Preparation and properties of nano-Al/MoO_3 thermite

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Received:
25 August 2018

Accepted:
11 October 2018

Available online:
6 November 2018

UDK 543.272.73, 661.666.4.

ABSTRACT

MoO_3 nanobelts were prepared by a facile hydrothermal method. The as synthesized MoO_3 nanobelts were used to integrate with nano-Al powder through two different approaches, mixing nano-Al with MoO_3 nanobelts ultrasonicly and combining nano-Al with MoO_3 self-assembly. The physical-chemical properties of the asprepared samples were carefully characterized by SEM, TEM, XRD, TGA/DSC and drop weight impact test. The results show that the morphology of MoO_3 is highly influenced by the additive sequence and the concentration of ammonium paramolybdate. The onset oxidation temperature of self-assembled nano-Al/MoO_3 is 478.5 ℃. Otherwise, the onset oxidation temperatures of nano Al powder, nano-Al/hydrothermal MoO_3 and nano-Al/referenced Fe_2O_3 prepared by ultrasonic method are 540.8 ℃, 484.2 ℃ and 514.8 ℃ respectively. And the total exothermic heats of self-assembled nano-Al/MoO_3 in the temperature of TG experiments are about 6696.0 J/g, and 801.6 J/g, 577.4 J/g and 4080.2 J/g higher than that of nano-Al/commercial MoO_3, nano-Al/hydrothermal MoO_3 and nano-Al/referenced Fe_2O_3.

Keywords: MoO_3 nanobelt, thermite, self-assembly, high-exothermic

1. Introduction

Integration of nano-aluminum and nano-metallic oxidizer was proved to be an efficient way to iprove the performance in ignition and energy release rate due to the shorter diffusion distance and larger contact area between fuel and oxidizer.

Researchers indicate that an Al/MoO_3 nanotherimte can provide favorable ignition property compared to pure aluminum in oxidizing atmospheres. Because any reduced molybdenum metal could likely be reoxidized at the high temperature. After that, MoO_3 still acts as an oxidizer in the oxygen-containing atmospheres.

If less MoO_3 content was used in the thermite, the composite could potentially provide the majority of high-energy aluminum with superior ignition characteristics [1, 2].

In this work, we used a facile hydrothermal method to prepare MoO_3 nanobelts, and then the as-synthesized MoO_3 nanobelts were used to integrate with nano-Al powder through two different approaches. The first way is to mix nano-Al with MoO_3 nanobelts by ultrasonication, and the other way is to combine the Al-nanoparticles with MoO_3 through a self-assembly method using polyvinylpyrrolidone (PVP) as a stabilizer.

The nano-aluminum can be arranged around metallic oxidizers in an ordered manner, and these thermites can provide more active sites and higher rate of energy release.

2. Experimental Part

Materials and Reagents

All the chemicals were of analytical grade and used as purchases without any further treatment.

The aluminum powder was obtained from Beijing Nachen Technology Co., Ltd with an average size of 100nm and a purity of 72%.

Referenced MoO_3 was purchased from Kaituo Muye Co., Ltd with an average size of 100 nm and a purity of 99.5% and was marked as MoO_3-0.

Referenced Fe_2O_3 was from Beijing Nachen Technology Co., Ltd with an average size of 100 nm and a purity of 99.9%.

Sample Preparation

Synthesis of MoO_3 nanobelt

The MoO_3 nanobelts were synthesized as follows: The MoO_3-1 nanobelt was synthesized through a hydrothermal method. 0.8 mmol (0.9885 g) of

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$(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ was added into 20 mL of deionized water. Then, 2 mmol (0.7278 g) of Hexadecyl trimethyl ammonium bromide (CTAB) was added to the above solution with constantly magnetic stirring. Next, 20 mL of HNO_3 (2.2 M) was added into the solution by drop-wise and subsequently a white precipitate formed.

Finally, the suspension was transferred to a 100 mL Teflon-lined autoclave for 20 h at 180 ℃. After the hydrothermal reaction, the light blue product was washed twice with etha-nol and acetone, respectively, and dried at 80 ℃.

The preparation process of MoO_3-2 nanobelt is similar to that of MoO_3-1 by exchanging the order of deionized water and HNO_3. Sample MoO_3-3 was obtained also by a hydrothermal method. 25 ml saturated water solution of $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ was ultrasonicated for 10 min. Then 2.2 mol/L HNO_3 was added into the solution and mixed with stirring. The molar ratio of CTAB to $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ was 1:2. After the reaction, the suspension was transferred into a Teflon-lined autoclave and kept at 180 ℃ for 40 h in a hot oven. The precipitate was separated by a centrifuge, washed with deionized water, ethanol and acetone for several times and dried at 80 ℃.

Synthesis of nanothermites

The Mo-Al-0 composite was prepared by adding MoO_3-0 and 100 nm Al (MoO_3/Al molar ratio: 1:3) into 20 mL hexane under the assistance of ultrasonication for 1 h. This formulation contains 36.0 wt.% aluminum nanoparticles and 64.0 wt.% MoO_3-0 nanoparticles. Mo-Al-1 composite was obtained by mixing MoO_3-1 and 100 nm Al (MoO_3 / Al molar ratio: 1:3) in 20 mL hexane by an ultrasonic method for 1 h. Mo-Al-2 composite was synthesized by self-assembly method. First, 0.1 g of PVP was solved in-to 100 mL isopropanol. Then, MoO_3-1 was added into the above solution and the mixture was ultra-sonicated for 4 h. Next, the mixture was washed by isopropanol for three times to remove the ultra PVP and dried at 120 ℃ for 1.5 h. Finally, the dried PVP-coated $MoO_3$was mixed with Al powders in hexane by ultrasonic for 1.5 h. Fe-Al-0 composite was fabricated by typical ultrasonic method. 100 nm Fe_2O_3 and 100 nm Al particles were added into 20 ml hexane in a sonic bath for 1 h. And the composite is composed of 33.6 wt.% aluminum nanoparticles and 66.4 wt.% Fe_2O_3.

Characterization

The phase structures of the as-synthesized samples were determined on a Bruker D8 Advance X-ray diffractometer (40 kV, 40 mA) with Cu Kα radiation (λ = 0.1542 nm).

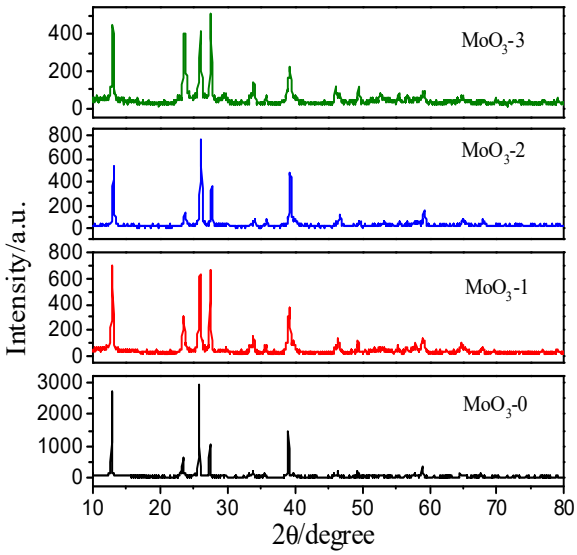

Fig. 1. XRD patterns of MoO_3-0, MoO_3-1, MoO_3-2 and MoO_3-3.

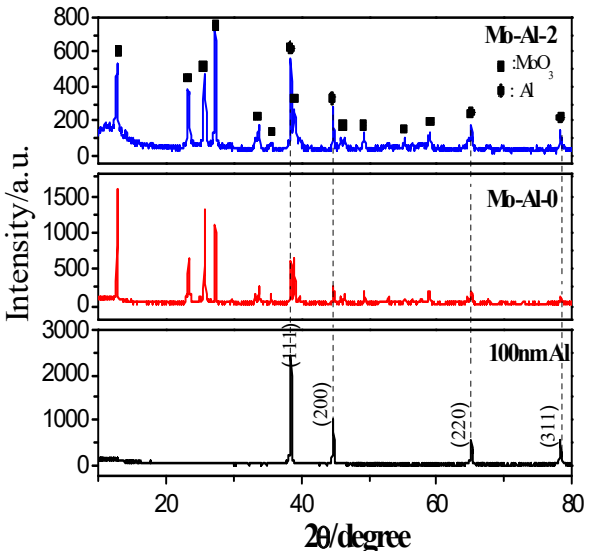

Fig. 2. XRD patterns of 100 nm Al, Mo-Al-0 and Mo-Al-2.

The morphology and mi-crostructure were observed by field-emission scanning electron microscopy (FE-SEM, Quanta™250) and transmission electron microscopy (TEM, JEOL JEM-2100).

A SDT Q600 V8.1 Build 99 thermal analyser was applied to measure the thermal property of the thermite. The measurement was conducted from 40 to 1000 ℃ in nitrogen atmosphere with a heating rate of 20 ℃/min.

3. Results and discussion

Characterization of MoO_3

All the samples show similar XRD patterns in Fig. 1 and all the diffraction peaks from 10 to 80° can

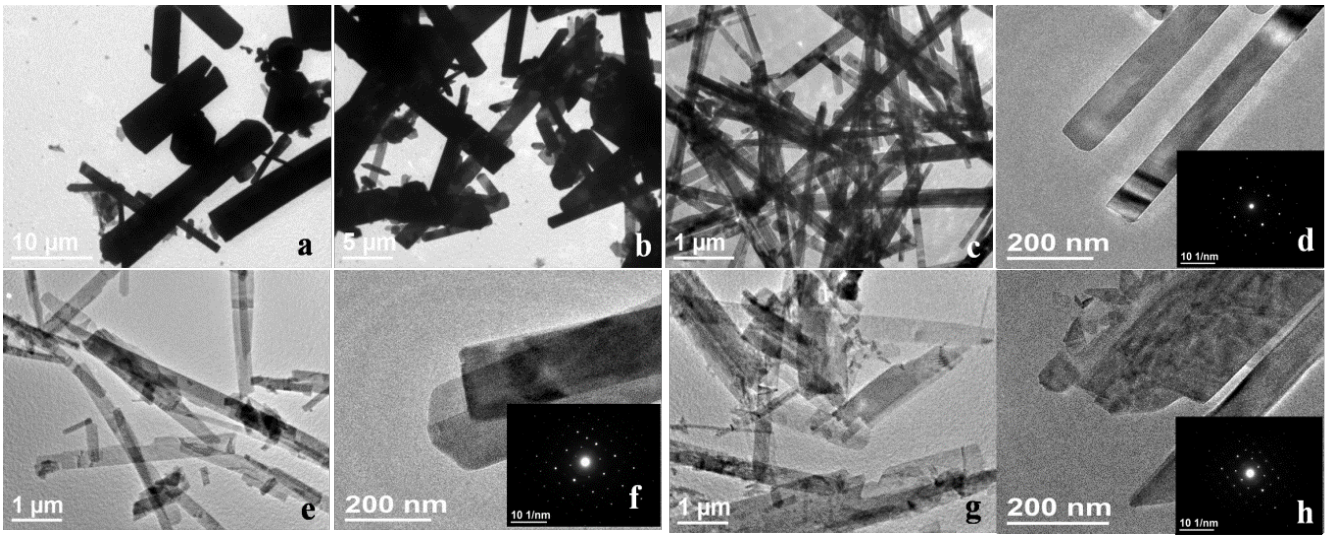

Fig. 3. TEM images of MoO_3-0 (a, b), MoO_3-1 (c, d), MoO_3-2 (e, f) and MoO_3-3 (g, h); The inset images in d, f and h are the SAED of MoO_3-1, MoO_3-2 and MoO_3-3.

be attributed to monoclinic MoO_3 (JCPDS NO. 05-0508). The main peaks at 2θ =12.9, 23.1, 25.8, 27.4 and 39.0° correspond to the diffractions of (0 2 0), (1 1 0), (0 4 0), (0 2 1) and (0 6 0) planes of MoO_3, respectively. The morphology evolution of MoO_3 prepared under different conditions was observed by TEM. As shown in Fig. 3 (a, b), the commercial MoO_3-0 particles are micron-sized belts with a size of width from 1 to 5 μm and length from 3 to 20 μm. The MoO_3-1 nanobelts have a mean width of ca. 60 nm (Fig. 3 (c, d)). And the shapes of MoO_3-2 and MoO_3-3 are not regular nanobelts with a large length range (Fig. 3 (e-h)). So the morphology of MoO_3 is influenced by the added order of raw ma-terials and the concentration of the $(NH_4)_6Mo_7O_{24}$ solution. The SAED images in the insets of Fig. 3 (d, f, h) show a single-like pattern, indicating that the MoO_3-1, MoO_3-2 and MoO_3-3 nanobelts grow along one special direction.

Characterization of nano-Al/MoO_3 thermites

The XRD pattern of 100 nm Al powder was displayed in Fig. 2. Typically, the diffraction peaks at 2θ = 38.5, 44.7, 65.1, and 78.2° can be indexed to (1 1 1), (2 0 0), (2 2 0) and (3 1 1) diffraction of Al (JCPDS No. 65-2869). The XRD patterns of Mo-Al-0 and Mo-Al-2 can be considered as the superimposition of that of MoO_3 and Al, which indicates the coexistence of MoO_3 and Al in the composite thermites. No diffraction peaks of any other impurity were detected in all the XRD patterns, suggesting that Al powder was stable during the preparation process of composite thermites.

Figure 4 shows the typical SEM images of nano-Al/MoO_3 composite thermites. As pre-sented in Fig. 4 (a, b), most of the Al nano-particles in Mo-Al-0 composite are agglomerated and there is no efficient contact between Al powder and MoO_3 nanobelts due

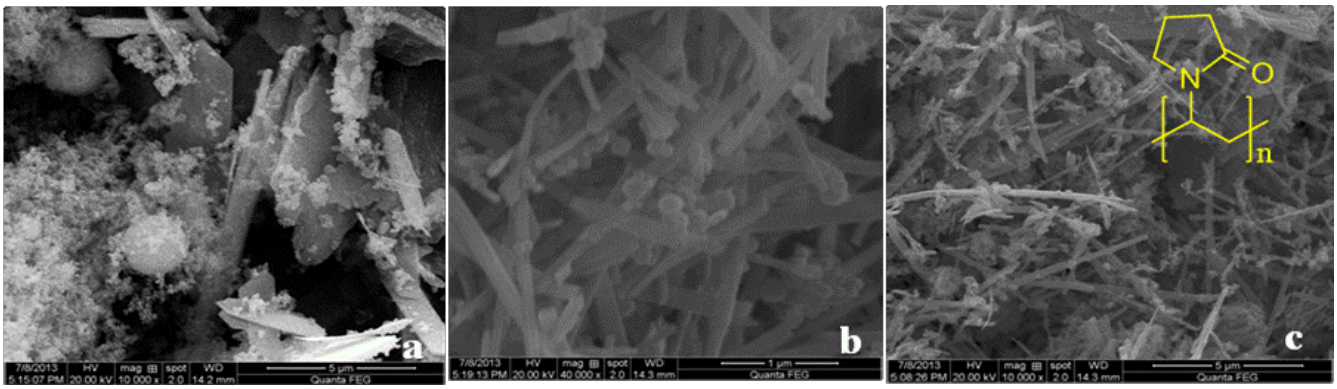

Fig. 4. The SEM images of Mo-Al-0 composite (a), Mo-Al-1 composite (b), and Mo-Al-2 composite (c); the inset in c is the formula of PVP. The molar ratios of Al powder to MoO_3 are kept at 3:1 in different samples.

Table 1
DSC results of 100nm Al and thermites in N_2

Samples	$H_{365-663}$ J/g	$H_{663-912}$ J/g	$H_{365-912}$ J/g	T_{p1}/°C	T_{p2}/°C	T_{p3}/°C	T_{onset}/°C	Remark
n-Al	2173.8	3597.7	6658.4	603.0	830.0	—	540.8	20 K/min ultrasonic,
Mo-Al-0	562.8	903.4	4652.4	572.6	672.3	783.7	474.8	20 K/min ultrasonic method,
Mo-Al-1	497.4	1166.8	4230.2	586.4	678.0	783.8	484.2	20 K/min self assemble,
Mo-Al-2	604.6	1468.1	4623.3	572.3	647.7	783.1	478.5	20 K/min ultrasonic,
Fe-Al-0	958.8	1657.0	2615.8	599.4	818.0	—	514.8	20 K/min

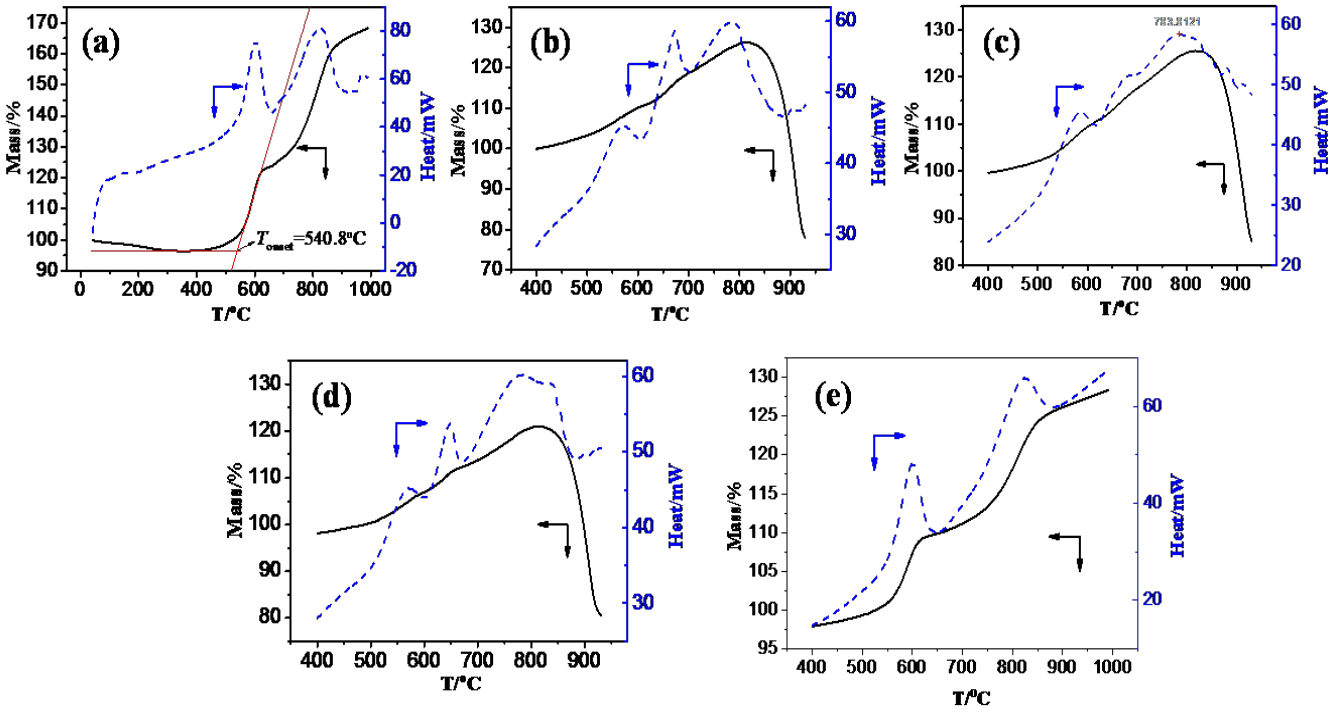

Fig. 5. TGA/DSC curves of 100 nm Al and composite thermites; (a) 100 nm Al, (b) Mo-Al-0; (c) Mo-Al-1; (d) Mo-Al-2; (e) Fe-Al-0.

to the big size of MoO_3-0 and the weak interaction. The dispersion of the Al nanoparticles in Mo-Al-1 was highly improved (Fig. 4b). Compared with Mo-Al-0 and Mo-Al-1, Al nanoparticles in Mo-Al-2 have better dispersion and uniformity around MoO_3-1 nanobelts. This is mainly attributed to the assistance of PVP, which can provide binding sites for Al nanoparticles on the surface of MoO_3 nano-belts.

Thermal properties of Mo-Al thermites

TGA/DSC was applied to measure the thermal properties of Mo-Al composite ther-mites, and Fig. 5 depicts the TGA/DSC curves of Al powder, Mo-Al-0, Mo-Al-1, Mo-Al-2 and Fe-Al-0. In order to compare the dif-ference between Al powder and thermites, on-set temperature and heat released are listed in Table 1.

As seen in Fig. 5 a, the absorbed O_2, H_2O and CO_2 in Al powder desorbed from 41 to 365.2 °C with a 3.6% mass loss. Nano Al melts at 663.2 °C, with an endothermic step. And then the melted nano Al reacts with N_2 from 663.2 to 912.7 °C. The released heat during this step is about 3597.7 J/g. The onset temperature (540.8 °C) was obtained by using the tangent lines of TGA curves.

DSC analysis (Fig. 5 b, c, d) shows an initial exothermic reaction at 365.2-663.2 °C, which is associated with the reaction between solid Al and N_2, and the subsequent two exo-thermic peaks correspond to the reactions between melted Al and N_2, and melted Al and MoO_3, respectively. TGA curves show a 20% weight gain from 400 to 800 °C. The thermites show a sharp mass loss at 825 °C, with a residual mass of 50%, implying the sublimation of MoO_3.

The Tonset of Mo-Al-0, Mo-Al-1 and Mo-Al-2 are 474.8 ℃, 484.2 ℃, and 478.5 ℃, which are lower than that of pure nano Al (540.8 ℃) and much lower than that of the thermites reported. As we can see from Fig. 5 (e) and Table 1, the Tonset of Fe-Al-0 is 514.8 ℃, which is 26 ℃ lower than that of pure nano Al, while 40 ℃, 30.6 ℃ and 36.3 ℃ higher than that of Mo-Al-0, Mo-Al-1 and Mo-Al-2, respectively.

Conclusion

The additive sequence of HNO_3 and DI water, and concentration of $(NH_4)_6Mo_7O_{24}$ solution have great influ-ences on the structure and morphology of MoO_3 nanobelts. High dispersive thermite is obtained by using self-assembly method. The onset temperature of nano aluminum decreased 56.6-66 ℃ in the presence of MoO_3 nanobelt. MoO_3 nanobelt can be used as catalyst for the ignition and combustion of nano aluminum.

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Подготовка и свойства нано-AL/MoO_3 термитов

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Аннотация

Нанополоски MoO_3 были получены с помощью поверхностного гидротермического метода. Синтезированные нанополоски MoO_3 были использованы для интеграции с порошком нано-Al двумя разными способами, путем смешивания нано-Al с нанополосками MoO_3 с применением ультразвука и смешивание нано-Al порошка в агрегатном состоянии с MoO_3 самосборочно. Физико-химические свойства подготовленных образцов были тщательно охарактеризованы SEM, TEM, XRD, TGA/DSC методами и испытывались на удар под собственным весом падения. Результаты показывают, что морфология MoO_3 сильно зависит от аддитивной последовательности и концентрации парамолибдата аммония. Начальная температура окисления самосборочного нано-Al/MoO_3 составляет 478,5 ℃. В противном случае начальные температуры окисления наноалюминиевого порошка, нано-Al/гидротермального MoO_3 и Al/Fe_2O_3, полученного ультра-звуковым методом, составляют 540,8 ℃, 484,2 ℃ и 514,8 ℃ соответственно. И общие экзотермические теплоты самосборочного нано-Al/MoO_3 в температуре TG-экспериментов составляют около 6696,0 Дж/г, а 801,6 Дж/г, 577,4 Дж/г и 4080,2 Дж/г что выше, чем у нано-Al/коммерческий MoO_3, нано-Al/гидротермальный MoO_3 и нано-Al/Fe_2O_3.
Ключевые слова: MoO_3 нанополоски, термический, самосборка, высокий экзотермический

Нано-AL/MoO_3 термитерін алу және олардың қасиеттері

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Аңдатпа

MoO_3 наножолақтары беттік гидротеримиялық әдіспен дайындалды. Синтезделген MoO_3 наножолақтары екі тәсіл арқылы нано-Al ұнтақтарымен араластыру үшін қолданылды: MoO_3 наножолақтарымен нано-Al ұнтағын араластыру кезінде ультрадыбысты қолдану және екі ұнтақты да агрегатты күйінде өздігінен араластыру. Дайындалған үлгілердің физика-химиялық қасиеттері SEM, TEM, XRD, TGA/DSC әдістерімен сипатталды және соққыға сынау өзіндік салмақпен құлау тәсілімен жүргізілді. Нәтижелер көрсеткендей, MoO_3 морфологиясы аммоний парамолибдатының жиынтықты реттілігі мен концентрациясына тікелей бағынышты. Нано-Al/MoO_3 өздігінен араласқан қоспасының бастапқы тотығу температурасы 478,5 ℃ болды. Ал керісінше, ультрадыбыстық әдіспен араластырудан кейінгі наноалюминий ұнтағының, нано-Al/гидротермальды MoO_3 және Al/Fe_2O_3 бастапқы тотығу температуралары, сәйкесінше, 540,8 ℃, 484,2 ℃ және 514,8 ℃ құрады. Және өздік араласқан нано-Al/MoO_3 қоспасының ТГ-тәжірибелері температуларындағы жалпы экзотермиялық жылуы 6696,0 Дж/г, а 801,6 Дж/г, 577,4 Дж/г және 4080,2 Дж/г құрады, және нано-Al/коммерциялық MoO_3, нано-Al/гидротермальдық MoO_3 и нано-Al/Fe_2O_3 қарағанда жоғары болды.
Түйінді сөздер: нанобөлшектер, теримиялық, өзінөзі жинау, жоғары экзотермиялық