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Stabilization of nickel-laden sludge by a high-temperature $NiCr_2O_4$ synthesis process

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ABSTRACT

The feasibility of stabilizing nickel-laden sludge by a high-temperature $NiCr_2O_4$ synthesis process was investigated with different sintering temperatures, salt contents, molar ratios, and reaction atmospheres. The crystalline phases of species were investigated by using an X-ray diffraction, and the surface characteristics of particles were observed by scanning electron microscopy. The leaching behavior of the stabilized sludge was evaluated by Toxicity Characteristic Leaching Procedure (TCLP) test. The results indicated that $NiCr_2O_4$ was formed at around 800 °C by transforming NiO and Cr_2O_3 into a spinel structure. Leaching concentrations of both nickel and chromium decreased with an increase in the sintering temperature. The existence of salt in the sludge disturbed the formation of spinel, but a moderate salt content contributed to stabilization efficiency. A Cr/Ni molar ratio >2 also contributed to the stabilization efficiency of heavy metals after the thermal process. $NiCr_2O_4$ was transformed from simulated sludge under both an N_2 and air atmosphere. The sintering strategy designed for nickel-laden sludge was proven to be beneficial in stabilizing nickel and chromium.

1. Introduction

According to statistical data of the Taiwanese Environmental Protection Administration, 164,309 tons of heavy metal sludge was generated in 2010 in Taiwan. Most of the sludge is from metal surface treatment, anodizing, plating, and printed circuit board manufacture. Concentrations of heavy metal ions in the sludge always exceed the legal limit according to the Toxic Characteristic Leaching Procedure (TCLP). The complicated composition and various toxic heavy metals that exist in sludge from different sources are also seen as a challenge for stabilization and reuse. Without suitable treatment, disposal of heavy metal sludge may contaminate soil and groundwater, and even endanger human health [1].

A conventional way of treating heavy metal sludge is cement solidification/stabilization prior to landfill for its cheap cost and easy operation [2]. However, cement solidification may only offer transient stabilization ability, and long-term leaching problems of heavy metals in acidic environments are of concern and are regarded as disadvantages of cementation stabilization [3]. In recent years, several studies successfully transformed heavy metal sludge into aluminate or ferrite spinel structures to obtain the objective of sludge stabilization [4–8]. With this technology, it is also feasible to reuse or recycle the waste sludge as new ceramic materials [9]. It was previously reported that copper can be incorporated into the alumina (Al_2O_3) and hematite (Fe_2O_3) structure to form $CuAl_2O_4$ and $CuFe_2O_4$ spinel by a thermal process [4,7]. By varying the sintering temperature and performing a long-term TCLP test, the strategy for stabilizing toxic sludge was unequivocally confirmed. Although copper-laden sludge forms the majority of heavy metal sludge, nickel-laden sludge is also regarded as an urgent target for proper treatment. Shih et al. successfully transformed nickel into $NiAl_2O_4$ and $NiFe_2O_4$ by sintering its oxide with alumina and hematite [3,6,10]. The successful reduction of nickel mobility and leachability in acidic environments has also been demonstrated at the same time. However, besides transforming heavy metal into aluminate or ferrite system spinel, chromite spinel is also considered an important spinel system with potential applications in material sciences [11]. In addition, the catalytic ability and magnetic properties exhibited by $NiCr_2O_4$ also provide potential for removing contaminants in environmental engineering [12,13]. And transforming the sludge into chromite spinel has not yet been particularly investigated to stabilize heavy metals in the past. Therefore, incorporating metal ions into a chromium oxide structure to form chromite spinel is also a potential worthy strategy to stabilize heavy metal sludge. However, crucial factors, optimal processing, and stabilization effects in the process still need to be investigated prior to its practical application.

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Conventionally, chromite spinel is prepared by the fusion of respective divalent metal oxides with Cr_2O_3 in appropriate molar ratios at high temperature [14]. The synthesis of chromite spinel was reported by the decomposition of co-precipitated hydroxides at 600–900 °C [15]. Spinel $ZnCr_2O_4$ was also successfully prepared from a mixture of ZnO and Cr_2O_3 by a conventional solid-state reaction at the temperature of 900 °C for 240 min [16].

In this study, we evaluated the technical feasibility of transforming heavy metal sludge into chromite spinel by a thermal process, and thus reduce the toxicity of hazardous wastes. The effects of temperature, conductivity, molar ratio, and reaction atmosphere on the transformation of $NiCr_2O_4$ from nickel species in simulated heavy metal sludge are discussed. The nickel leachability of $NiCr_2O_3$ was also evaluated to understand the stabilization effects.

2. Materials and methods

2.1. Preparation of simulated sludge

Because of the complex composition of real heavy metal sludge, simulated nickel-laden sludge was prepared and applied in this study. A co-precipitation method was conducted to prepare the simulated sludge. Nickel chloride ($NiCl_2·6H_2O$) and chromium chloride ($CrCl_3·6H_2O$) were mixed in a specific ratio by stirring in deionized water to prepare a solution containing high concentrations of nickel and chromium. Then the pH was adjusted to a range of 7–8 with continual stirring and the addition of NaOH and HNO_3. The precipitate composed of nickel hydroxide and chromium hydroxide was used as the simulated heavy metal sludge. The simulated sludge was dried at 105 °C, and ground to pass through a 74 μm sieve (ASTM 200 mesh). In each sintering trials, the sludge sample was pressed into a small pellet with 13 mm diameter in advance under a compression pressure of 2 t/cm^2. All chemicals used in this study were of reagent grade.

2.2. Desalination process

The existence of chlorine ions may result in a decrease in spinel formation efficiency. In this experiment, the content of chloride salt in the simulated sludge was repeatedly adjusted by washing with deionized water, and the slurry was centrifuged at 8000 rpm for 6 min. The conductivity of the upper layer solution was measured to indicate the amount of salt in the sludge. Then the simulated sludge with a conductivity of 0.2–14 ms/cm was dried, pelletized and subjected to the sintering process.

2.3. Sintering temperature, molar ratio, and atmospheric effect

To interpret the effect of temperature on the formation of the chromite spinel structure, simulated sludge with a Cr/Ni molar ratio of 2 and conductivity of 1.4 ms/cm was sintered at varied temperatures ranging 500–1200 °C for 3 h at a heating rate of 10 °C/min in an air atmosphere. In addition to the sintering temperature, the molar ratio of Cr/Ni is also an important controlling parameter for synthesizing spinel and the stabilization efficiency. The simulated sludge with a conductivity of 3 ms/cm and different Cr/Ni molar ratios of 1–6 was sintered at 1200 °C for 3 h. The furnace was filled with two reaction atmospheres (nitrogen and air) during the thermal process. After sintering, samples were air-quenched at room temperature and ground into powders to pass through a 74 μm sieve for product characteristic analysis.

2.4. Product analysis

The stabilization efficiency of heavy metals after the sintering process was determined through a toxicity characteristic leaching procedure (TCLP). Concentrations of heavy metals were analyzed by inductively coupled plasma-atomic emission spectrometry (ICP-AES, Jobin Yvon, JY24) with triplicate analyses, and average values are presented. The phase transformation of heavy metal sludge and the formation of spinel structures were investigated by X-ray diffraction (XRD, Rigaku RINT2000) and scanning electron microscopy (SEM, Hitachi S-2400). The crystalline phases found in the products were identified based on the Joint Committee on Powder Diffraction Standards-International Centre for Diffraction Data (JCPDS-ICDD), including NiO (PDF #47-1049), Cr_2O_3 (PDF #06-0504), and $NiCr_2O_4$ (PDF #23-0432).

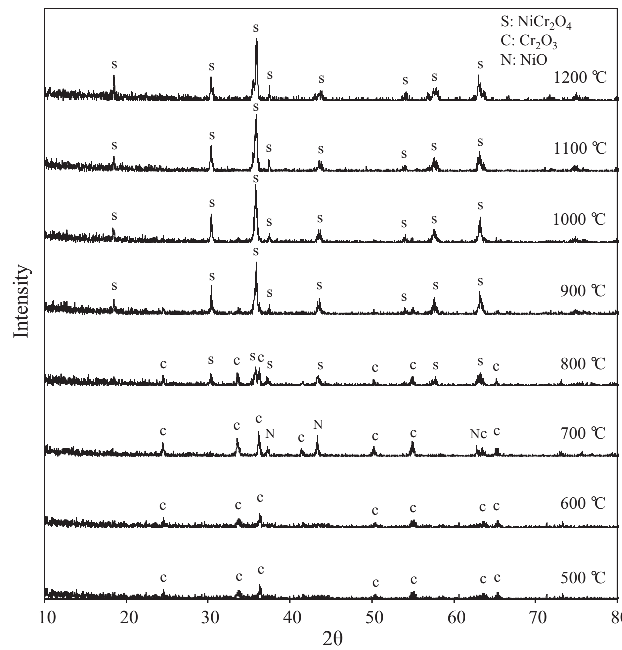

Fig. 1. XRD patterns of samples (with a Cr/Ni ratio of 2 and a conductivity of 1.4 ms/cm) sintered at different temperatures.

3. Results and discussions

3.1. Temperature effect

From previous studies, it was supposed that temperature is one of the most important factors affecting the formation of nickel spinel during the thermal process. Fig. 1 shows the XRD pattern (with 2θ range of 10–80°) of the simulated sludge with a Cr/Ni molar ratio of 2 and conductivity of 1.4 ms/cm sintered at different temperatures. No crystal phase was observed in the XRD pattern of samples before processing. The crystal phases of Cr_2O_3 and NiO were formed at respective sintering temperatures of 500 and 700 °C due to dehydration of chromium hydroxide and nickel hydroxide during the high-temperature process. As the sintering temperature rose to 800 °C, characteristic peaks of $NiCr_2O_4$ were observed in the XRD pattern with decreasing intensities of Cr_2O_3 and NiO. This showed that NiO began to diffuse and was inset into the lattice of Cr_2O_3, and the spinel structure was generated at around 800 °C. The characteristic peaks of Cr_2O_3 had almost completely disappeared at 900 °C, which means that the sludge had been almost completely transformed into nickel chromite spinel after the thermal process. The formation mechanisms of $NiCr_2O_4$ are expressed by the following chemical reactions:

$$2Cr(OH)_3 \rightarrow Cr_2O_3 + 3H_2O \quad (1)$$

(2)$Ni(OH)_2 \rightarrow NiO + H_2O$
(3)$Cr_2O_3 + NiO \rightarrow NiCr_2O_4$

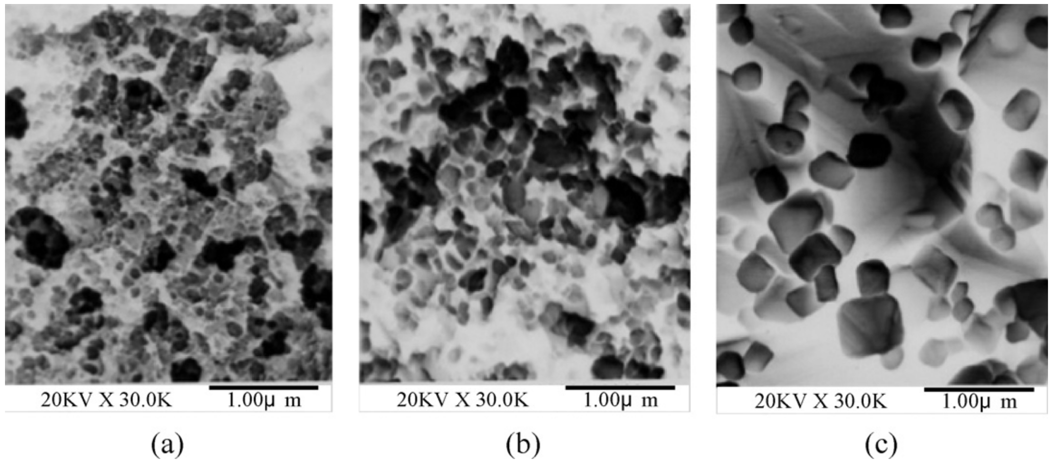

Fig. 2. SEM micrographs of samples (with a Cr/Ni ratio of 2 and a conductivity of 1.4 ms/cm) sintered at (a) 500, (b) 800, and (c) 1200 °C.

The peak intensity of nickel chromite spinel also increased with an increasing temperature to 1200 °C. However, this phenomenon was different from those of other spinel systems, such as aluminate and ferrite spinel, which dissociate to a delafosite phase at temperatures of >1100 °C [4,5].

Fig. 2 shows the microstructures of sludge sintered at 500, 800, and 1200 °C. By analyzing the surface characteristic of sintered sludge from the SEM pictures, it can be seen that a heterogeneous porous structure was present at 500 °C. This observation proves that no reaction had occurred at this temperature, coincident with the XRD results. When the temperature increased to 800 °C, surface particles began to fuse and congregate with fewer porous structures. As the sintering temperature rose to 1200 °C, clear crystalline facets with tetrahedral and octahedral structures were observed, indicating that the sludge had been significantly transformed into the spinel structure. Changes in the microstructure at different temperatures may also affect the leachability of nickel ions in the TCLP test.

To investigate the stabilization efficiency of the simulated sludge after the thermal process, TCLP tests were performed to compare the leachability of samples sintered at different temperatures. Leaching concentrations of nickel and chromium from sintered samples at different temperatures was presented in Fig. 3. Leaching concentrations of nickel and chromium of the sample sintered at 500 °C were about 1391 and 526 mg/L, respectively. The leaching tendencies of both metal ions significantly declined with an increase in the sintering temperature. When the temperature exceeded 1100 °C, leaching concentrations of nickel and chromium were <10 and 2.5 mg/L, respectively. Therefore, the results confirmed that the sintering strategy designed for nickel-laden sludge is beneficial in stabilizing heavy metals.

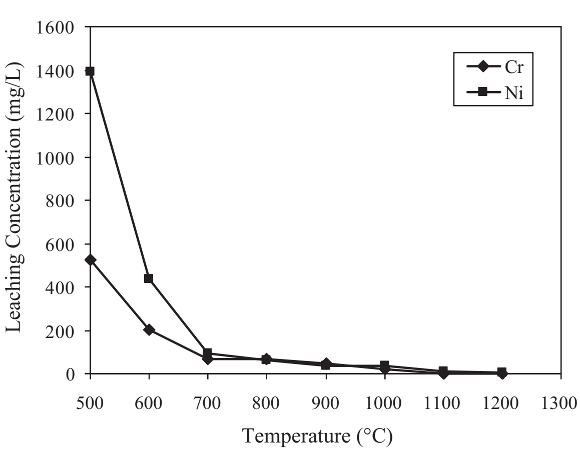

Fig. 3. Leaching concentrations of samples (with a Cr/Ni ratio of 2 and a conductivity of 1.4 ms/cm) sintered at different temperatures.

3.2. Desalination effect

To understand the desalination effect when forming chromite spinel and the stabilization efficiency, the conductivity of the simulated sludge was adjusted from 0.2 to 1, 3, 8, and 14 ms/cm, and the sludge was sintered at 1200 °C for 3 h. Fig. 4 illustrates the effect of the salt content on the formation of the $NiCr_2O_4$ crystalline phase. Characteristic peaks of $NiCr_2O_4$ were only observed at lower conductivities, and the peak intensity of $NiCr_2O_4$ decreased with an increased salt content. The result also showed that only characteristic peaks of Cr_2O_3 and $NiCr_2O_4$ were observed in this system when the conductivity was >3 ms/cm. The crystalline phase of nickel oxide did not form due to the presence of the salt content. In a condition of high conductivity, the salt content might obstruct the diffusion of nickel oxide into the chromium oxide structure at high temperatures. In addition, the chromite spinel has an affinity of chromium ions for octahedral sites [17]. Therefore,

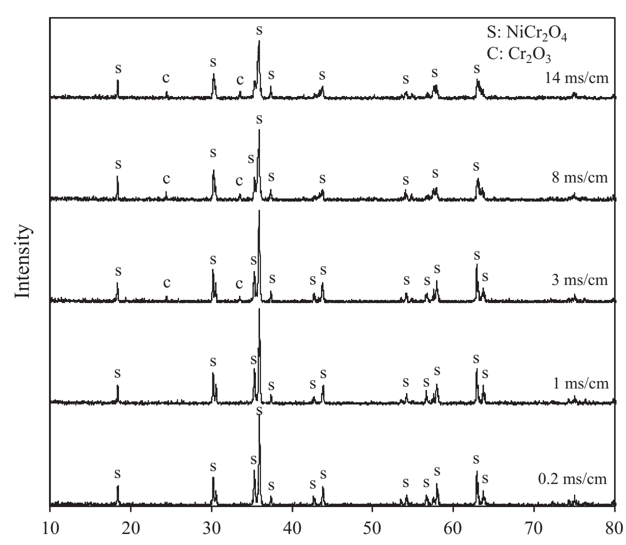

Fig. 4. XRD patterns of samples (with a Cr/Ni ratio of 2) with different conductivities sintered at 1200 °C.

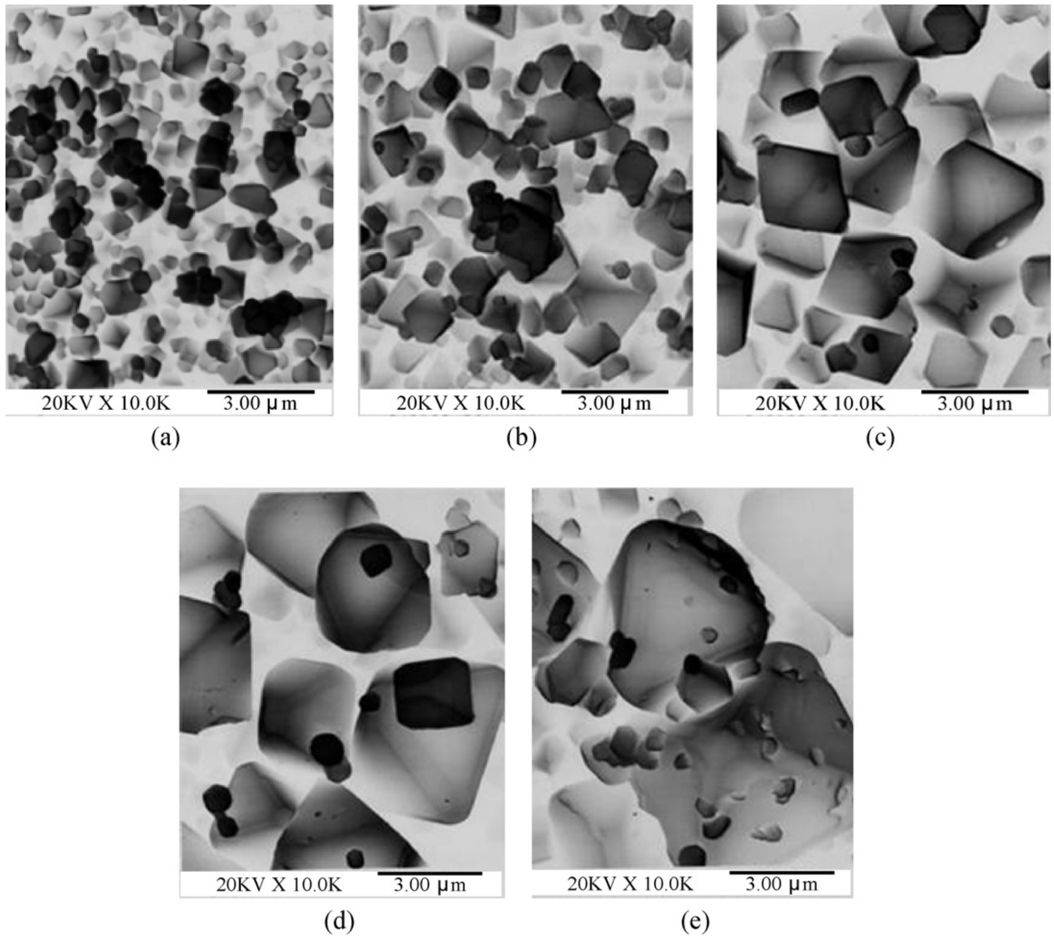

Fig. 5. SEM micrographs of samples (with a Cr/Ni ratio of 2) with different conductivities of (a) 0.2, (b) 1, (c) 3, (d) 8, and (e) 14 ms/cm.

plenty of sodium ions might have occupied vacancies in octahedral sites in the spinel structure, which caused the formation of Cr_2O_3 and deferred the formation of $NiCr_2O_4$. A similar result was also observed by Selim et al. who reported that the presence of sodium ions interfered with the solid reaction between CuO and Fe_2O_3 [18]. It was supposed that removing the salt content from the system would diminish the distance between NiO and Cr_2O_3, thus improving $NiCr_2O_4$ formation efficiency.

Fig. 5 shows SEM results of sintered sludge with different desalination levels at 1200 °C for 3 h. The particle size of spinel crystal increased with an increasing salt content. However, a portion of nonreactive particles was observed on the surface of the spinel crystals as the conductivity rose to 14 ms/cm, which might have affected the leaching behavior of the sintered sludge. Therefore, the existence of chloride in the sludge would affect the spinel particle size and then the stabilization efficiency of spinel after the thermal process. To investigate the desalination effect on the nickel stabilization efficiency, TCLP tests were also performed to compare the leachability of samples with different salt contents. Nickel and chromium leaching concentrations of sintered sludge with different conductivities are presented in Fig. 6. It was found that leaching concentrations of both nickel and chromium decreased with an increase in the conductivity. However, the concentration of chromium slightly increased as the conductivity rose to 14 ms/cm. From the above results, it was concluded that the behavior of a higher leaching concentration was relative to a smaller particle size with a higher specific surface of the spinel at low conductivities. In addition, the lower transformation efficiency would also cause an increase in the leaching concentration at high conductivity. Therefore, the existence of chloride in the sludge affected the leaching behavior of heavy metals and the transformation efficiency of $NiCr_2O_4$.

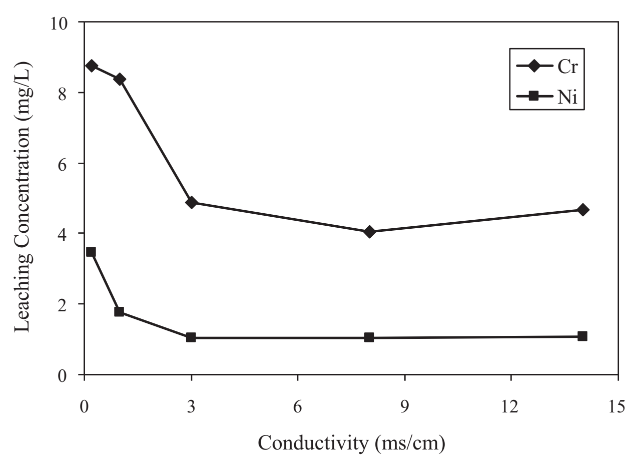

Fig. 6. Leaching concentrations of samples (with a Cr/Ni ratio of 2) with different conductivities sintered at 1200 °C.

3.3. Molar ratio

The initial trivalent ion/divalent ion molar ratio was also concluded to have a significant influence on the formation of spinel materials during the thermal process in the previous study [19].

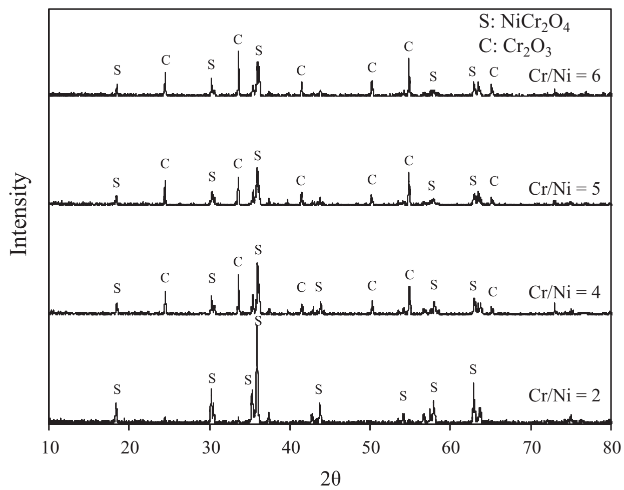

Fig. 7. XRD patterns of samples (with a conductivity of 3 ms/cm) with different molar ratios sintered at 1200 °C.

Although the stoichiometric value of the Cr/Ni molar ratio for spinel synthesis is 2, field sludge generally contains additional divalent and/or trivalent metal oxides. To investigate the appropriate molar ratio for spinel transformation and nickel stabilization, the Cr/Ni molar ratio was set to 1–6, and samples with a conductivity of 3 ms/cm were sintered at 1200 °C for 3 h. Changes in the crystalline phase with different molar ratios are shown in Fig. 7. The results showed that significant nickel chromite spinel was observed, but no nickel oxide was detected in any of the sintered samples, indicating that nickel oxide was completely transformed into nickel chromite after the thermal process. With an increase in the quantities of chromium oxide, a dilution effect might lead to a decrease in the intensity of nickel chromite spinel. The results also indicated that too much chromium oxide was added to the simulated sludge with a high Cr/Ni molar ratio for the formation of nickel chromite spinel.

Fig. 8 shows the relationship between the leaching concentration of TCLP tests and Cr/Ni molar ratio of sintered samples. The leaching concentration of nickel significantly decreased as the molar ratio increased from 1 to 2. The results indicated that samples with a molar ratio of 1 had a higher leaching concentration of nickel because of insufficient chromium oxide to transform the nickel oxide into chromite spinel. After increasing the amount of chromium oxide in the simulated sludge, the leaching concentration of nickel dramatically decreased because of sufficient chromium oxide which provided a higher transformation efficiency of nickel oxide. Therefore, it was concluded that a Cr/Ni molar ratio of >2 will contribute to the stabilization efficiency of heavy metals in the sludge after thermal processing.

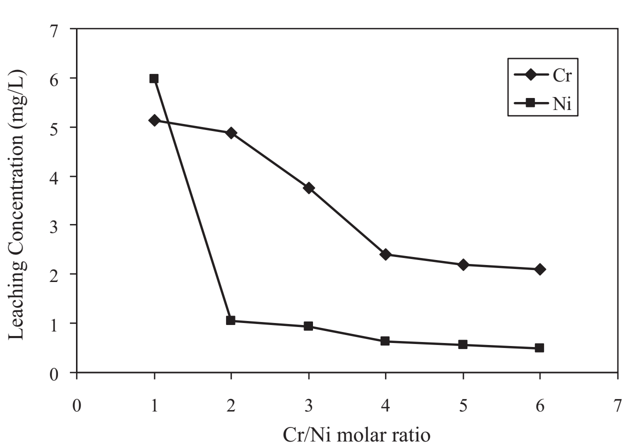

Fig. 8. Leaching concentrations of samples (with a conductivity of 3 ms/cm) with different molar ratios sintered at 1200 °C.

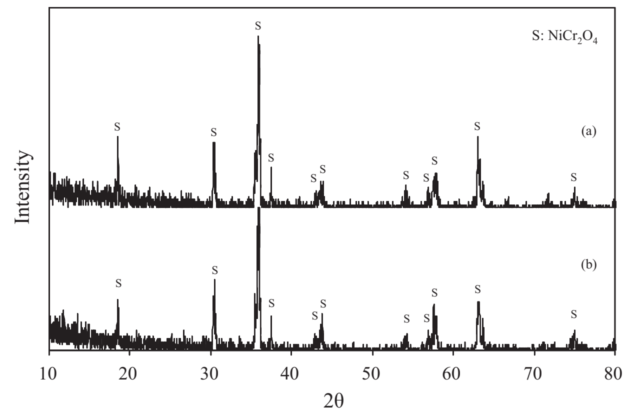

Fig. 9. XRD patterns of samples (with a Cr/Ni ratio of 2 and a conductivity of 0.2 ms/cm) sintered at 1200 °C under two atmospheres of (a) N_2 and (b) air.

3.4. Atmospheric effects

Most experiments to synthesize spinel materials are conducted with a high-temperature process under an air atmosphere. The previous study also indicated that the oxygen partial pressure affects

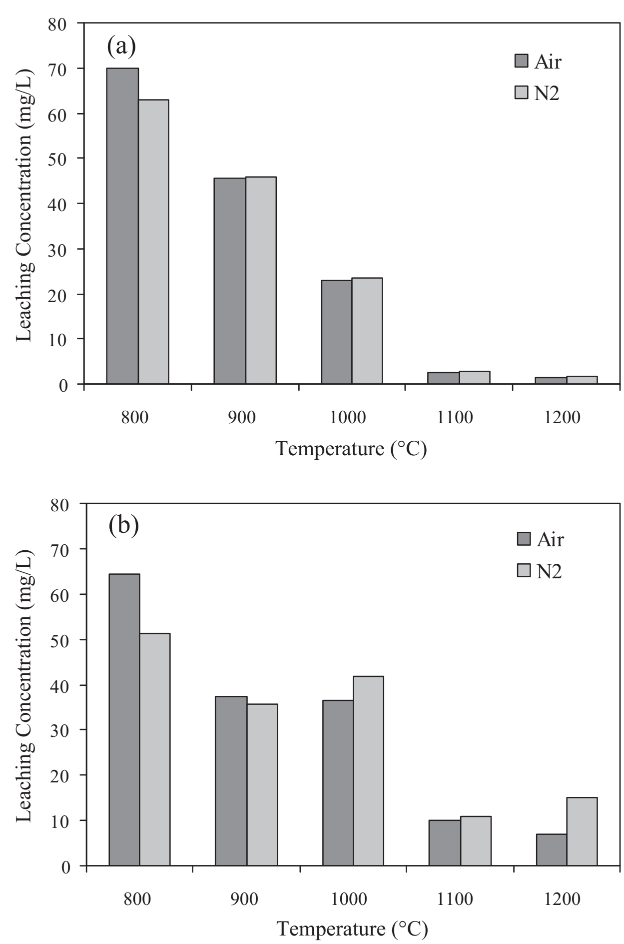

Fig. 10. Leaching concentrations of samples (with a Cr/Ni ratio of 2 and a conductivity of 0.2 ms/cm) sintered at different temperatures under two atmospheres.

the physical properties of spinel materials in high-temperature processes [20]. In order to understand the effects of the reaction atmosphere on forming chromite spinel and the stabilization efficiency, two different gases, air and nitrogen were used in the study. Fig. 9 shows the XRD patterns of simulated sludge with a Cr/Ni molar ratio of 2 and a conductivity of 1.4 ms/cm sintered at 1200 °C under two atmospheric gases for 3 h. The results showed that the crystal phase of $NiCr_2O_4$ was appreciably detected in the two sintered samples under both N_2 and air, but no obvious difference between the two samples was observed.

The leaching behaviors of nickel and chromium in samples sintered at different temperatures under two atmospheres are shown as Fig. 10. Leaching concentrations of both nickel and chromium decreased with an increase in the sintering temperature. However, there was also no obvious difference between the two different atmospheres, which was coincident with the XRD results. Therefore, it was concluded that these two reaction atmospheres did not affect the transformation efficiency of chromite spinel or the stabilization of heavy metals.

4. Conclusions

The nickel-laden sludge was transformed into nickel chromite spinel ($NiCr_2O_4$) by thermal treatment. From the investigation, the following conclusions were reached.

(1) The simulated nickel-laden sludge prepared by a co-precipitation method could be transformed into nickel chromite spinel ($NiCr_2O_4$) by thermal treatment at ~800 °C. The simulated sludge showed in the SEM micrographs was transformed from porous structures to crystalline facets with tetrahedral and octahedral structure with an increasing sintering temperature, which also proved the formation of spinel. Leaching concentrations of both nickel and chromium also decreased with an increase in the sintering temperature according to the TCLP test. Therefore, this sintering strategy designed for laden-sludge was proven to be beneficial in stabilizing heavy metals.

(2) The existence of salt in the sludge disturbs the formation of spinel. However, leaching concentrations of both nickel and chromium decreased with an increase in the salt content owing to smaller particle sizes, which indicated that a moderate level of salt in the sludge contributed to stabilization efficiency during the thermal process.

(3) The leaching concentration of nickel significantly decreased as the molar ratio increased from 1 to 2 because of sufficient chromium oxide to transform nickel oxide into chromite spinel. The results also indicated that a Cr/Ni molar ratio of >2 contributed to the stabilization efficiency of heavy metals in the sludge after the thermal process.

(4) The reaction atmosphere during thermal treatment did not show obvious effects on the formation of chromite spinel. Similar results were also observed with the TCLP test, which means that nickel chromite spinel was transformed from simulated sludge under either an N_2 or air atmosphere.

References

[1] C.-H. Hsieh, S.-L. Lo, C.-Y. Hu, K. Shih, W.-H. Kuan, C.-L. Chen, Thermal detoxification of hazardous metal sludge by applied electromagnetic energy, Chemosphere 71 (2008) 1693–1700.

[2] C.-H. Hsieh, S.-L. Lo, P.-T. Chiueh, W.-H. Kuan, C.-L. Chen, Microwave enhanced stabilization of heavy metal sludge, Journal of Hazardous Materials 139 (2007) 160–166.

[3] K. Shih, T. White, J.O. Leckie, Spinel formation for stabilizing simulated nickel-laden sludge with aluminum-rich ceramic precursors, Environmental Science & Technology 40 (2006) 5077–5083.

[4] N.-H. Li, S.-L. Lo, C.-Y. Hu, C.-H. Hsieh, C.-L. Chen, Stabilization and phase transformation of $CuFe_2O_4$ sintered from simulated copper-laden sludge, Journal of Hazardous Materials 190 (2011) 597–603.

[5] C.-Y. Hu, K. Shih, J.O. Leckie, Formation of copper aluminate spinel and cuprous aluminate delafossite to thermally stabilize simulated copper-laden sludge, Journal of Hazardous Materials 181 (2010) 399–404.

[6] K. Shih, T. White, J.O. Leckie, Nickel stabilization efficiency of aluminate and ferrite spinels and their leaching behavior, Environmental Science & Technology 40 (2006) 5520–5526.

[7] Y.Y. Tang, S.S.Y. Chui, K. Shih, L.R. Zhang, Copper stabilization via spinel formation during the sintering of simulated copper-laden sludge with aluminum-rich ceramic precursors, Environmental Science & Technology 45 (2011) 3598–3604.

[8] Y. Tang, K. Shih, K. Chan, Copper aluminate spinel in the stabilization and detoxification of simulated copper-laden sludge, Chemosphere 80 (2010) 375–380.

[9] C.-L. Chen, S.-L. Lo, W.-H. Kuan, C.-H. Hsieh, Stabilization of copper-contaminated sludge using the microwave sintering, Journal of Hazardous Materials 168 (2009) 857–861.

[10] K. Shih, J.O. Leckie, Nickel aluminate spinel formation during sintering of simulated Ni-laden sludge and kaolinite, Journal of the European Ceramic Society 27 (2007) 91–99.

[11] Z. Wang, S.K. Saxena, P. Lazor, H.S.C. O'Neill, An in situ Raman spectroscopic study of pressure induced dissociation of spinel $NiCr_2O_4$, Journal of Physics and Chemistry of Solids 64 (2003) 425–431.

[12] H. Ishibashi, T. Yasumi, Structural transition of spinel compound $NiCr_2O_4$ at ferrimagnetic transition temperature, Journal of Magnetism and Magnetic Materials 310 (2007) e610–e612.

[13] M. Yazdanbakhsh, I. Khosravi, E.K. Goharshadi, A. Youssefi, Fabrication of nanospinel $ZnCr_2O_4$ using sol–gel method and its application on removal of azo dye from aqueous solution, Journal of Hazardous Materials 184 (2010) 684–689.

[14] S.S. Manoharan, N.R.S. Kumar, K.C. Patil, Preparation of fine particle chromites: a combustion approach, Materials Research Bulletin 25 (1990) 731–738.

[15] B.M. Abu-Zied, Preparation of cadmium chromite spinel: a combustion approach, Colloids and Surfaces A: Physicochemical and Engineering Aspects 211 (2002) 27–42.

[16] Z.V. Marinkovic Stanojevic, N. Romcevic, B. Stojanovic, Spectroscopic study of spinel $ZnCr_2O_4$ obtained from mechanically activated $ZnO–Cr_2O_3$ mixtures, Journal of the European Ceramic Society 27 (2007) 903–907.

[17] F. Müller, O.J. Kleppa, Thermodynamics of formation of chromite spinels, Journal of Inorganic and Nuclear Chemistry 35 (1973) 2673–2678.

[18] M.M. Selim, T.M.H. Saber, N.A. Youssef, Thermal and spectroscopic study on the solid–solid interaction between CuO and Fe_2O_3 and the effect of sodium ions, Reactivity of Solids 8 (1990) 189–196.

[19] H.-C. Lu, J.-E. Chang, P.-H. Shih, L.-C. Chiang, Stabilization of copper sludge by high-temperature $CuFe_2O_4$ synthesis process, Journal of Hazardous Materials 150 (2008) 504–509.

[20] Y. Choi, N.I. Cho, H.C. Kim, Y.D. Hahn, Magnetic properties of Ni–Zn ferrite powders formed by self-propagating high temperature synthesis reaction, Journal of Materials Science: Materials in Electronics 11 (2000) 25–30.