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O.I. Oranska, Yu.I. Gornikov, A.V. Brichka, S.Ya. Brichka

THERMAL ANALYSIS, PHASE AND MORPHOLOGICAL TRANSFORMATIONS IN THE COMPOSITES ALUMINOSILICATE NANOTUBES/ACETATES OF Ni, Cu, Zn

Chuiko Institute of Surface Chemistry of National Academy of Sciences of Ukraine
17 General Naumov Str., Kyiv, 03164, Ukraine, E-mail: el_oranska@mail.ru

The thermal stability and solid-phase reactions in composites halloysite nanotubes – acetates of Ni, Cu, Zn in the temperature range from 20 to 1100 °C have been investigated. It has been shown that chemical reactions occur with metal oxides formed due to thermal degradation of acetates and components of aluminosilicate matrix formed during dehydration and dehydroxylation of halloysite nanotubes. Reaction products are nanocrystalline ZnAl₂O₄ distributed in a matrix of amorphous SiO₂ and CuO solid solution in α-cristobalite. Degree of destruction of the tubular structure of nanotubes in the composites with acetate increases as follows: Ni²⁺ < Zn²⁺ < Cu²⁺.

Keywords: halloysite nanotubes, oxides NiO, CuO, ZnO, nanocrystalline ZnAl₂O₄, solid-phase reactions, tubular structure

INTRODUCTION

Currently, not only natural aluminosilicate (halloysite) nanotubes (HNT), but HNT-composites are used in various fields of medicine, industry, and agriculture. In general, composites are produced by modifying the outer surface of the nanotubes by impregnating the organic and inorganic substances in the inner cavities of the nanotubes, as well as by introduction of HNT into the mixture as component [1–3]. When using composites based on HNT and metal-containing components as catalysts or their substrates, for the manufacture of ceramic and construction materials and special purpose coatings, knowledge of their physico-chemical properties over a wide temperature range is important. Mechanical mixing of the components in the solid state is one of the most effective and available methods for producing composites with HNT. Study on thermal stability and solid-state reactions that occur in such systems with increasing temperature is of great scientific and practical interest.

In this work, the interaction between the acetates of transition metals and aluminosilicate halloysite nanotubes (HNT) with formula Al₂[Si₂O₅](OH)₄·nH₂O during heating up to 1000 °C has been studied. Materials and knowledge of their thermal properties are important for creation and exploitation of

heterogeneous catalysts [4]. Previously, it was shown that the chemical reactions in the composites HNT/NiO, CuO, ZnO proceeded after destruction of the hexagonal structure of nanotubes at the temperatures above 600 °C [5]. This study will enhance the understanding of the mechanism of interaction between the components of the composites.

MATERIALS AND METHODS

The test samples were composites of halloysite nanotubes “ND Life” and metal acetate reagents: Ni(CH₃COO)₂·4H₂O (NiAc) TU 6-09-3848-87, Cu(CH₃COO)₂·H₂O (CuAc) GOST 5852-79, Zn(CH₃COO)₂·2H₂O (ZnAc) GOST 5823-78. The content of metal acetate in the mixture was 1 mmol/g HNT. Composites were prepared by mechanical mixing the components.

Thermal analysis was performed using a Q-1500D (MOM firm, Hungary) derivatograph in the temperature range of 20–1000 °C with linear heating rate of 10 deg/min. Phase composition of the cooled samples was determined by X-ray diffraction using a DRON-4-07 diffractometer with Bragg-Brentano geometry, filtered CuK_α radiation in the angular range 2θ of 10–80°. Particle morphology was studied with a scanning electron microscopy instrument MIRA3 LMU, TESCAN with a resolution of 1 nm. The specific surface area

was measured by low temperature nitrogen desorption.

RESULTS AND DISCUSSION

It is known that thermal decomposition of aluminosilicate nanotubes occurs in several stages with mass loss corresponding to the removal of the interlayer water at about 100 °C and intralayer hydroxyls at 500–600 °C [6]. For HNT "ND Life" one more stage of decomposition with weight loss at 310 °C is characteristic (Fig. 1 *a*). According to X-ray diffraction and thermal studies, halloysite nanotubes include an appreciable amount of gibbsite $\text{Al}(\text{OH})_3 \cdot 3\text{H}_2\text{O}$, as accompanying mineral [7]. This is evidenced by the corresponding diffraction peaks in the diffraction pattern of initial HNT (Fig. 1 *b*). Heating the sample to about 300 °C leads to decomposition of gibbsite to form

alumina, which corresponds to a mass loss and endoeffect on TG and DTA curves. Heating the sample to 800 °C leads to crystallization of the alumina in the form of $\gamma\text{-Al}_2\text{O}_3$ spinel, which is indicated by the appearance of corresponding peaks in the diffractogram of the sample (Fig. 1 *b*). Al_2O_3 crystallization proceeds without visible thermal effect on the DTA curve. When the sample is heated up to 1050 °C, clear exothermic peak at 995 °C is observed on the DTA curve. X-ray diffraction data indicate the formation of a crystalline phase with a structure similar to $\gamma\text{-Al}_2\text{O}_3$ in this case. According to [8], this effect is associated with a phase transition in the amorphous aluminosilicate matrix, product of dehydration and dehydroxylation of HNT, leading to the formation of Al-Si spinel with formula $2\text{Al}_2\text{O}_3 \cdot 3\text{SiO}_2$.

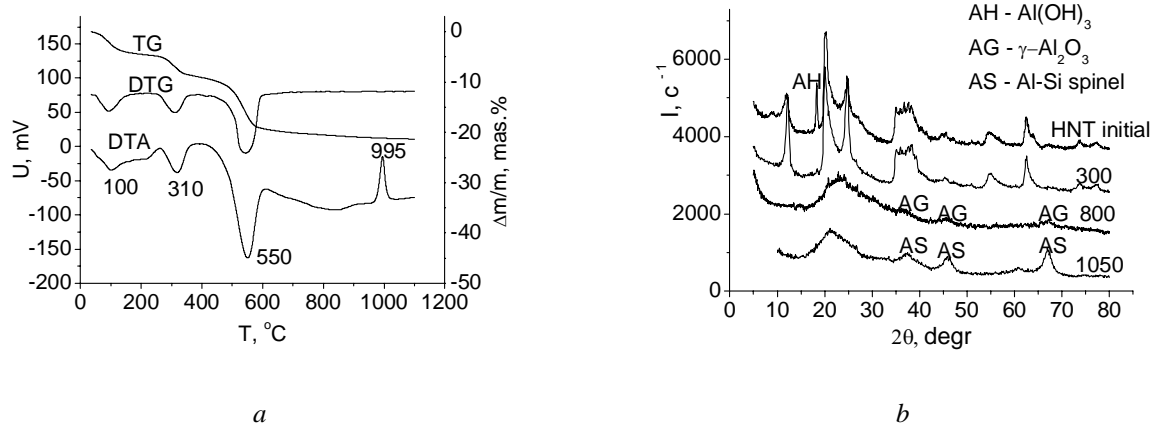


Fig. 1. Thermal curves of HNT (*a*), XRD patterns of initial and HNT heated at different temperature (*b*)

Derivatograms of hydrated metal acetates are shown in Fig. 2 *a–c*. They are characterized by two temperature regions where the mass loss corresponds to the removal of adsorbed water at 100–150 °C and removal of the destruction products of acetates at 250–430 °C. Among the acetates, CuAc has the highest temperature removal of hydrate water 145–150 °C and the lowest acetate decomposition temperature 280–293 °C. Oxides ZnO, CuO, and NiO are products of decomposition of metal acetates and they are formed at the temperatures lower than that of HNT decomposition.

Derivatograms of mixtures of metal acetates and HNT are presented in Fig. 2 *d–f*. Observed changes of mass and thermal effects on TG and DTA curves correspond to successive processes, such as removal of adsorbed water, interlayer water

in the HNT, removal of acetate of hydration water, hydroxyls of gibbsite, decomposition products of acetate, intralayer hydroxyls of HNT, formation of NiO, CuO, and ZnO and exothermic process at 925 °C for mixture ZnAc-HNT. On DTG curves of mixtures, a shift of the acetate destruction temperatures to lower values is observed. Probably, this is related to superposition of the dehydration process of gibbsite in the same temperature range.

XRD data of the mixtures cooled after heating in furnace of derivatograph up to 1000 °C indicate a series of phase transformations (Fig. 3). There are amorphous silica, Al-Si spinel, and NiO in NiAc-HNT mixture. Thus, on DTA curve of the sample exoeffect at about 1000 °C observed for initial HNT is registered. In the sample CuAc-HNT amorphous silica, α -cristobalite and mullite are detected. The latter is usually formed in

aluminosilicates at higher temperatures (~1200 °C). Crystalline CuO is not found since, apparently, it forms a solid solution in α -cristobalite, as shifts of diffraction peaks of SiO₂ are indicated [9]. It is known from the literature that the temperature of mullite formation in the presence of CuO reduces to values closed to the decomposition temperature of the copper oxide,

~ 1030 °C [10, 11]. ZnAc-HNT mixture, unlike other mixtures heated to 1000 °C, contains zinc aluminate ZnAl₂O₄ with spinel type structure and amorphous silica. As noted earlier, there is a narrow exothermic peak at 925 °C on DTA curve of this sample, similar to that recorded for the initial HNT at 995 °C.

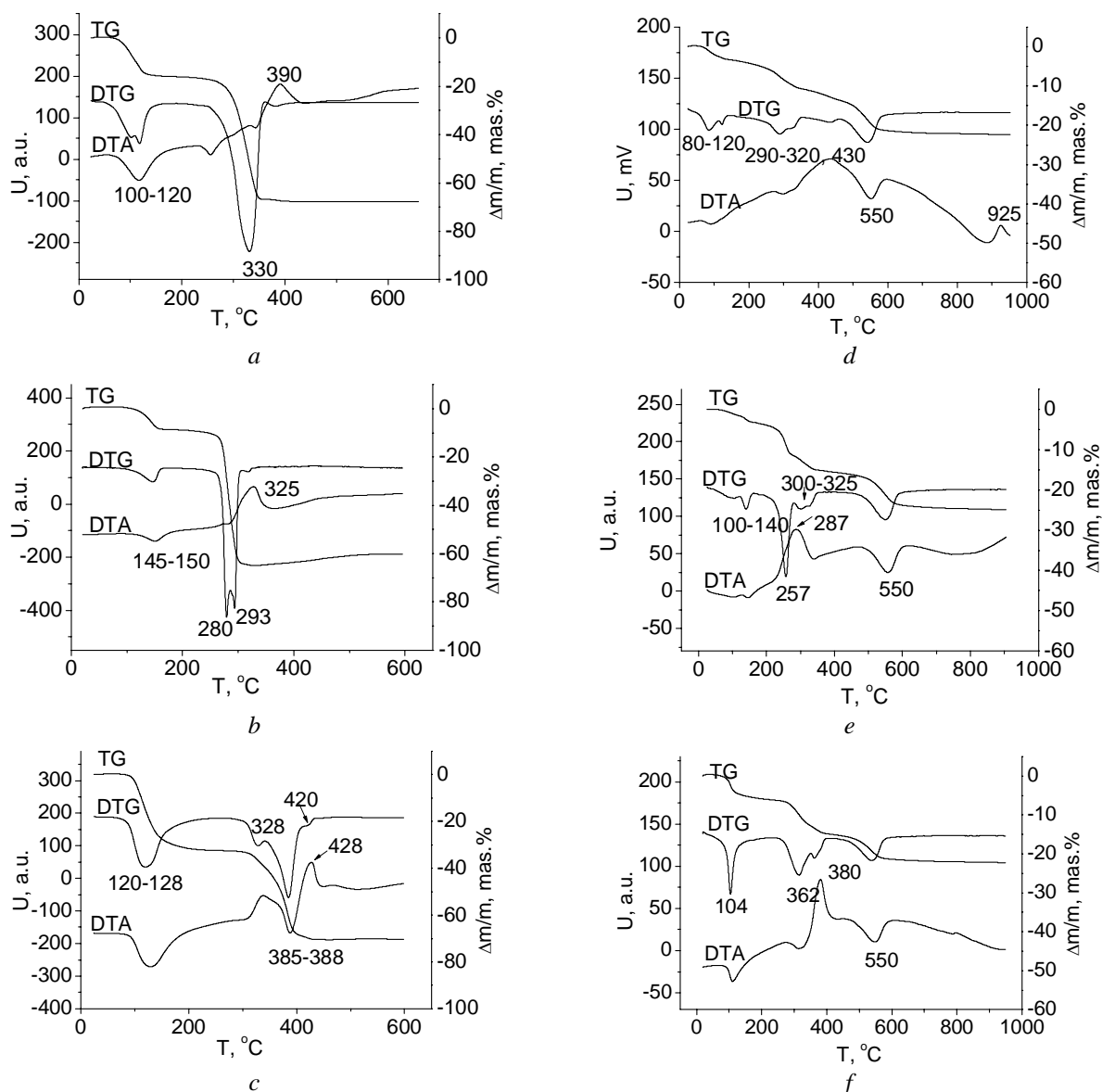


Fig. 2. Thermal curves of ZnAc (a), CuAc (b), NiAc (c), ZnAc-HNT (d), CuAc-HNT (e), NiAc-HNT (f)

The formation of zinc aluminate can be explained from the viewpoint of increasing the reactivity of the solids in the solid phase reactions occurring simultaneously with structural transformations in the system – increased reactivity of solid-state during and as a consequence of the

transformation of the crystal is known as Hedvall effect [12–15]. Thus, according to XRD of the mixtures, heated to 500 and 600 °C (Fig. 4), reducing of crystalline ZnO content with increasing heating temperature (Fig. 4) and the disappearance of diffraction peaks of ZnO, when the heating

temperature of 800 °C is observed. At the same time, the content of crystalline CuO and NiO in the mixtures CuAc-HNT and NiAc-HNT is not reduced by heating to 600 °C. Consequently mixture ZnAc-HNT becomes amorphous near 800 °C and at 925 °C it transforms in to spinel ZnAl₂O₄. Based on these data, one can suggest that the interaction between ZnO and aluminosilicate matrix begins after HNT dehydroxylation and ZnO dissolves in areas enriched in aluminum, including areas of Al₂O₃ formed by the decomposition of gibbsite.

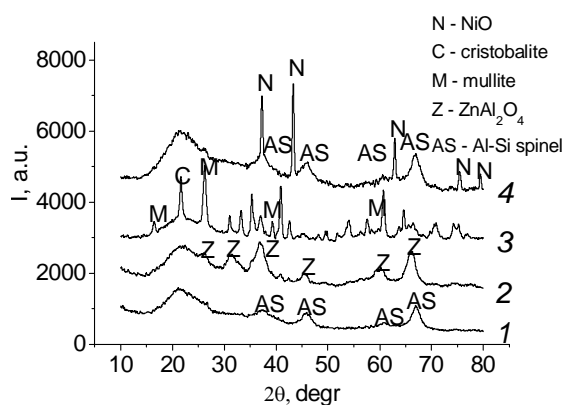


Fig. 3. XRD patterns of HNT (1), ZnAc/HNT (2), CuAc/HNT (3), NiAc/HNT (4) heated to 1050 °C

XRD analysis of CuAc-HNT mixture heated from 600 to 1050 °C shows reduction of crystalline CuO and formation of Al-Si spinel near the decomposition temperature of CuO ~1030 °C, the formation of mullite and CuO solid solution in α -cristobalite. Therefore for mixture CuAc-HNT the interaction of CuO and Al-Si-O matrix of dehydroxylated HNT is also characteristic and it occurs mainly in regions enriched with silica, not

alumina. Increasing the temperature of heating the mixture NiAc-HNT from 600 to 1000 °C leads to growth of crystallinity of NiO and, simultaneously, to formation of Al-Si spinel. Therefore, in mixture NiAc-HNT no interaction of NiO with elements of Al-Si-O matrix occurs in this temperature range.

Therefore, the phase composition of the composites of HNT and metal acetates of Zn, Cu, Ni depends on the heating temperature and on the reactivity of oxides ZnO, CuO, NiO with respect to the elements of Al-Si-O matrix.

Based on the values of the average crystallite size 6–7 nm calculated by Scherrer equation, crystalline phase Al-Si spinel and ZnAl₂O₄ formed at about 1000 °C can be attributed to nanocrystalline one distributed in the silica matrix.

The specific surface area, S_{spec} , of the samples, initial and annealed at 320, 700, and 1050 °C of HNT, ZnAc-HNT, and CuAc-HNT annealed at 1050 °C, is 54, 53, 80, 37, 17, and less than 1 m²/g, respectively. Based on almost identical values S_{spec} samples of HNT – initial and annealed at 320 °C – decomposition temperature of gibbsite, it can be assumed that gibbsite crystals do not form separate particles, but are embedded into the layered structure of HNT. S_{spec} of HNT, ZnAc-HNT, and CuAc-HNT annealed at 1050 °C has a smaller value associated with the destruction of HNT and phase transformations in the samples. A larger value S_{spec} of HNT annealed at 700 °C, compared to the initial HNT, is apparently due to the increase in the number of defects and voids on the surface of the particles as a result of HNT dehydroxylation at 550 °C.

S_{spec} data correlate well with SEM data presented in Fig. 5.

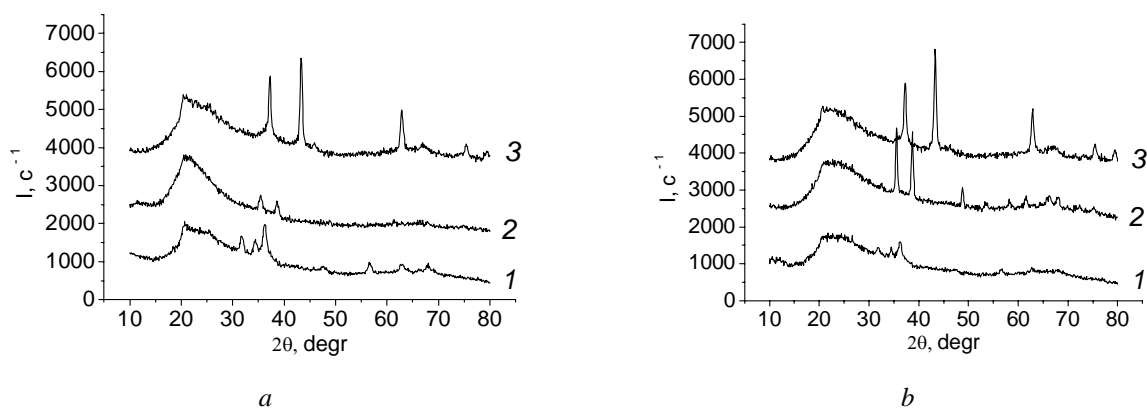


Fig. 4. XRD patterns of ZnAc-HNT (1), CuAc-HNT (2), NiAc-HNT (3) heated to 500 (a) and 600 °C (b)

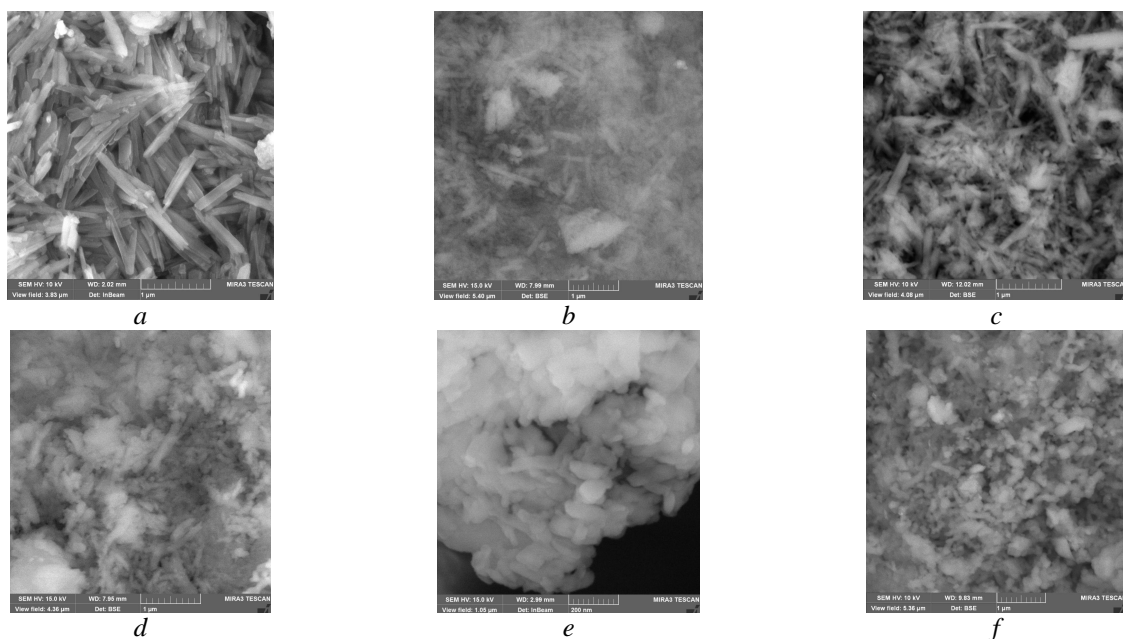


Fig. 5. SEM images: initial (a) and heated to 700 °C (b), 1050 °C (c) HNT, and composites ZnAc-HNT (d, e different magnification) and CuAc-HNT (f) heated at 1050 °C

Images in Fig. 5 *a–c* illustrate the morphologic changes of HNT particles heated to 700 and 1050 °C. It is seen that the transformation in aluminosilicate matrix of HNT at 700 and 1050 °C leads to partial destruction of the tubular structure of initial HNT. Similar transformations occur in the mixture NiAc-HNT heated up to 1000 °C (data not shown). In a mixture of ZnAc-HNT heating to 1050 °C followed by destruction of the tubular structure form ellipsoidal particle with size of 100–200 nm assembled into aggregates of various shapes and lengths (Fig. 5 *d–e*). The greatest destruction of the tubular structure of HNT occurs in CuAc-HNT mixture heated up to 1050 °C, which is characterized by the formation of two crystalline phases - mullite and CuO solid solution in α -cristobalite (Fig. 5 *f*).

CONCLUSIONS

Based on the results of a combined study on composites of HNT and metal acetates under heating to ~1050 °C using TG, DTG, DTA methods, XRD, SEM, low temperature nitrogen desorption analysis, following findings are made:

1. Presumably gibbsite, part of the HNT mark "ND Life", is not present as a separate phase. Heating of HNT to 1000 °C is followed by an exothermic phase transition in the Al-Si-O matrix at 995 °C to form a nanocrystalline Al-Si spinel

(average crystallite size 6 nm) and amorphous SiO₂.

2. In the mixtures HNT-metal acetate, the interaction of oxides NiO, CuO, ZnO formed upon decomposition of acetates at 300–400 °C with HNT aluminosilicate matrix occurs at the temperatures exceeding the destruction temperature of HNT (550 °C).

3. The result of the interaction of zinc oxide and aluminosilicate matrix is the formation of nanocrystalline zinc aluminate spinel ZnAl₂O₄ (the average crystallite size of 7 nm) in a matrix of amorphous silica with particles of an ellipsoidal shape and size along the long axis of 100–200 nm, followed by exothermic effect at 925 °C.

4. In the mixture CuAc-HNT, CuO reacts with silica to form a solid solution in α -cristobalite. Al-Si spinel is formed at the same time, what happens without exoeffect. With increasing the temperature to the decomposition of CuO ~1030 °C, Al-Si spinel is converted into mullite accompanied by the complete destruction of the tubular structure of HNT.

5. In the mixture NiAc-HNT, crystallization of NiO and Al-Si spinel occurs independently. Spinel formation takes place without noticeable exothermic effect. High-temperature morphological changes in the mixture are similar to those observed in the initial HNT.

Термічний аналіз, фазові та морфологічні перетворення в композитах алюмосилікатні нанотрубки/ацетати Ni, Cu, Zn

О.І. Оранська, Ю.І. Горніков, А.В. Бричка, С.Я. Бричка

Інститут хімії поверхні ім. О.О. Чуйка Національної академії наук України
вул. Генерала Наумова, 17, Київ, 03164, Україна, el_oranska@mail.ru

Досліджена термічна стабільність і твердофазні реакції в композитах галлуазитні нанотрубки – ацетати Ni, Cu, Zn в області температур від 20 до 1100 °С. Показано, що хімічні реакції в композитах перебігають за участю оксидів металів, які утворились в результаті термічної деструкції ацетатів, та елементів алюмосилікатної матриці, яка утворилася при дегідратації і дегідроксилюванні галлуазитних нанотрубок. Продуктами взаємодії є нанокристалічний $ZnAl_2O_4$, розподілений у матриці аморфного SiO_2 , і твердий розчин CuO в α -кристобаліті. Ступінь руйнування тубулярної структури нанотрубок збільшується в ряду композитів з ацетатом: $Ni^{2+} < Zn^{2+} < Cu^{2+}$.

Ключові слова: галлуазитні нанотрубки, оксиди NiO, CuO, ZnO, нанокристалічний $ZnAl_2O_4$, твердофазні реакції, тубулярна структура

Термический анализ, фазовые и морфологические превращения в композитах алюмосиликатные нанотрубки/ацетаты Ni, Cu, Zn

Е.И. Оранская, Ю.И. Горников, А.В. Бричка, С.Я. Бричка

Інститут хімії поверхні ім. А.А. Чуйко Національної академії наук України
Ул. Генерала Наумова, 17, Київ, 03164, Україна, E-mail: el_oranska@mail.ru

Исследована термическая стабильность и твердофазные реакции в композитах галлуазитные нанотрубки – ацетаты Ni, Cu, Zn в области температур от 20 до 1100 °С. Показано, что химические реакции в композитах протекают при участии оксидов металлов, образовавшихся в результате термической деструкции ацетатов, и элементов алюмосиликатной матрицы, образовавшейся при дегидратации и дегидроксилировании галлуазитных нанотрубок. Продуктами взаимодействия являются нанокристаллический $ZnAl_2O_4$, распределенный в матрице аморфного SiO_2 , и твердый раствор CuO в α -кристобалите. Степень разрушения тубулярной структуры нанотрубок увеличивается в ряду композитов с ацетатом: $Ni^{2+} < Zn^{2+} < Cu^{2+}$.

Ключевые слова: галлуазитные нанотрубки, оксиды NiO, CuO, ZnO, нанокристаллический $ZnAl_2O_4$, твердофазные реакции, тубулярная структура

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