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PREPARATION AND PROPERTIES OF NANO-AL/MOO3 THERMITE

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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 as-prepared 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 improve 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 nano-therimte 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 Sections

2.1 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 100nm 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 100nm and a purity of 99.9%.

2.2 Sample Preparation

2.2.1 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 $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ 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 100mL Teflon-lined autoclave for 20 h at 180℃. After the hydrothermal reaction, the light blue product was washed twice with ethanol 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 ℃.

2.2.2 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 100nm 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 into 100 mL isopropanol. Then, MoO_3-1 was added into the above solution and the mixture was ultrasonicated 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.

2. 3 Characterization

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

3.1 Characterization of MoO_3

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

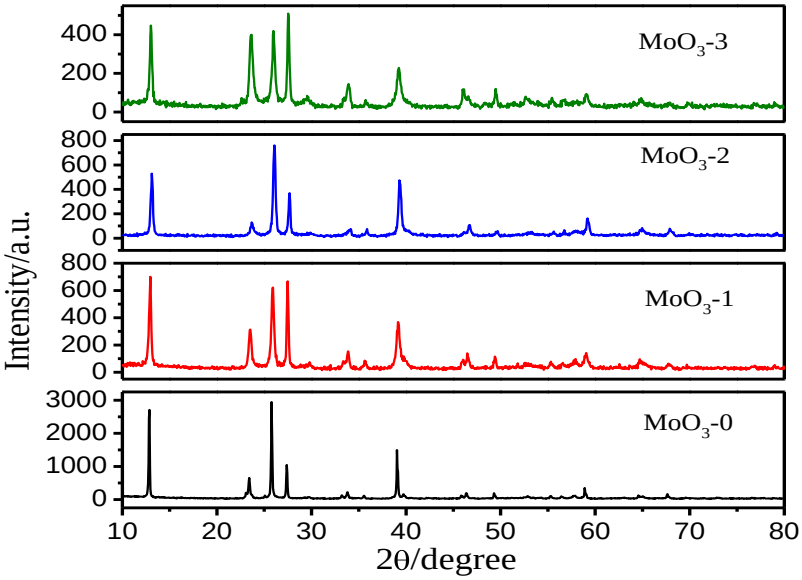

Fig. 1 XRD patterns of MoO_3-0, MoO_3-1, MoO_3-2 and MoO_3-3

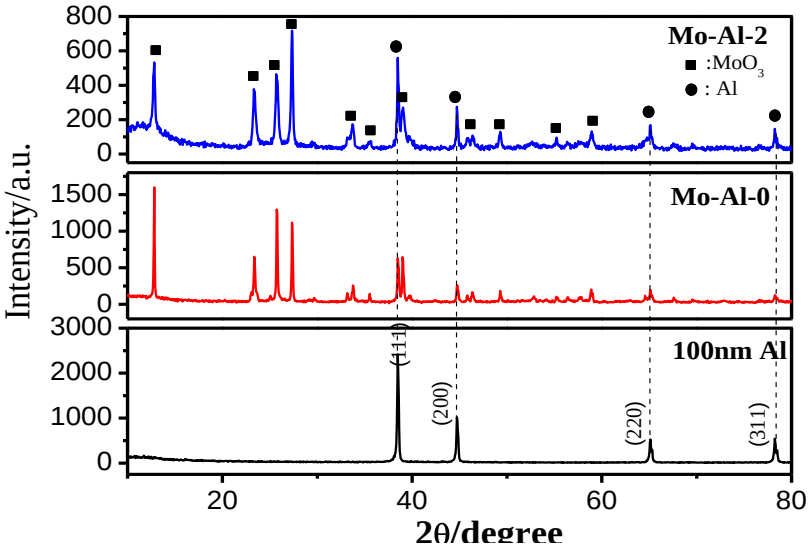

Fig. 3. XRD patterns of 100 nm Al, Mo-Al-0 and Mo-Al-2

The morphology evolution of MoO_3 prepared under different conditions was observed by TEM. As shown in Figure 2 (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 (Figure 2 (c, d)). And the shapes of MoO_3-2 and MoO_3-3 are not regular nanobelts with a large length range (Figure 2 (e-h)). So the morphology of MoO_3 is influenced by the added order of raw materials and the concentration of the $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$ solution. The SAED images in the insets of Figure 2 (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.

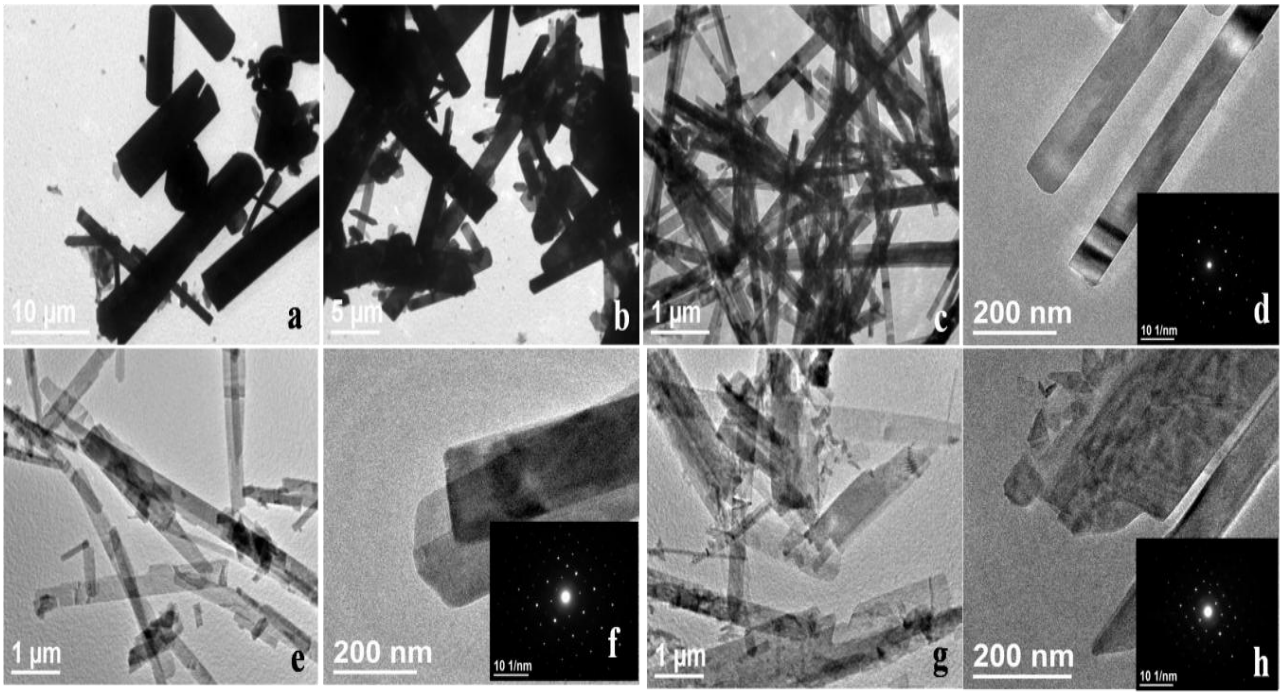

Fig. 2. TEM images of MoO_3-0(a, b), MoO_3-1(c, d), MoO_3-2(e, f) and MoO_3-3 (g, h) ;
The inset images in d, f and h are the SAED of MoO_3-1, MoO_3-2 and MoO_3-3

3.2 Characterization of nano-Al/MoO_3 thermites

The XRD pattern of 100 nm Al powder was displayed in Figure 3. 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 presented in Figure 4(a, b), most of the Al nanoparticles in Mo-Al-0 composite are agglomerated and there is no efficient contact between Al powder and MoO_3 nanobelts due 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 (Figure 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 nanobelts.

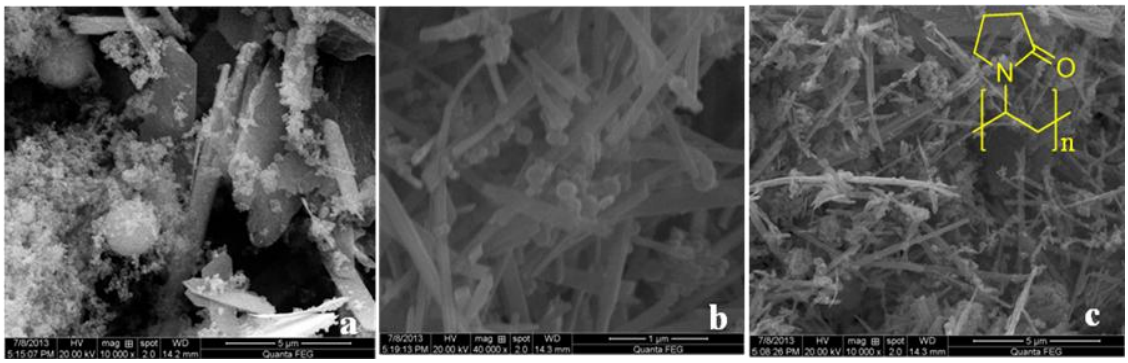

Fig. 4. The SEM images of Mo-Al-0 composite (a), Mo-Al-1 composite (b), and Mo-Al-2 composite (c); the inset in c is the formula of PVP. The molar ratios of Al powder to MoO_3 are kept at 3:1 in different samples.

3.2.3 Thermal properties of Mo-Al thermites

TGA/DSC was applied to measure the thermal properties of Mo-Al composite thermites, and Figure 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 difference between Al powder and thermites, onset temperature and heat released are listed in Table 1.

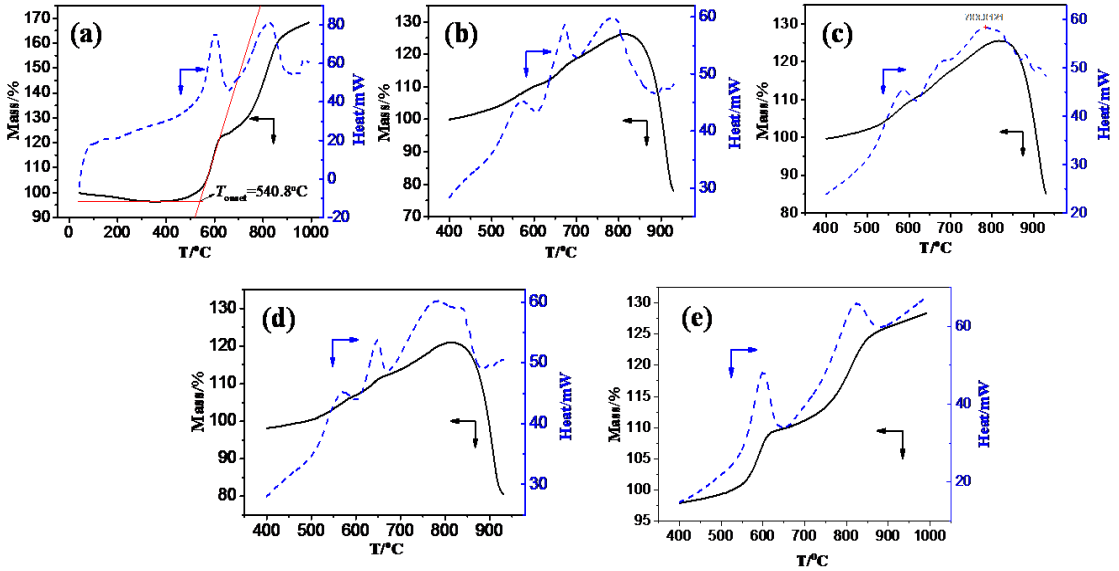

Fig. 5 TGA/DSC curves of 100nm Al and composite thermites;
(a) 100 nm Al, (b) Mo-Al-0; (c) Mo-Al-1; (d) Mo-Al-2; (e) Fe-Al-0

Table 1. DSC results of 100nm Al and thermites

Samples	$H_{365\text{-}663}$ J/g	$H_{663\text{-}912}$ J/g	$H_{365\text{-}912}$ 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	N_2, 20K/min
Mo-Al-0	562.8	903.4	4652.4	572.6	672.3	783.7	474.8	ultrasonic, N_2, 20K/min
Mo-Al-1	497.4	1166.8	4230.2	586.4	678.0	783.8	484.2	ultrasonic method, N_2, 20K/min
Mo-Al-2	604.6	1468.1	4623.3	572.3	647.7	783.1	478.5	Self assemble, N_2, 20K/min
Fe-Al-0	958.8	1657.0	2615.8	599.4	818.0	—	514.8	ultrasonic, N_2, 20K/min

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

DSC analysis (Figure 5, b, c, d) shows an initial exothermic reaction at 365.2-663.2 ℃, which is associated with the reaction between solid Al and N_2, and the subsequent two exothermic 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 ℃. The thermites show a sharp mass loss at 825 ℃, with a residual mass of 50 %, implying the sublimation of MoO_3. The T_{onset} 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 Figure 5 (e) and Table 1, the T_{onset} 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.

As displayed in Figure 5 (b, c, d), there are three main peaks in the DSC curves of thermites. The first peak corresponds to the reaction between solid Al powder and N_2. At about 660 ℃, weight gain accompanied by a second exothermic peak. This second stage of mass gain and related exothermic stage may be due to the reaction between melted Al and MoO_3 nanobelts. The third exothermic peak may be caused by the second oxidation of melted Al. The peak temperature decreases from 830 ℃ to 783.7 ℃, 783.8 ℃ and 783.1 ℃ for Al powder, Mo-Al-0, Mo-Al-1 and Mo-Al-2. Another phenomenon is found that there is an additional exothermic peak at roughly 830 ℃ in the DSC curves of Mo-Al-0 and Mo-Al-1 composites. This may result from the reaction between new formed MoO_3 (Reduced Mo during the thermite reaction) and left melted Al. It is worth noting that, there is no exothermic peak in the DSC curve of Mo-Al-0, which may be attributed to the large particle size of MoO_3. As described in Table 1, The reaction of Mo-Al-2 releases much higher heat than Mo-Al-0 and Mo-Al-1. The total heat released of Mo-Al-2 is 6696.0 J/g and 577.4 J/g, 801.6 J/g and 4080.2 J/g higher than that of Mo-Al-0, Mo-Al-1 and Fe-Al-0, respectively.

4 Conclusion

The additive sequence of HNO_3 and DI water, and concentration of $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$ solution have great influences 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 ^{0}C in the presence of MoO_3 nanobelt. MoO_3 nanobelt can be used as catalyst for the ignition and combustion of nano aluminum.

Reference

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ТЕРМАЛЬНОЕ ПОЛУЧЕНИЕ И СВОЙСТВА НАНО AL/MOO_3

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Аннотация
Нано полоски MoO_3 были подготовлены мягким гидротермическим методом. Синтезированные нано полоски MoO3 были использованы для того чтобы смешать с нано порошком Al двумя способами: смешивая нано порошок Al с нано полосками MoO_3 с применением ультразвука и смешивая нано порошок Al в агрегатном состоянии с MoO_3. Физико-химические свойства подготовленных образцов охарактеризованы SEM, TEM, XRD, TGA/DSC методами и испытывались на удар под собственным весом падения. Температура начала окисления нано смеси Al/MoO_3 будет 478.5℃, с ультразвуковым перемешиванием - 514.8℃.
Ключевые слова: нано полоски, термичный, агрегатное, экзотермичный

НАНО AL/MOO_3 ТЕРМАЛДЫ АЛУ ЖӘНЕ ҚАСИЕТТЕРІ

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Аннотация
MoO_3 нано жолақтары жұмсақ гидротеримялық әдіспен дайындалды. Синтезделген MoO_3 нано жолақтары екі тәсіл арқылы Al нано ұнтақтарымен араластыру үшін қолданылды: MoO3 нано жолақтарымен Al нано ұнтағын араластыру кезінде ультрадыбысты қолдану және екі ұнтақты да агрегатты күйінде араластыру. Дайындалған үлгілердің физика-химилық қасиеттері SEM, TEM, XRD, TGA/DSC әдістерімен сипатталды және соққыға сынау өзіндік салмақпен құлау тәсілімен жүргізілді. Al/MoO_3 нано қоспасының бастапқы тотығу температурасы 478.5℃, ал ультрадыбыстық араластырудан кейін 514.8℃ болды.
Түйінді сөздер: нано жолақтар, теримялық, жиынтық, экзотермиялық