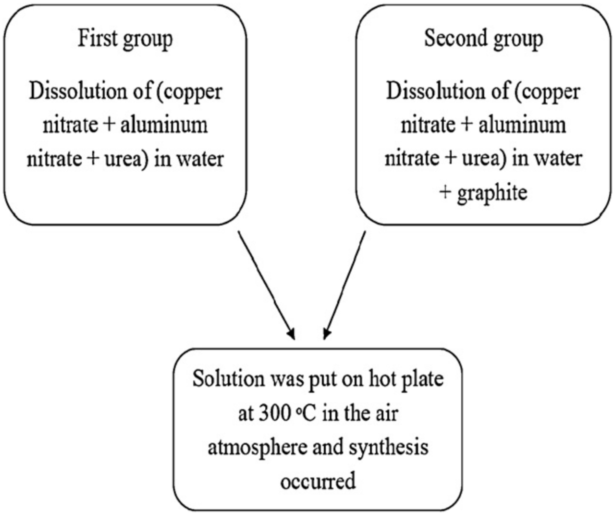

Fig. 1. Fabrication chart for first and second group.

The fuel to oxidizer ratio (F/O) was calculated through the method reported by Jain and Adiga [12]. The F/O ratios were chosen in two amounts of 1.0 and 1.5 and Eq. (1) was used in order to produce metallic copper and alumina.

$$4.4Al(NO_3)_3 + 10.5Cu(NO_3)_2 + 32CO(NH_2)_2 = 10.5Cu + 2.2Al_2O_3 + 32CO_2 + 64H_2O + 49.1N_2 \quad (1)$$

Examinations were divided into two parts. In the first group, copper, aluminum nitrate and urea were solved in minimum amount of distilled water. Then solution was heated up to 300 °C. For both ratios after evaporation of water and formation of gel, ignition occurred immediately. In second group of experiments, graphite was added to the raw materials as an auxiliary material and followed the similar method reported for first group. Eq. (2) shows the role of carbon on reduction of copper oxide. The details of both experiment groups were summarized in Fig. 1.

$$CuO + C = Cu + CO \quad (2)$$

XRD was used to identify the produced phases. XRD patterns were obtained using a Philips X'pert diffractometer with Cu Kα radiation ($\lambda = 0.15406$ nm) in the range of $2\theta = 4$–$80°$ by the step of 0.02°. Microscopic evaluation was done using both using scanning electron microscope (SEM) model VP 1450 and transmission electron microscope (TEM) model 912 AB.

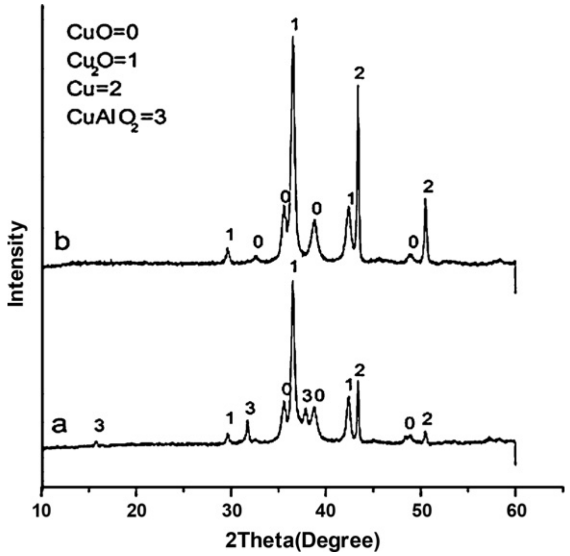

Fig. 2. XRD patterns for ratios F/O: (a) 1, (b) 1.5.

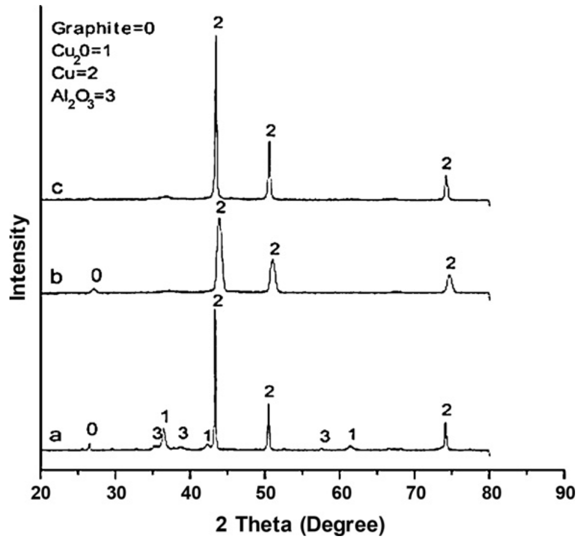

Fig. 3. XRD patterns for, (a) F/O = 1 and graphite stoichiometric amount, (b) F/O = 1.5 and graphite stoichiometric amount, (c) F/O = 1.5 and 25% graphite stoichiometric amount.

3. Result and discussion

3.1. None graphite contained experiments

First group experiments were started with stoichiometric ratio. Fig. 2 shows the XRD patterns of the produced materials using SCS route at different the F/O ratio (i.e. 1 and 1.5). XRD pattern in Fig. 2a, shows various copper oxides (CuO and Cu_2O) and even spinel compound of $CuAlO_2$. Existing of the mentioned phases can be attributed to the amount of fuel. This is because the used fuel can be hydrolyzed at higher temperature (above 80 °C) [13]. Since ignition temperature for this system is more than 200 °C, some fuel hydrolyzes before starting the reaction (Eq. (3)).

$$CO(NH_2)_2 + H_2O = CO_2 + 2NH_3 \quad (3)$$

But, after decomposition of copper and aluminum nitrates according to Eqs. (4) and (5) [14,15], NH_3 and NO_2 can react together as seen in Eq. (6) [16].

$$2Cu(NO_3)_2 = 2CuO + 4NO_2 + O_2 \quad (4)$$

$$2Al(NO_3)_3 = Al_2O_3 + 6NO_2 + 1.5O_2 \quad (5)$$

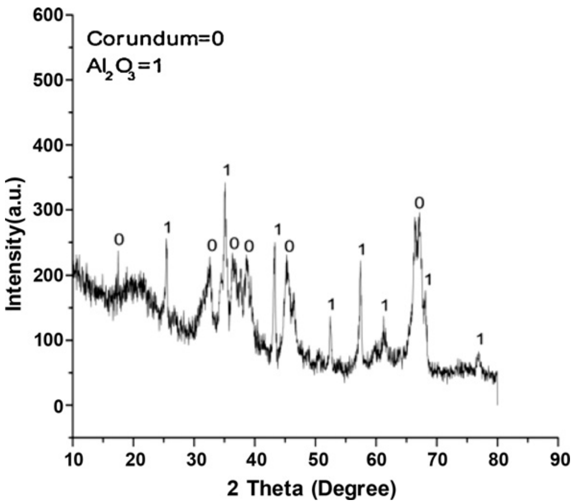

Fig. 4. XRD pattern from the synthesis product, after solving in nitric acid.

$$8NH_3 + 10NO_2 = 9N_2 + 12H_2O + 4O_2 \quad \Delta H = -2865.4\,\text{kJ} \tag{6}$$

In the case of extra fuel in the solution, the copper oxide can be reduced to metallic copper because of the presence of reducing agents, including H and C components, unlike alumina, which is almost a stable oxide [17]. The reaction between the remained urea and oxygen is shown in Eq. (7) [18].

$$CO(NH_2)_2 + 1.5O_2 = CO_2 + 2H_2O + N_2 \quad \Delta H = -543\,\text{kJ} \tag{7}$$

The enthalpies appeared in both Eqs. (6) and (7) act as internal source of energy and this is why the temperature increases suddenly during process.

Whereof the reaction occurs at air atmosphere, the presence of oxygen leads metallic copper to copper oxides. With looking at in more details in Fig. 2, it may be concluded that the type of oxide phase depends on the F/O ratio, because with increasing the F/O ratio, ability of solution to reduce can be promoted. In fact, the presence of oxide phases refers to high temperature and vicinity of the products with oxygen during and after combustion. In the F/O ratio1.5 intensity of the peaks are higher than that of stoichiometric ratio. As a matter of fact, the reduction ability of solution promotes as fuel content increases. As it is clear in Fig. 2, increasing the F/O ratio causes to decrease the probability of spinel production. The main reason of this phenomenon can be referred to the fact that spinel phase can be produced at temperature about 1000 °C [19]. Briefly, the interested result achieved in the current research is, producing copper oxides will not be postponed as the F/O ratio changes (Fig. 2b).

3.2. *Experiments in the presence of graphite*

In the second group, graphite was added to the raw materials to facilitate in situ reduction during combustion synthesis of Cu–Al_2O_3 nanocomposite. Indeed the presence of graphite reduces the oxide copper as mentioned in the Eq. (2) or prevents the oxidation of produced copper.

Although other reactions between graphite and copper oxides may be occurred (Eqs. (8–10)), but calculation of graphite content was done according to Eq. (2).

$$Cu_2O + C = 2Cu + CO \tag{8}$$

$$CuO + C + \tfrac{1}{2}O_2 = Cu + CO_2 \tag{9}$$

$$Cu_2O + C + \tfrac{1}{2}O_2 = 2Cu + CO_2 \tag{10}$$

Similar to what proposed in the first group, the experiments were done at different the F/O ratios (1 and 1.5). Fig. 3 shows the dependency of produced materials on the F/O ratio in the presence of graphite. As it is shown in Fig. 3a, the amount and intensity of copper oxides decrease in comparison to Fig. 2a, because of the reduction role of graphite. The interesting result is lack of $CuAlO_2$ peak in the presence of graphite. It seems the presence of graphite decreases the combustion temperature and facilitates the reduction of copper oxides.

In Fig. 3b the result of addition stoichiometric amount of graphite to the solution with the F/O ratio 1.5 is shown. Disappearing of all copper oxides is very interesting and only copper and graphite peaks appear. May be the reason of being an extra graphite in the XRD spectrum can be referred to the fact that some synthesized copper particle ca not oxidize during or after SCS. This is why the partial amounts of graphite remain.

In order to eliminate the extra graphite, the amount of added graphite was decreased up to 25% stoichiometric. XRD pattern of this kind of reaction is appeared in Fig. 3c.

As seen the above equation was set to produce composite with 25 wt% of alumina but in none of XRD patterns alumina peaks has not appeared (except in Fig. 3a). It returns to more attractive power

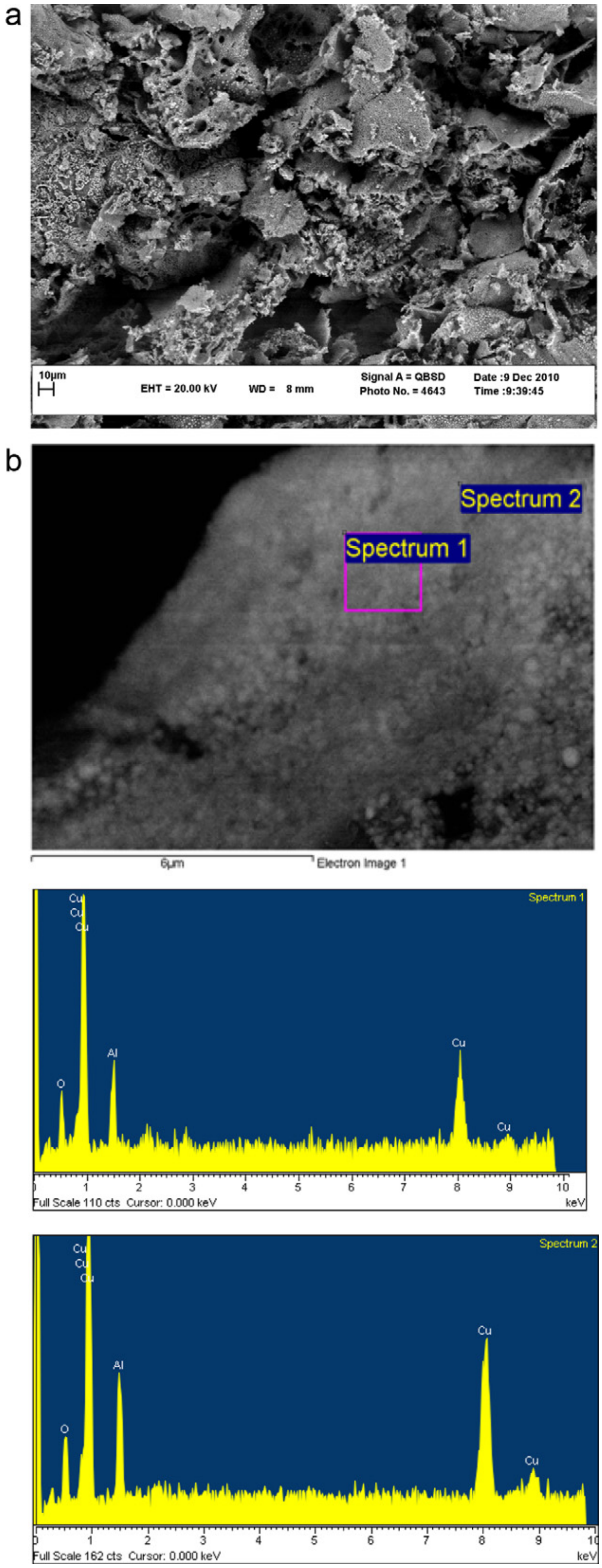

Fig. 5. (a) The SEM micrograph of Cu–Al_2O_3 nanocomposite. (b) The same micrograph at higher magnification micrograph and EDS patterns of Cu–Al_2O_3 nanocomposite.

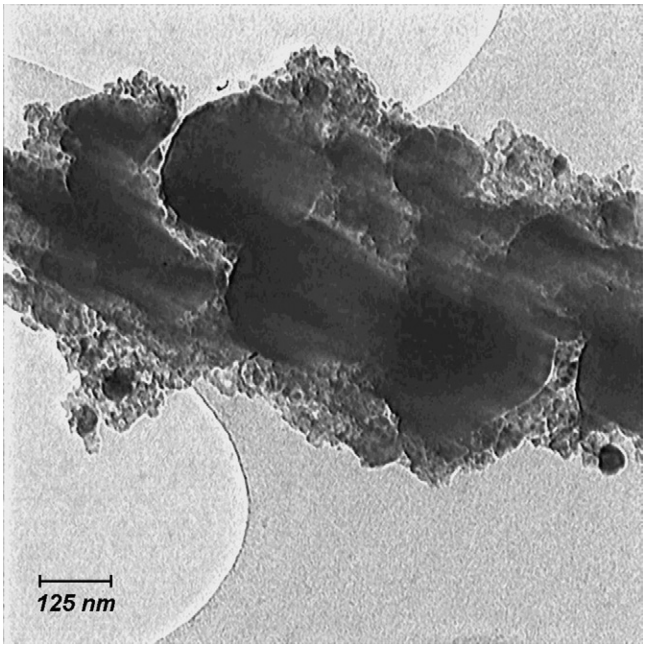

Fig. 6. TEM micrograph of Cu–Al_2O_3 nanocomposite.

Table 1
Role of graphite on the combustion temperature.

Mode	Combustion temperature (°C)
Without graphite	784
With presence of graphite	718

of X-ray for metallic copper with respect to aluminum oxide. In order to see aluminum oxide peaks, powder of synthesized product was solved in nitric acid (HNO_3 to water ratio 1:1) and afterward the residue material washed in distilled water [20]. Then residue material was dried in oven at temperature of about 65 °C for 40 min. The XRD pattern of dried powder is given in Fig. 4, as seen the alumina peak appeared and proved its present in all samples.

Crystal size for aluminum oxide and metallic copper was calculated by Scherer's equation (Eq. (11)).

$$D = \left(\frac{0.9\lambda}{\beta \cos\theta}\right) \qquad (11)$$

where D is the crystallites size in nm, λ the radiation of wavelength (Cu Kα1, 0.15406 nm), β the full width at half of the maximum in radians and θ is the Bragg-angle. The results show that the crystal size of aluminum oxide and metallic copper are 28 and 330 nm respectively for samples with the F/O ratio equals 1.5. Table 1 shows the dependence of combustion temperature on graphite content. As seen addition, graphite causes to decrease combustion temperature and leads to decrease the production of copper oxides. As a matter of fact, role of graphite becomes highlight as system temperature increases, particularly after ignition. In the other word at room temperature and even less than ignition temperature graphite has not any significant effect on reduction process and plays like an inert material. In fact at higher temperature, graphite acts as a reduction agent to reduce copper oxides or prevents the oxidation of produced copper.

SEM micrographs of Cu–Al_2O_3 nanocomposite are shown in Fig. 5a and b. The EDS patterns for copper–alumina nanocomposite are illustrated in Fig. 5b. In the patterns the copper, aluminum and oxygen peaks can be seen. Comparison Fig. 3 and Fig. 5 implies that theses peaks belong to copper and alumina (in the XRD patterns (see Figs. 3c and Fig. 4) only metallic copper and alumina exist). Whereas, the diameter spectrum is more than nano scale, both of synthesis products (copper and alumina) have been seen in the EDS patterns, even with spot spectrometry (Fig. 5b spectrum 2). In order to clarify the fabrication of nano sized alumina from copper matrix TEM micrograph can be useful (see Fig. 6). As seen nano sized alumina distribute in the copper matrix. The micrographs prove that the nanocomposite can be produced just in one-step, i.e. without any additional step for reduction. As seen whereof volume fraction of alumina is more in the final products, but some agglomerated alumina can be seen (Fig. 6). The reason for agglomeration of alumina returns to high surface energy of nano sized particles. Indeed, it causes some producing alumina stick together to decrease the surface energy. Nonetheless, many amount of production alumina remains in the nano scale.

4. Conclusions

In this investigation, solution combustion synthesis has been used for the fabrication of Cu–Al_2O_3 nanocomposite. The research has some results such as:

- Fabrication of Cu–Al_2O_3 nanocomposite via solution combustion synthesis route can be done just in one-step.
- In experiments without graphite, the high combustion temperature and vicinity of products with oxygen prevent producing metallic copper.
- Adding graphite as an auxiliary material can produce in situ reducing atmosphere to prevent copper oxidation.
- With increasing graphite and decreasing the combustion temperature, spinel $CuAlO_2$ phase was eliminated.

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