



Formation of copper aluminate spinel and cuprous aluminate delafossite to thermally stabilize simulated copper-laden sludge

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ARTICLE INFO

Article history:

Received 19 November 2009

Received in revised form 5 May 2010

Accepted 6 May 2010

Available online 12 May 2010

Keywords:

Sludge

Copper

Spinel

Alumina

Kaolinite

ABSTRACT

The study reported herein indicated the stabilization mechanisms at work when copper-laden sludge is thermally treated with γ -alumina and kaolinite precursors, and evaluated the prolonged leachability of their product phases. Four copper-containing phases – copper oxide (CuO), cuprous oxide (Cu₂O), copper aluminate spinel (CuAl₂O₄), and cuprous aluminate delafossite (CuAlO₂) – were found in the thermal reactions of the investigated systems. These phases were independently synthesized for leaching by 0.1 M HCl aqueous solution, and the relative leachabilities were found to be CuAl₂O₄ < CuAlO₂ << Cu₂O < CuO. The sintering condition and formation mechanism employed to stabilize copper into CuAl₂O₄ and CuAlO₂ are extensively discussed here. With a 3 h of short sintering, it was found that CuAl₂O₄ could be effectively formed between 850 and 950 °C by the γ -alumina precursor. Although kaolinite had a lower incorporation capability than γ -alumina, it was found to transform a considerable amount of copper into CuAl₂O₄ between 950 and 1000 °C. At higher temperatures, CuAlO₂ was produced only in the γ -alumina system as the occurrence of Cu₂O-cristobalite solution in the kaolinite system precluded the production of CuAlO₂. The hypothesis that the spinel formation mechanism has two stages was supported by the results of the changing Cu/Al mole ratio in the system, and the rate-limiting step was identified as the diffusion process in the second stage.

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1. Introduction

Hazardous copper ions can cause severe damage to the stomach, intestines, and liver. They can also cause anemia in humans [1] and are highly toxic for some aquatic biota [2–4]. The various production processes relating to circuit board printing, metal surface treatment and mining operations comprise the primary sources for the discharge of hazardous copper. In Taiwan, for instance, over 100,000 tons of copper-laden sludge is produced annually, and because copper is highly leachable that sludge increases the risk of water and soil pollution.

A conventional method of treating hazardous metal sludge is to stabilize/solidify (SS) solid waste by using cement prior to landfill. This method is attractive because of its low initial cost [5]. However, a large amount of cementitious material is required to make solidified waste sufficiently strong to prevent the leaching of hazardous metals from broken products, and this significantly increases the volume of cement needed for landfill [6–8]. It has also been found that the metal incorporation mechanisms in cement

products are not unconditionally stable and that the reactions of incorporation may be reversible. Many observations have demonstrated that these cement products have been unable to prevent the leaching of heavy metals in acidic environments, i.e., at pH levels of less than 4.0 [9,10], or under conditions of aggressive CO₂ attack [5]. Moreover, the cost of disposing of cemented sludge that contains hazardous metals has significantly increased due to the introduction of stringent regulations that limit the number of landfills qualified for receiving such waste. Therefore, alternative heavy metal stabilization strategies that depend on irreversible stabilization mechanisms and enable the reuse of stabilized products are needed.

The stabilization of metal sludge via thermal treatment has the potential to convert hazardous metal-laden sludge from the waste stream into reusable products. The goal is to significantly reduce the metal leachability of products via an irreversible transformation of metals into their mineral phases after thermal treatment [11–18]. Shih et al. successfully stabilized nickel by sintering its oxide with alumina (Al₂O₃), hematite (Fe₂O₃), and kaolinite (Al₂Si₂O₅(OH)₄) [11,17,18]. They found that the sintering of simulated sludge at 1000 °C with alumina and at 600 °C with hematite, respectively, resulted in the formation of nickel aluminate spinel and nickel ferrite spinel. The long-term leachability of nickel dropped

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dramatically in its alumina and ferrite spinel phases, when compared to the leachability levels associated with nickel oxide (NiO). Copper has been found to react with alumina at high temperatures [14,19–21], and thus the strategy of sintering copper-laden sludge with aluminum-rich precursors shows promise of stabilizing copper as well. However, crucial factors in this process – such as incorporation mechanisms, kinetics, stabilization effects, and optimal processing – warranted thorough investigation prior to practical application.

The aim of this study reported here was to evaluate the technical feasibility of incorporating copper-laden sludge into marketable construction ceramics, and thus to reduce the hazard of environmental pollution without additional costs. By adopting sintering time and temperature regime to levels followed in the industrial manufacture of construction ceramics, the study investigated the copper incorporation behavior of two aluminum-rich precursors, γ -alumina and kaolinite, and evaluated the copper leachabilities of copper-bearing phases to understand their stabilization effects.

2. Materials and methods

Copper oxide powder was purchased from Fisher Scientific. The γ -alumina was prepared from HiQ-7223 alumina powder manufactured by Alcoa Corp., with a reported average particle size (d_{50}) of 54.8 nm. As received, the HiQ-7223 alumina was confirmed by powder X-ray diffraction (XRD) to be in the boehmite phase (AlOOH ; ICDD PDF #74-1895). Following heat treatment at 975 °C for 3 h, it was successfully converted to a γ -alumina dominant material [22,23]. Acid washed USP grade kaolinite powder from Fisher Scientific yielded a BET surface area of $9.0 \pm 2.9 \text{ m}^2/\text{g}$, and its powder XRD pattern matched kaolinite ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$; ICDD PDF #78-1996).

Copper incorporation experiments were conducted using copper oxide to simulate the high temperature phase of copper in sludge, sintering it with the γ -alumina or kaolinite precursor. Copper oxide and the precursors were mixed by ball milling in water slurry for 24 h and then dried at 105 °C for 2 days. The dried solids were further homogenized by mortar and pestle grinding. Shaped into pellets of 13 mm diameter at 6 MPa, the solids were sintered at targeted temperatures ranging from 600 to 1200 °C. After sintering, the pellets were air-quenched and ground into powders for XRD analysis. In practice, construction ceramics may incorporate very low levels of metal sludge, so that product properties are not compromised. However, to investigate the incorporation mechanism of copper, the raw materials in this study were prepared with Cu/Al mole ratios of 0.5 unless specified.

After identifying the potential copper-containing phases (CuO , Cu_2O , CuAl_2O_4 , CuAlO_2) in the products, the study evaluated their intrinsic leachability under prolonged acidic attack. The pure phases of cuprous aluminate (CuAlO_2) and copper alumina spinel (CuAl_2O_4) were prepared by sintering the $\text{CuO}/\text{Al}_2\text{O}_3$ powder mixture with Cu/Al mole ratios of 1 and 0.5 at 1050 and 950 °C, respectively, for 20 days. Cuprous oxide (Cu_2O) was prepared by sintering copper oxide (CuO) powder at 1050 °C for 1 day. Phase transformation during sintering was monitored by powder XRD patterns with an angular range (2θ) of 10–80° using X'Pert PRO X-ray Diffraction System (PANalytical). The Cu X-ray tube was operated at 45 kV and 40 mA, and a hybrid monochromator, consisting of an X-ray mirror and a Ge crystal, was used for the incident beam. The data were collected with a step size of 0.01° and a counting time of 10 s per step. The leachability under acidic environment was evaluated by using 0.1 M hydrochloric (HCl) solution as the extraction fluid. Each testing vial was filled with 10 mL of extraction solution and 0.5 g of powder sample, and then agitated by an end-over-end rotator at 60 rpm for periods of 1 h–11 days. At the end of each period, the leachates were filtered with 0.2- μm syringe

filters with pH measured, and the concentration of copper derived with a TJA IRIS Advantage/1000 Radial ICP spectrometer calibrated against CLARITAS certified reference solution (SPEX CertiPrep, Inc.). The reported leachability data were normalized by the BET surface areas of powder samples prior to leaching test, using a Beckman Coulter SA3100 surface area and pore size analyzer.

3. Results and discussions

3.1. Leachability of the product phases

Fig. 1 shows the XRD patterns of copper oxide (CuO), cuprous oxide (Cu_2O), copper aluminate spinel (CuAl_2O_4), and cuprous aluminate (CuAlO_2) used for the leaching test in this study. All

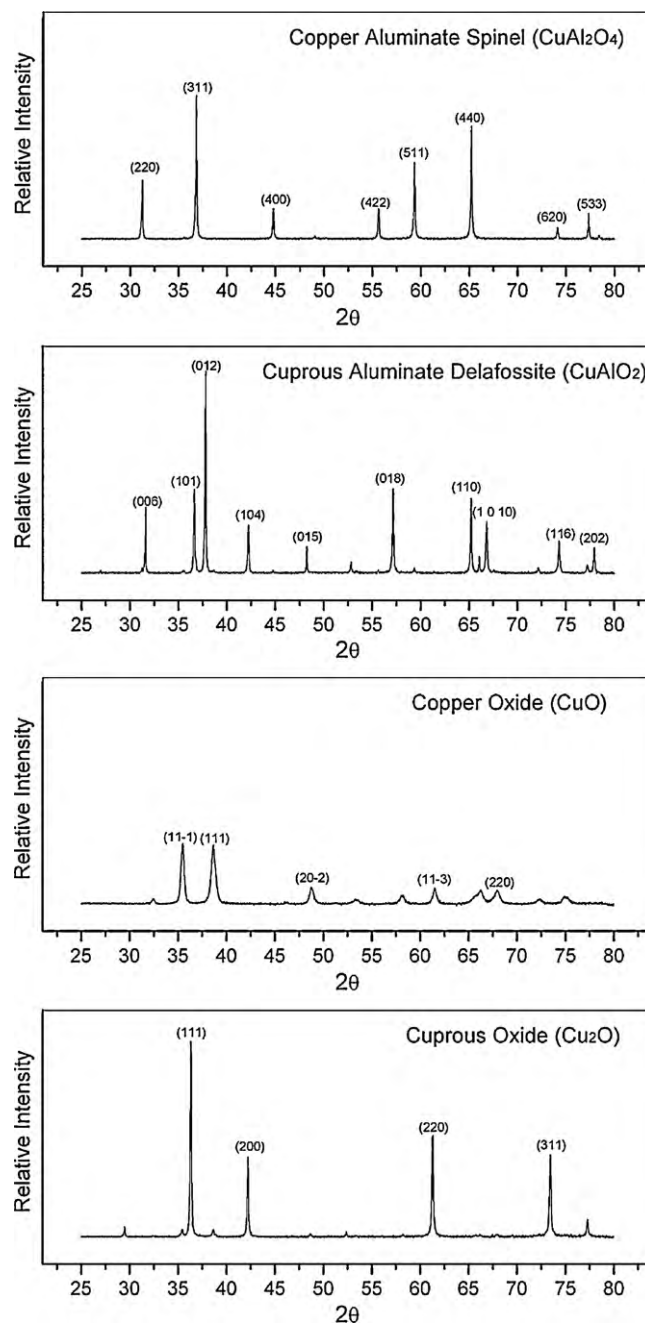


Fig. 1. XRD patterns and the major diffraction planes (hkl) of the four copper phases (CuAl_2O_4 , CuAlO_2 , CuO , Cu_2O) generated in this study. The Cu–Al phases were produced by thermal reactions between CuO and $\gamma\text{-Al}_2\text{O}_3$.

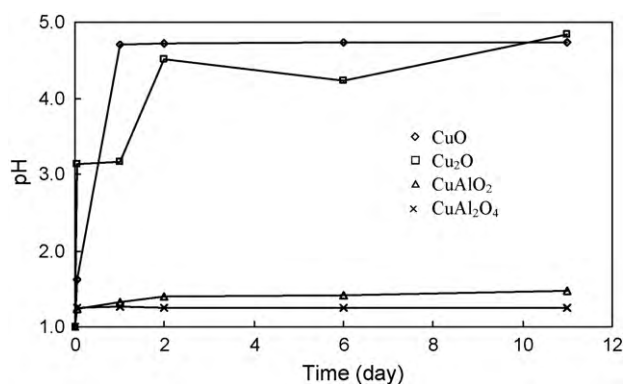


Fig. 2. The pH values of sampled leachate from the four copper-containing phases in this study. The leaching fluid was 0.1 M HCl aqueous solution, and each leaching vial was filled with 10 mL leaching fluid and 0.5 g dry powder. The vials were then agitated by tumbling end-over-end at 60 rpm between 1 h and 11 days.

four single-phase samples were synthesized without observable remaining reactants from their XRD patterns. The results of solution pH after the 1 h–11 days leaching tests are plotted in Fig. 2. Both CuO and Cu₂O showed a significant increase of pH in the extraction solution after 1–2 days of leaching, whereas CuAl₂O₄ and CuAlO₂ showed nearly no increase of pH in the solution at the end of the leaching experiment. The increase in pH resulted from the dissolution of crystal cations that exchanged with protons in the solution (effectively, an acid/base reaction). This was accompanied by the destruction of crystals by the acidic solution. The significant increase in leachate pH revealed both CuO and Cu₂O to be more vulnerable to proton-mediated dissolution.

Long-term leaching is dominated by surface reactions, and thus the leaching rate is likely to be proportional to the surface area. Fig. 3 shows the variation of leached copper normalized with

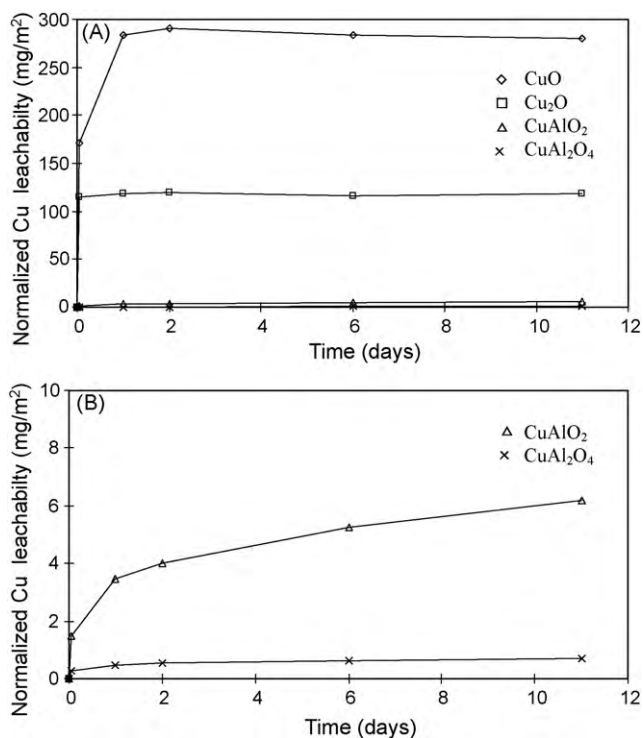


Fig. 3. Leached copper of the four copper-containing phases (A) and copper-aluminates (B) normalized by their surface areas. The surface areas of CuO, Cu₂O, CuAlO₂ and CuAl₂O₄ are 0.230, 0.509, 2.813 and 2.203 m²/g, respectively. The leaching condition was the same as described in Fig. 2.

respect to the surface area of leached samples. The normalized copper quantities leached from CuO and Cu₂O were much higher than those from CuAl₂O₄ and CuAlO₂, and this was consistent with the more significant pH change in the extraction solutions of CuO and Cu₂O. Although both CuAl₂O₄ and CuAlO₂ were in low leachability, CuAl₂O₄ showed relatively less leachable copper compared to CuAlO₂. Therefore, the results suggest that the use of CuAl₂O₄ would be a better strategy for stabilizing copper, considering the copper phase transformation during thermal treatment.

3.2. Phase transformation of copper from sintering with the γ -alumina precursor

Fig. 4 shows the XRD pattern details within $2\theta = 35\text{--}40^\circ$ for the samples sintered from the γ -alumina precursor at a temperature range of 600–1200 °C for 3 h. Within this 2θ range, several major diffraction planes of the copper phases can be used to observe the phase transformation process, including (1 1 – 1) of CuO (35.50°), (1 1 1) of CuO (38.69°), (3 1 1) of CuAl₂O₄ (36.84°), (1 0 1) of CuAlO₂ (36.60°), and (0 1 2) of CuAlO₂ (37.77°). The peak of copper aluminate spinel (CuAl₂O₄) appeared after the sintering temperature exceeded 700 °C; this peak intensity increased with increased temperature until 950 °C. In contrast, the relative intensity of copper oxide, as the starting material, began to decrease at the temperature of 700 °C, and disappeared as the sintering temperature went over 1000 °C. The results revealed that, with 3-h of short sintering for copper oxide doped γ -alumina, the phase of copper aluminate

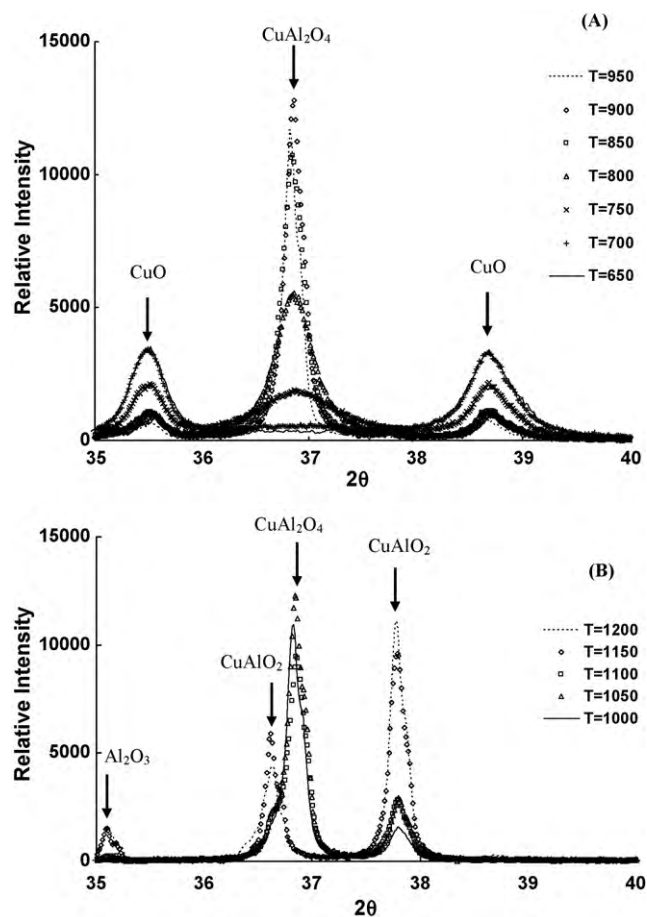


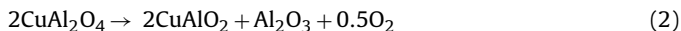
Fig. 4. XRD pattern details ($2\theta = 35\text{--}40^\circ$) showing the phase change of copper oxide sintered with γ -alumina precursor (Cu/Al mole ratio = 0.5) at temperature range A. 600–900 °C and range B. 1000–1200 °C for 3 h. (A)

spinel became observable in the XRD pattern at temperatures above 700 °C:



The lowest temperature for observing the copper aluminate spinel in this experiment differed from the results of the equilibrium experiments carried out by Jacob and Alcock [24], where the formation of copper aluminate spinel was reported to start at 612 °C. Since the nucleation of the reaction product (copper aluminate spinel) is slow at relatively low temperatures [19], the diffusion of the metal ions to the bulk grain was slower than to the grain boundaries and the surfaces of pores. The interaction between the reactants was confined to the first monolayer of their grains, which may be described as a solid-state reaction on surface. Therefore, the thickness of this type of “surface spinel species” was too thin to be detected by XRD. A similar result was reported by Gadalla and White, who used thermogravimetric analysis to detect the formation of copper aluminate [25]. Jacob and Alcock utilized an electrochemical method to detect the formation of copper aluminate spinel [24] in their equilibrium experiment, and reported a relatively lower temperature for initiating the formation of copper aluminate spinel. In aiming to stabilize hazardous metal in the product, the temperature for obtaining well-crystallized phase was more critical than just achieving surface reaction in the early stage.

The disappearance of spinel phase at higher temperatures was due to the formation of the cuprous aluminate delafossite (CuAlO_2) by the following reactions:



The CuAlO_2 peaks appeared when the sintering temperature was over 1000 °C, as illustrated in Fig. 4. The reaction (2) occurred thermodynamically if the sintering temperature was over 1175 °C and if the mole ratio of Cu to the Al (Γ) was under 0.5 [24,26]. If Γ was over 0.5, then the excess CuO in reaction (1) would react with CuAl_2O_4 to form CuAlO_2 as the sintering temperature was around 1000 °C. Further excess of CuO would be reduced to Cu_2O as described by reactions (3) [24,26]. Although Γ was equal to 0.5 in our experiment, CuAlO_2 could also form because the rates of CuAl_2O_4 and CuAlO_2 formation depended on the crystallographic orientation of the surface of alumina particles, especially if the system was not in thermodynamic equilibrium. At the transitional range where CuAl_2O_4 and CuAlO_2 coexist, copper prefers to form CuAl_2O_4 by reacting with the (0001) plane of alumina, and CuAlO_2 by reacting with the (1120) plane [26].

3.3. Phase transformation of copper from sintering with the kaolinite precursor

Fig. 5 demonstrates the XRD patterns of the samples at various sintering temperatures with the kaolinite precursor. The peak of copper aluminate spinel started to appear at the temperature of around 800 °C and the intensity of the spinel peak increased with the rise of sintering temperature to the level of 950 °C. However, comparing Figs. 4A and 5A, it was found that the relative intensity of CuAl_2O_4 from the kaolinite precursor (Fig. 5A) was much less than the intensity of CuAl_2O_4 from the γ -alumina precursor (Fig. 4A). The significant signal from CuO diffraction peaks showed that the transformation rate of copper from CuO to CuAl_2O_4 spinel by the kaolinite precursor was much slower than the rate discerned from the γ -alumina precursor. Moreover, unlike those from the γ -alumina precursor, the CuAlO_2 phase was not found at higher temperatures (>1000 °C), as shown in Fig. 5B.

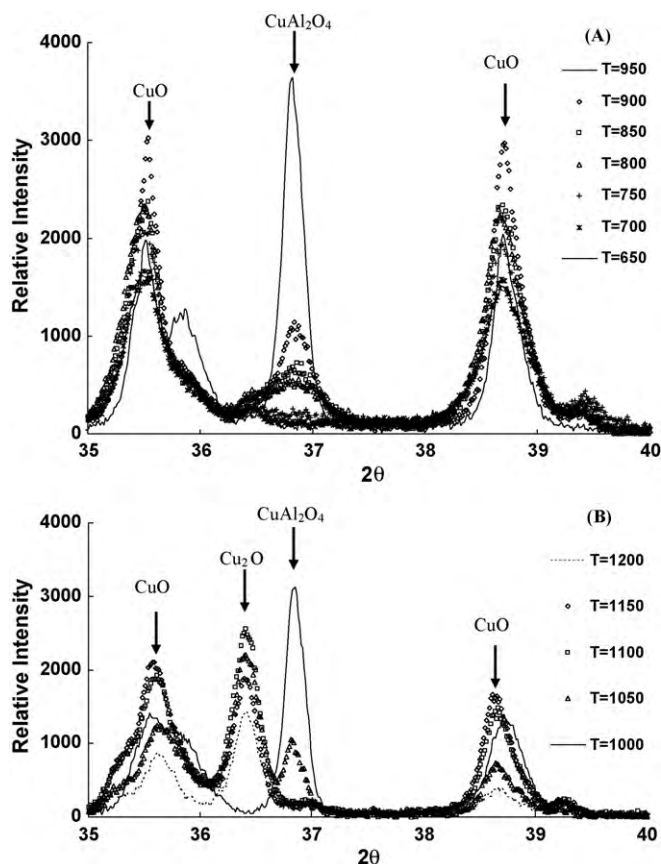
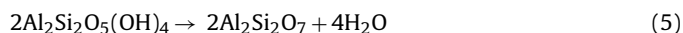


Fig. 5. XRD patterns (between $2\theta = 35\text{--}40^\circ$) of CuO + kaolinite samples (Cu/Al mole ratio = 0.5) sintered at various temperatures (A: 600–950 °C; B: 1000–1200 °C) for 3 h.

Bolt et al. reported that the formation rate of spinels may depend on the site-preference energy and the surface rupture of alumina substrate during sintering [19]. Site-preference energy is the energy change involved in the diffusion of metal ions through a series of alternating tetrahedral and octahedral vacancies. Energy changes of vacancies in the kaolinite precursor should be much higher than that of γ -alumina because of the additional Si–O tetrahedral structure in the kaolinite system. Moreover, the surface of the γ -alumina particle is severely disrupted ($\sim 1\ \mu\text{m}$) after annealing because of the transformation of γ -alumina to α -alumina [18,19]. The severe rupture increases the surface area and increases the diffusion rate. The spinel formation rate at 500–1000 °C from a kaolinite precursor is thus much slower than that from a γ -alumina precursor.

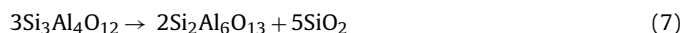
In this study, kaolinite underwent a series of phase transformations during thermal treatment. Endothermic dehydration, which began at 550–600 °C, generated metakaolin, $\text{Al}_2\text{Si}_2\text{O}_7$, and resulted in continuous hydroxyl loss ($-\text{OH}$) up to a temperature of 900 °C:



Further heating to 925–950 °C converted metakaolin to a defect aluminum–silicon spinel, $\text{Si}_3\text{Al}_4\text{O}_{12}$, which is sometimes also referred to as a γ -alumina type structure:



Upon calcination to ~ 1050 °C, the spinel phase ($\text{Si}_3\text{Al}_4\text{O}_{12}$) nucleated and transformed into mullite ($\text{Si}_2\text{Al}_6\text{O}_{13}$) and cristobalite (SiO_2):



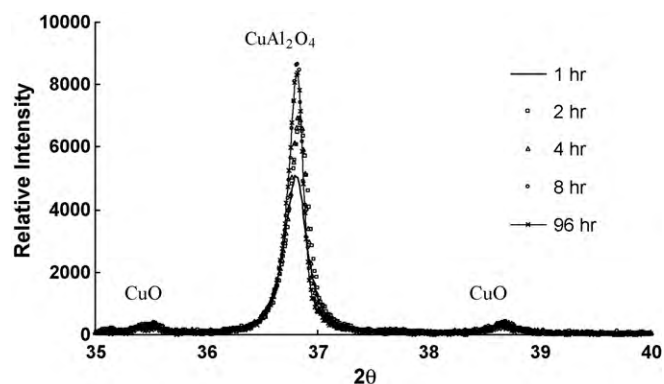


Fig. 6. XRD pattern details ($2\theta = 35\text{--}40^\circ$) of $\Gamma = 0.5$ (Cu/Al mole ratio = 0.5) CuO + γ -alumina sample sintered at 950°C for 1–96 h.

A significant signal increase of the copper aluminate spinel peak appeared at $950\text{--}1000^\circ\text{C}$ (Fig. 5), where the defect aluminum–silicon spinel structure was dominant in the system. Unlike sintering with the γ -alumina precursor, the CuAlO_2 phase was not formed in this case at higher temperatures because of the participation of cristobalite in the system. Cuprous oxide was found to dissolve in cristobalite at higher temperatures [27]. The active energy needed for the Cu_2O -cristobalite solution and mullite to form CuAlO_2 was too high in this temperature range. A similar phenomenon was observed in the recent work of Xiao et al. on a three-oxide system [28].

3.4. Effect of Cu/Al mole ratio (Γ)

Besides the precursor materials, sintering condition is also an important aspect of the energy cost and industrial feasibility of this practice. Fig. 6 shows the XRD patterns with various dwelling times at 950°C for samples mixed with γ -alumina precursor and CuO at Cu/Al mole ratio of 0.5 ($\Gamma = 0.5$). Copper oxide was significantly transformed to copper aluminate spinel (CuAl_2O_4) after sintering for 2 h from the γ -alumina precursor. However, a minor copper oxide signal was still detectable even after sintering the sample for 96 h. This observation is also supported by our work in preparing the sample for leaching study, as it took 20 days of 950°C sintering to achieve a CuAl_2O_4 product without a detectable CuO signal. When $\Gamma = 0.5$, a result of complete transformation within a short period indicated that a fast Cu–Al spinel reaction and extensive diffusion process had occurred. The result of a significantly high transformation rate in the first couple of hours revealed that the reaction between alumina and copper oxide was reasonably fast. However, the rate-limiting step of achieving complete transformation was the diffusion process at a later stage. After the formation of CuAl_2O_4 at the interface between alumina and copper oxide particles, the remaining Al and Cu atoms on each side had to counter-diffuse through the CuAl_2O_4 zone to trigger further spinel reaction. As a relatively more stable phase in the system, CuAl_2O_4 acted as a diffusion barrier and resulted in the major rate-limiting step to achieving complete spinel transformation of the bulk sample. When the CuAl_2O_4 zone grew thicker at a later stage, the transformation rate was hampered as it became more difficult for Al and Cu to counter-diffuse. Furthermore, when $\Gamma = 0.5$, the nature of local inhomogeneity became more profound because the excess of both reactants in their regions had to diffuse over a longer distance to initiate spinel reaction.

The use of $\Gamma = 0.5$ was in accordance with the stoichiometric ratio of CuAl_2O_4 spinel and was simply chosen to test the theoretical maximum capacity of incorporating copper into spinel phase. In practice, construction ceramics incorporate much lower levels of

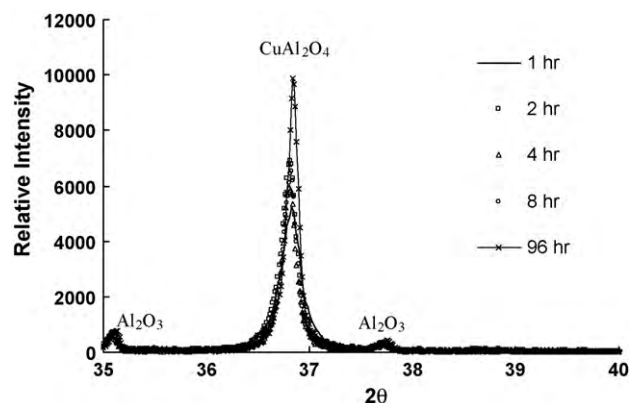


Fig. 7. XRD pattern details ($2\theta = 35\text{--}40^\circ$) of $\Gamma = 0.333$ (Cu/Al mole ratio = 1/3) CuO + γ -alumina sample sintered at 950°C for 1–96 h.

targeted metals, so that overall product property is not affected. To preliminarily test the influence of metal level on the incorporation kinetics, a sample of $\Gamma = 0.333$ was prepared for a 950°C sintering experiment for the same 96-h period (Fig. 7). It was found that the copper oxide was not detectable shortly after 1 h of sintering. This result further suggests that the first stage spinel formation reaction was relatively fast, and once the diffusion process had been facilitated, the overall incorporation efficiency of copper was significantly increased. Over 950°C , prolonged sintering is not needed for the complete elimination of CuO if sufficient alumina is available for the reaction. This can be easily achieved in practical applications by incorporating copper into construction ceramics, where the doped copper from sludge will surely be much less than the available aluminum in the system.

4. Conclusion

The copper aluminate spinel (CuAl_2O_4), which is the less leachable copper phase during thermal treatment of simulated copper-laden sludge and a γ -alumina precursor, can be effectively formed between 850 and 950°C . It was found that at $950\text{--}1000^\circ\text{C}$, the kaolinite precursor could also transform a considerable amount of copper into the copper aluminate spinel although the efficiency was less than that by γ -alumina. The observed result can be explained by the smaller site-preference energy of the γ -alumina precursor and the severe rupture of the top layer of the γ -alumina substrate during sintering. At higher temperatures ($>1100^\circ\text{C}$), cuprous aluminate delafossite (CuAlO_2) was produced in the copper–alumina system, but not in the copper–kaolinite system. This may have occurred because the Cu_2O dissolved in cristobalite at high temperatures, thereby precluding the stabilization of copper via CuAlO_2 with the kaolinite precursor. The experiment of changing the Cu/Al mole ratio (Γ) of raw materials revealed that spinel formation for bulk sample has to go through two stages, a fast first stage of spinel reaction and a slow second stage of diffusing through product (spinel) zone for further reaction. Nevertheless, reducing the Cu/Al mole ratio was found to significantly increase the system capability to completely transform the copper into spinel.

Comparing to the results of previous studies working on the aluminate spinel stabilization for nickel [17,18], the copper aluminate system demonstrates better potential to achieve the spinel stabilization at a lower but narrower temperature range. As sintering temperature reaches 1200°C , the high yield of nickel aluminate spinel will be maintained throughout further sintering process. However, the best operational temperature for achieving CuAl_2O_4 spinel is suggested within the range of $950\text{--}1000^\circ\text{C}$ by this study. With higher sintering temperatures, the reduction of

copper will initiate additional phase transformation mechanisms to form CuAlO_2 or cuprous/copper oxide. This mechanistically driven behavior is particularly important in considering the application for different ceramic products. For instance, the stabilization by nickel aluminate spinel may be used in porcelain and refractory products, but the stabilization by copper aluminate spinel may be better suited for lower temperature tiles and bricks.

Acknowledgement

The Alcoa Corporation is acknowledged for providing HiQ®-7223 alumina. We would also like to thank the supports from the Singapore Stanford Partnership and University of Hong Kong Seed Funding.

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