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Preparation of Nano Al_5O_6N via Shock Wave Plasmas Technique

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1. Introduction

1.1 Plasmas technique

Preparation of nano-materials can be divided into three types: gas-phase-, solid state- and liquid-methods. Material researchers have made some achievements in their own fields using different methods. Among them, the gas-phase evaporation method in vacuum is usually filled into the low-pressure inert gas interior (N_2, He, Ne, Ar, etc.). Heating sources such as resistance, plasma, electron beam, laser and high frequency induction are used to make raw material gasificated or to form into plasma, which will lose energy during the collision with the inert gas atoms and then condensed into fine particles by quencher [1]. The technique of plasma plays an important role in preparing nano-materials, especially the metal particle nano-materials, which are prepared by gas-phase methods.

The conception of "plasma" was first reported by Langmuir in 1927, which was firstly applied to investigate the electric discharge phenomena of mercury vapor under low pressure. Plasma is a highly ionized gas mixture, which is consists of electrons, ions, atoms and molecules. The whole system is neutral as positive and negative charges are equal. So, it has different properties from the common gases. The inner electrons, irons, and even neutral particles have higher energy, and all reactions are proceeding under high excited state. This is totally different from the typical chemical reactions, for example, in plasma the inert gas could be highly chemical active and form XeF_6 and O_2F_2 and so on.

According to the degree of gas dissociation, plasma can be divided into high-temperature plasma (high temperature can reach tens of thousands to tens of millions centigrade) and low-temperature plasma (hundreds to tens of thousands centigrade). Low temperature plasma can be divided into thermal plasma (thousands to tens of thousands centigrade) and cold plasma (hundreds centigrade). To prepare ultrafine particle by plasma, chemical reaction can take place (plasma physical method) or not (plasma chemical method).

1.1.1 Plasma physical method

In plasma physical method ultra-fining particles can be obtained by the phase transformation through the energy of plasma. Firstly, the metal powders melt and evaporate into gas using plasma. , Then, the metal powders condense and grow into ultra-fine particles when cooling down. This technique is the most effective to prepare metal and metal alloy nano-particles with high purity and small uniform size.

Wang et al.[2] have prepared the single crystalline phase nano-Tantalum ultrafine particles using the direct-current arc plasma (DC). They designed a Tantalum-to-Tantalum solution using Tantalum stick as the cathode and Tantalum, which could evaporate in a fixed water-cooled copper anode. Then the mixed argon and hydrogen were filled into the vacuum chamber. The Tantalum evaporated under high temperature of arc plasma produced by hydrogen arc, and then smoke-like Tantalum nano-particles precipitated on the low temperature surface. Finally, black nano-Tantalum metal particles were collected after purification. The single crystalline Tantalum nano-particles obtained using this method have a black color, homogeneous particle with an average diameter of 10 nm, and good dispersion. Until now, the nano-powders of Au, Fe, Ni, Ag and Zn have been prepared using the method of direct-current arc plasma (DC).[3-5]

1.1.2 Plasma chemical method

In Plasma chemical processing, some chemical reactions can happen to generate and refine new products. The vapors of volatile metal halide or hydride or metal organics are usually used as raw materials in this method. The nonmetal oxides such as carbides, nitrides and borides ultrafine powders could be synthesized through gas-phase thermal decomposition or other chemical reactions with the energy generated from plasma.

Han et al.[6] prepared silicon nitride nano-spheres with high purity, loose structure and size distribution of 20~30 nm by radio frequency plasma vapor deposition(R.F, CVD) technique, using $SiCl_4$ and NH_3 as raw materials. Waterfall flows of Titanium atoms generated from the Titanium anticathode and cathode by (O_2 + Ar)arc plasma, and were oxidized to form TiO_2 nano-crystals in the ionized oxygen plasma region, which has been reported before. The prepared TiO_2 nano-powders were highly dispersed sphere-like particles with an average diameter around 20 nm, and the grains were mixed structure of anatase and rutile.[7]

Radio frequency plasma would not produce the impurities of electrode materials in plasma because it dose not use electrode. It could use gas during the preparation process. At the same time, the residence time of the compounds would increase due to the larger plasma space, and the reactants could be completely reacted and heated. Shang Shuyong et al.[8] in Sichuan University have prepared the Aluminum nitride ultra-fine powders by DC arc thermal plasma using micro aluminum powders as raw material. During the preparation process, aluminum powders were inputted by nitrogen as carrier gas, so, the flow of powder and the distribution of temperature in the reaction tube were achieved by adjusting the flow rate of nitrogen gas. Nitrogen and Aluminum reacted in the reaction chamber, and after that, ammonia was added at the end of the chamber to form aluminum nitride powers. Then, the powers rapidly quenched, nucleated, grown up and finally were collected by bag collector. As-prepared Aluminum nitride was pure and the particles with an average diameter of 100nm were highly dispersed.

Studies have shown that high temperature plasma method is fast, easy to achieve mass production, and it can prepare almost any kind of nano-materials, especially for nano metal materials. The prepared nano-material is zero-dimensional and homogeneous.

1.1.3 Issues in typical plasma methods

Although plasma method has certain advantages in the preparation of nano-materials, there is also a drawback of exorbitant energy consumption, which limits its space of industrialization.

The plasma methods can be divided into the method of direct-current arc plasma (DC), radio frequency plasma (RF) and hybrid plasma (HP) according to the ways of generating plasma. As heat induced plasma, they all have the properties of high temperature, containing plenty of electrons, ions and other active particles, controllable atmosphere etc., which offers the many new possibilities for material processing and creates new opportunities for scientific research on material properties. However, further production has revealed the drawback of excessive energy consumption of thermally induced plasma.

It can reach a high core temperature but small scale high temperature zone via direct-current arc plasma (DC). The plasma generator or reactor always have huge temperature gradient (10^5~10^6 K/m) and velocity gradient (10^4~10^5 m/ s•m), so it is difficult to move the particles exactly to the high temperature zone of the generator or reactor of arc plasma and make the target materials gain proper and effective heat. It is more difficult to load the gas reactants into the high temperature zone of plasma reactor to mix and react completely.

Radio frequency plasma generator or reactor has a bigger high temperature zone, which is good for reaction. The lower velocity of plasma in reactor (usually 10 m/s scale), controllable atmosphere, and no electrode pollution are benefit to obtain clean products. However, Radio frequency plasma reactor itself has large energy consumption and low energy efficiency (less than 50%), so it is difficult to reduce product cost. Furthermore, the input particles or gas reactants need to be organized elaborately in consideration of the complex flow field in reactor.

Recently, the schemes of tandem connection of direct-current arc and radio frequency plasma, parallel connection of multi direct-current arc and direct-current arc using ring-like anode have been used to enlarge the high temperature zone and offer a better material producing surroundings or improve the yields of product. However, all above schemes inevitably make the system more complex and make investment larger. Therefore, it is necessary to explore novel plasma to make up for its shortages.

1.1.4 Design of novel plasma

Making a general survey of DC, RF and combination of the two methods, although the plasma is generated in different ways, they all prepare ultra fine powders in the same principle. Raw material particles (solid or liquid) are rapidly heated by the thermal plasma with high temperature, containing various electrons, ions and active particles in excited state. Then the particles are evaporated or cracked to complete the necessary reactions of gas reactant, and finally grow up to form the goaled product after quenching, nucleating. The process is shown in Fig.1.

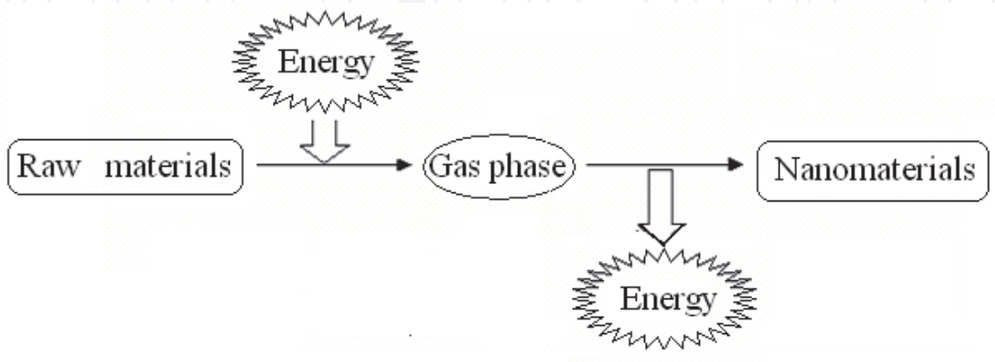


Fig. 1. A schematic illustration of preparing nano-materials using plasma

The process from solid to gas then nano-powders is determined by the preparation of goals with regard to the preparation craft, which can be seen from Fig.1. The exploration of space is very small, but the different energy ways to generate plasma and the following forms of energy release have left a wide thinking space to the researchers.

1.1.5 Shock wave plasmas technique

There are various methods and ways to generate plasma, which are related to lots of microcosmic processes, physical effects and experimental methods. The most common methods used to generate plasma in chemical fields are mainly listed as follows: [9]

(1) Gas discharge plasmas

The gas molecules are ionized through colliding with the accelerated charged particles especially the electrons in the electric field. Plasma forms by disruptive discharge of gas under the effect of cathode secondary emission and other mechanisms. The plasma currently actually used in laboratory and production is produced by gas discharge. In particular, the most widely used is radio frequency discharge.

(2) Photo ionization and laser emission ionization

The plasma is formed by ionizing the molecule through gathering the energy of incident photons. The precondition is that the photon energy should be larger than the first ionization energy. The laser emission belongs to photo ionization in itself, but it not only possesses single photon ionization but also multi photon ionization in ionized mechanism, which results in difference in ionization mechanism from normal photo ionization methods. For example, In multi photon ionization, the atoms or molecules ionized by absorbing numerous of photons at the same time. So argon plasma can be obtained by irradiating the argon gas using ruby laser. In recent years, application of laser plasma in chemical fields such as chemical deposition by laser plasma has gained an obvious ascended trend, because it is easy to achieve plasma with high temperature and high density.

(3) Irradiation

The plasma could also be generated by irradiating the gas with various rays or particles beams such as the α、β、γ rays produced by radioisotope, X-rays given off from X-ray tube and beams of electron or ion accelerated by accelerator, etc.. The plasma generated via α rays is equivalent to the gas molecules collided and ionized with nuclear power particles. β rays is a beam of election current, the generated ionization is equivalent to ionize by high speed election collision. While γ rays and X rays could be recognized as photo ionization. The collision ionization of gas molecules is obtained by accelerated particles such as beams of electrons and ions. The ion beams show lots of advantages due to the controllable accelerated energy, intensity of flow and impulse.

(4) Combustion method

This is a method already well known as thermal ionization, which generates ionization by the collision between the atoms and molecules with sufficient kinetic energy with the help of thermal motion, and the generated plasma called flame plasma.

(5) Shock wave methods

The plasma generated by the adiabatic compression of gas called shock wave during the process that shock waves pass through the sample gas. Actually, it belongs to thermal ionization.

1.2 Preparation of nanometer Al_5O_6N via shock wave plasmas technique

1.2.1 Introduction

It has drawn much attention from the society since the Al_5O_6N with spinel structure was found[10-17]. Compared with the normal Al_2O_3, the crystal lattice in Al_5O_6N recombines, because the atom "O" is displaced by the atom "N". It results that the Al_5O_6N not only keeps the excellences from the white gem, such as higher tenacity and rigidity, but also has the outstanding isotropic characteristics, which avoids briefringent effect from aeolotropism within the use of Al_2O_3 poly-crystal. As a result, it is hopeful for Al_5O_6N to replace the large cost white gem in the armed techno-field, and become the preferred material in the aspect of high-speed missile rectifier and the bulletproof glass of the new pattern armored-car [18]. At present, the transparent ceramics of Al_5O_6N has been produced for business in foreign countries, and it is also being studied step by step in China. From the literatures all over the world, it is not hard to see that the very point to prepare the Al_5O_6N transparent ceramics is getting ceramics powder with higher purity and agglutinating activity. It is easy to get Al_5O_6N ceramics powder with higher purity by the existing technic, but it is difficult to get better agglutinating activity. The study of nano-tech shows that when the ceramics come to the nano scale, the agglutinating activity will be improved effectively. The nano particles have very small size, big BET surface area and high rate of diffusion, which results in the speedup of densification in the process of agglutination and reducer of the agglutinating temperature and time greatly. For example, the common Al_2O_3 ceramics agglutinate under 1750°C . However, when doped with 0.1%~0.5% nano Al_5O_3 powder, the agglutinating temperature can be reduced to less than 1500°C , and at the same time, the intensity and tenacity of the 85 and 95 ceramics doped with nano Al_5O_3 can also be improved to 1.5 times[3]. Therefor, whether agglutinated immediately or used as the filler in the process, the preparation of high purity nano Al_5O_6N transparent ceramics is helpful for raising the agglutinating activity of Al_5O_6N.

It is difficult to prepare nano Al_5O_6N powder with high purity, because the high temperature becomes the huge bottleneck to avoid agglomeration. We use a new method named blast wave plasma to prepare the Al_5O_6N quickly by the detonation of the mixed explosives. However, as the reaction is so fast and complex, it is difficult to study its process in detail. Here, we designed some contrast experiments, analyzed the reaction mechanism of detonation for nano Al_5O_6N with the energetic material TNT and the metal Al powder as the starting materials in water, which will establish the theoretical basis for the development of the technology.

1.2.2 Design of the experiments

1.2.2.1 Construction of shock wave plasma field

Actually, the reported direct-current discharge, radio frequency discharge and microwave discharge are gas discharges generating plasma to convert the electric energy to thermal energy. The electron beams and ion beams plasma belong to irradiation method. From the ways to achieve energy, the gather of transient state super high energy from the detonation of energetic material provides the possibility of generating plasma, and the preparation of nano-materials using shock wave plasma could be designed based on this.

The energy of shock wave plasma is obtained from powerful thermal energy and strong shock wave instantaneously released by the detonation of material with high energy such as TNT, RDX, PETN, HMX etc.. The transient state production of solid powder materials was achieved by powerful shock wave, super high pressure and temperature in

microenvironment formed by the strong plasma field. The preparation of nano-materials by shock wave plasma has brought in the extreme conditions of powerful shock wave, super high pressure and compulsory rapidly cooling besides the necessary high temperature, which is different from other plasma fields. The introduction of the extreme conditions is hopeful to achieve the chemical reaction or physical process, which is hard to achieve under normal conditions, and brings new energy to the techniques of nano-material preparation.

Using explosion of energetic materials to synthesize materials began with the preparation of nano-diamond.[19] Soviet scientists first reported the detonation synthesis of nano-diamond in 1984, and then the synthesis prelude using detonation was opened. They gained a trial-production in 1990 by detonating 140 kg explosive charge in the explosion chamber with a diameter of 12 m [20]. Since then, the U.S., Japan, Germany and other developed countries have also reported the synthesis of nano-diamond by detonating one after another[21,22]. Since 1992, Jin Zengshou in Lanzhou Institute of Chemical Physics, Xu Kang in Gansu Research Institute of Chemical Industry and Hui Shourong in Beijing Institute of Technology have also done the research [23,24]. However, the experimental scale and performance of the products were behind that of the developed countries. The related explosion synthesis mechanism was discussed on this basis. The detonation of energetic materials is a transient state process of high temperature and high pressure, and so, it is very difficult to measure directly. Many researchers have to find the relative evidence of the synthesis mechanism only from the detonation products.

Samara[25] supposed that the detonation of energetic materials was a fast reaction process that firstly generated the mixture of electriferous atoms or elementide called low temperature plasma, and then formed stable phase of diamond in thermodynamics. Ree et al.[26] thought that carbon phase in the detonation products was first separated from fluid phase to form semi-stable state graphite and changed to become diamond by phase transformation. Tinov et al.[27] considered that the molecules of explosive reaction decomposed to be various atoms, and a part of carbon atoms combined to form graphite in the reaction zone, then produced diamond through phase transformation. Yamada et al[28] observed extremely round spherical carbon particles in detonation products by electron microscope analysis. Accordingly, he presented the generate mechanism of diamond phase under high temperature and pressure was that the initial gas state carbon condensed to liquid carbon drop in the detonation reaction zone because of supersaturating, and the liquid carbon drop formed diamond by phase transformation. Hui Shourong got the similar results by electron microscope analysis.

From the mechanism studied by the former researchers, it is not difficult to find that the plasma can be obtained during the detonation process with a phase transformation from gas carbon to liquid carbon drop and even graphite. Therefore, it is completely possible to construct the transient state shock wave plasma field with the help of detonation process in energetic materials.

1.2.2.2 Selection of energetic materials

The main energetic materials here is TNT, which has the scientific name of 2,4,6-trinitrotoluene, and molecular formula of $C_7H_5N_3O_6$, relative molecular weight of 227.13, and -73.96% for the oxygen balance. Its structure is shown in Fig.2.

The pure TNT is colorless needle-like crystal. Its industrial products are yellowish flaps with physical properties of low hygroscopic, non-volatile at room temperature and difficult to dissolve in water, slightly dissolve in ethanol, CCl_4 and CS_2. TNT is neuter. It can't corrode

metal or react with heavy metal oxide obviously. It performs satisfactorily for pressing and casting, and has good stability for experiment.

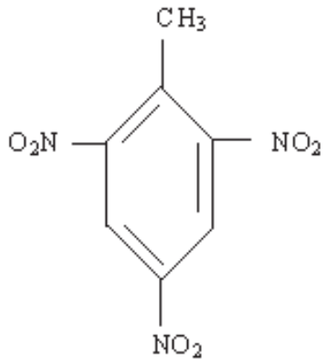


Fig. 2. Structure of TNT

TNT is a typical negative oxygen balanced explosive, which would produce large amount of carbons, and the reaction equation is as follows:

$$C_7H_5N_3O_6 = 2.5H_2O + 3.5CO + 1.5N_2 + 3.5C \quad (1\text{-}1)$$

Different from normal condition, the free carbon and nitrogen generated through the detonation of TNT have high activity, which creates beneficial material conditions for design and synthesis of nano-materials. In this sense, TNT is the energy source as well as important material source. The powerful shock, super high pressure and temperature have provided several effective ways to form the transient state of high thermal energy plasma field.

1.2.2.3 Selection of cooling medium in shock wave plasma field

Among the reported methods for plasma, gasified materials or gaseous products lose energy while colliding with the atoms of inert gas, and then they are cooled rapidly to form ultra-fine particles, which is a process of energy release. The fast energy release can make the particles in plasma field reach a thermodynamic stable state and avoid agglomeration.

The theoretical study of underwater ordnance shows that [29] the shock wave generated by explosive under water could be rapidly absorbed by aqueous medium. The spread velocity of shock wave in water is several times larger than that of sound (about 1520 m/s) in water. Therefore, the shock wave could be far away from the centre of explosion and the energy provided by shock wave in plasma field decreases fast to achieve the partly energy release, as the shock waves transmit fast in water. At the same time, impulse bubbles formed by explosion also help to the energy release rapidly. So, we choose water as the cooling medium in the research as it can not only cool down faster, but also possess the advantages of easy acquired, economy and environmental friendly.

Above all, with the general requirements in the area of material preparation encourages environmental protection and energy saving in nowadays, the dual features of transient state energy field and material field in shock wave plasma field make this method possess good development prospects. The reactions which are difficult to achieve in normal conditions are expected to be achieved when combining the chemical theory with the extremely preparation conditions. It is important and meaningful to the development of novel materials, and it enriches the theories of explosion physics and chemistry.

1.2.3 Experimental procedures

1.2.3.1 Preparation of Al_5O_6N nano-powders

All reagents were commercially available and used without further purification. In a typical experiment, the negative oxygen explosive TNT and the metal Al powder(average diameter 200 mu, 99.0%W) were mixed together with a mass ratio of 4:1, and the mixture was loaded into a mould and pressed into a column shape with a density of 1.60g/cm^3.

Then the column mixture was put into a 1 L stainless autoclave, which was special-designed according to the temperature and pressure during detonation. After filling 500 mL water, the autoclave was sealed and the column mixture was ignited through the detonator outside. The detonation resultant was collected and filtered with 230 mesh screen to remove the coarse impurity. The filtrate was filtered again after depositing for 5 h to obtain the dark precursor. After treatment in inorganic acid for 1 h at 80°C , dark solid was obtained by filtration, washing with absolute ethanol and distilled water, and drying at 60°C for 2 h. The carbon in the dark precursor was removed through calcination at 600–700°C for 1 h to obtain gray powder. The calcination temperature schedule of the precursor was decided through a differential thermal analysis/thermogravimetry (DTA/TG, model STA449C, NETZSCH, Germany company), using an ascending rate of 10 K/min from 23°C to 800°C and a velocity of air flow of 20 mL/min.

1.2.3.2 Instruments

Crystalline phase was determined by X-ray diffraction (XRD, model D/Max-IIIB, Shimadzu) instrument with Cu Ka radiation (λ = 0.15418 nm). The scanning rate of 0.05^0/S was applied to record the pattern in the 2θ range of 10–70^0. The crystal size was calculated with Scherer's formula.

Laser Common Focus Raman Spectrum Instrument (model Renishaw-1000, England) was used to analyze the degree of graphitization of carbon particles in the mixture at ambient temperature, employing an argon ion laser at an excitation wavelength of 514.5 nm. The scan area ranges from 100~2000 cm^{-1}. The capacity of the incident light is 5 mW. The slit breadth of the monochromator is 24 μm. The diameter of the light spot is 1~2 μm.

Morphological feature and particle size of the products were investigated by a high-resolution transmission electron microscope (HRTEM, model JEM-2100, Japan), using an accelerating voltage of 200 kV.

Analysis of element content was done with Thermo ESCALAB 250 XPS instrument (America) using Al Kα radiation (hυ = 1486.6 eV).

1.2.3.3 The antioxidancy of Al_5O_6N

Differential thermal analyzer (DTA, model STA449C, NETZSCH) is employed to analyze the temperature course of nano Al5O6N at the reaction of oxygenation and denitrify. The heating rate is 10K/min.The flow rate of air is 20mL/min. The sample' quality is 10.181 mg. The scan area ranges from 23~1360°C and the sample pond is made by Al_2O_3.

1.2.4 Results and discussion

1.2.4.1 XRD analysis of the precursor

The key idea of our method for the synthesis of Al_5O_6N is to carry out a shock wave plasma process including the detonation of explosive column, decomposition of chemistry substances, dispersion and rebuilding of free atoms or gas ions. The precursor including

carbon and Al_5O_6N was produced during this process. Fig.3 displays the typical XRD pattern of the precursor.

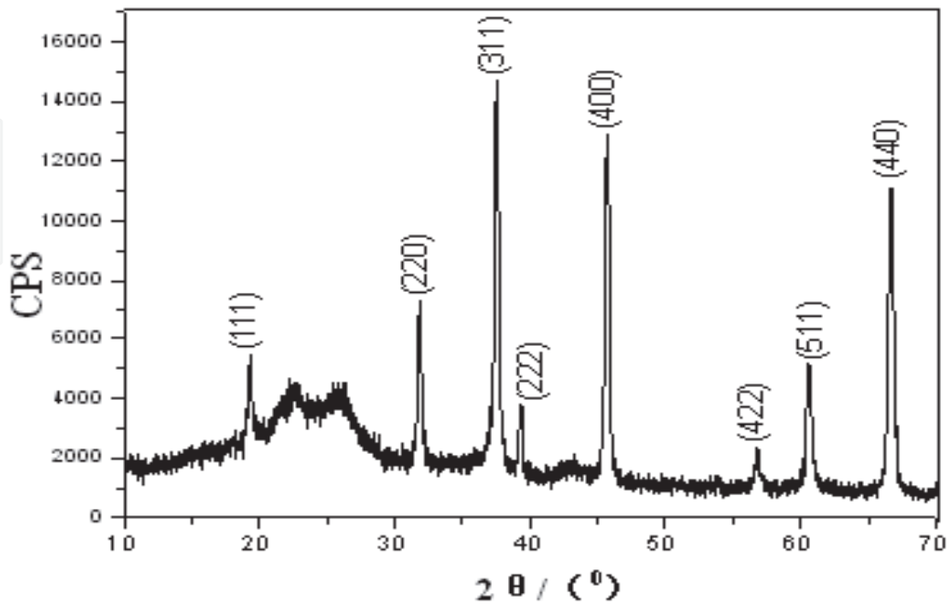


Fig. 3. XRD pattern of the precursor

It shows that the half band widths are 4.586, 2.808, 2.394, 2.288, 1.984, 1.621, 1.526, 1.402 and the position and intensity are according with JCPDS 48-0686, which confirms that the major constituent of the powder is Al_5O_6N.

The main peaks have an obvious broaden phenomena and the strongest diffraction appearing at 37.54^0 with the half band width of 0.440 can be indexed to (311) plane. According to Scherer equation, the average size of the particles is 28 nm. The whole spectrum has a higher diffraction mount and in $20\sim30^0$ exits some low and broad peaks, which indicates the product contains ultrafine imperfectly crystallize carbon in the detonation process, especially in the diffraction position at 25.5^0 where exists a low and broad graphite diffraction.

1.2.4.2 Raman analysis of the precursor

The following laser common focus Raman spectrum in Fig.4 approves the crystallographic structure of the carbon in the precursor. Fig.4 shows that there exists two wide peaks at 1344.81 cm^{-1} (D-band) and 1575.94 cm^{-1} (G-band). The D-peak at 1344.81 cm^{-1} is related to a resonant Raman process, generally at 1370 cm^{-1}, it represents a peak of disordered graphite with primary imperfections, and the decrease of its intensity indicates the increase of degree of graphitization. The G-peak at 1575.94 cm^{-1} is associated with an E_{2g} mode of graphite and related to the vibration of sp^2 -bonded carbon atoms in a two- dimensional hexagonal lattice, such as in a graphite layer, which is consistent with the reported data [30]. Comparing with the Raman spectrum of nature monocrystal graphite, in which there is only one acute peak at 1580 cm^{-1} (G-band), the Raman spectrum of the precursor is unsymmetrical and the peaks are widened obviously, which indicates that the carbon in the precursor consists of amorphous carbon and nanographite. The above analysis proves that the precursor is the composite of nanometer Al_5O_6N and incomplete crystalline nanographite.

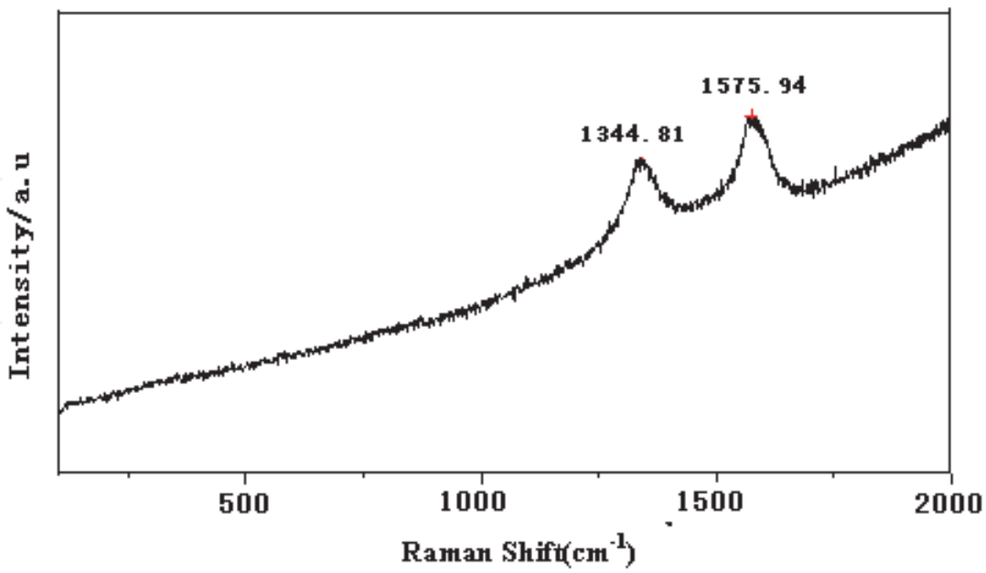


Fig. 4. Raman spectrum of the precursor

1.2.4.3 TEM images of the precursor

Fig.5 shows the TEM image of the sample prepared in the optimum technology. It is concluded that the sample is particle-like with a uniform diameter from 20~40 nm and has no obvious accumulation.

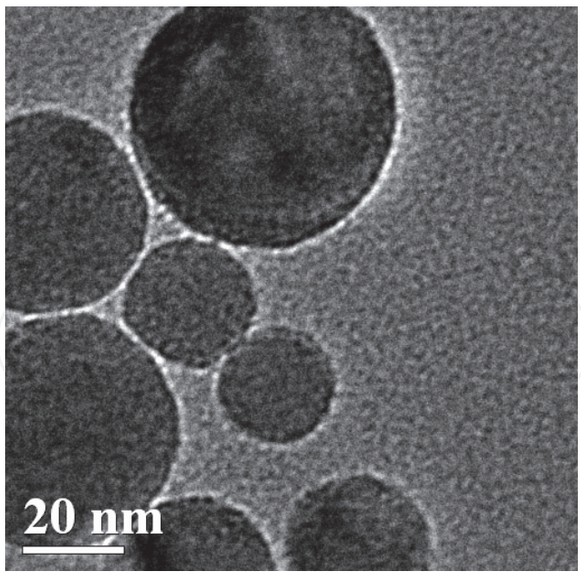


Fig. 5. HRTEM image of the precursor

1.2.4.4 DTA/TG analysis of the precursor

The carbon in the precursor can be removed through calcining process at proper temperature, which can be decided through DTA/TG analysis of the precursor in Fig.6. The

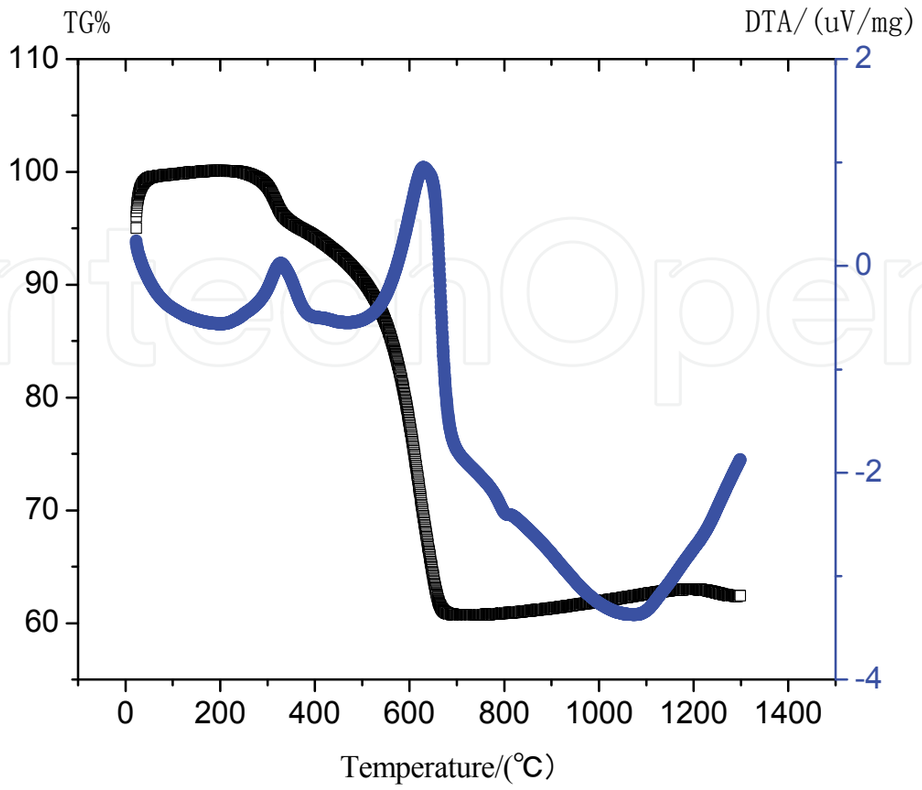
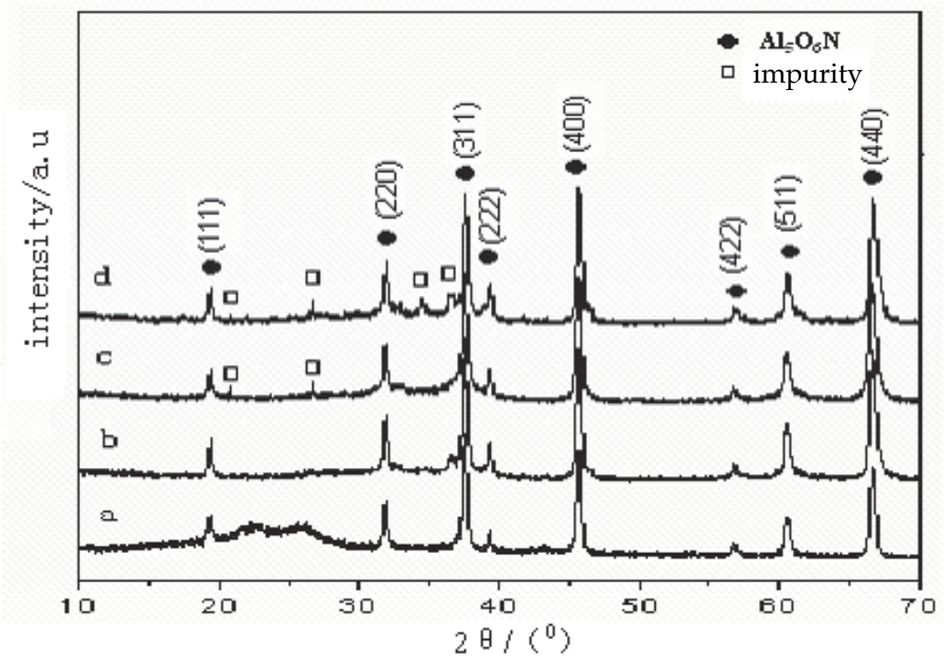


Fig. 6. TG-DTA curves of the precursor

thermal mass loss curve shows that the mass increases slightly at the beginning of elevating temperature, which is due to the flowing oxygen adsorbed by the oxygen-vacancy of the Al–O–N system. Subsequently the mass decreases from 327°C to 672°C . There are two obvious turning points at 327°C and 672°C , which are corresponding with the two obvious exothermic peaks of DTA curve, a weak exothermic peak at 327°C and a strong exothermic peak at 628°C . The mass loss of 3% at 327°C attributes to the slow oxidation of amorphous carbon and the mass loss of 34% at 672°C attributes to the rapid oxidation of nanographite, which shows that most of the carbon in the precursor is graphite. The above results are also consistent with the foregoing XRD analysis and Raman spectrum analysis of the precursor. The DTA/TG analysis shows the mass content of carbon is 38% and the Al_5O_6N is 62%. At the same time, the DTA/TG analysis result can also be considered as an evidence of calcining temperature schedule. According to Fig.6, carbon can be removed by calcining the precursor at the temperature about 600°C .

1.2.4.5 Influence of different calcining temperature

Fig. 7 shows the XRD patterns of the as-synthesized Al_5O_6N powders calcined at 600°C, 700°C and 800°C . Pattern (b) in Fig. 7 shows that the as-synthesized powder calcined at 600°C for 1 h is fully crystalline cubic structure and all of the reflections can be indexed to the crystal planes of a standard cubic Al_5O_6N crystal (JCPDS 48-0686). There exists no other crystalline peaks except Al_5O_6N in the pattern. According to Scherer's equation, the mean particle size of the Al_5O_6N crystal is estimated to be 28.21 nm, which is consistent completely with that of the precursor, seeing pattern in Fig.1. It indicates that the Al_5O_6N



(a) the precursor (b) 600°C (c) 700°C (d) 800°C

Fig. 7. XRD patterns of products obtained by calcining the precursor at different temperatures

crystal has not grown up and the carbon indicates that the Al_5O_6N crystal has not grown up and the carbon is completely eliminated after calcined at 600°C for 1 h. Increasing calcining temperature has no obvious effect on the particle size, while some new crystalline diffraction peaks appear at 25.558, 34.878 and 37.568, seeing pattern (c) and (d) in Fig.7. These new peaks are identified to be a-Al_2O_3 crystal, which can be attributed to the oxidation of Al_5O_6N crystal at 700°C and 800°C for 1 h. Therefore, the calcining temperature should be controlled at about 600°C to assure that product has the pure Al_5O_6N phase.

1.2.4.6 TEM image of the sample

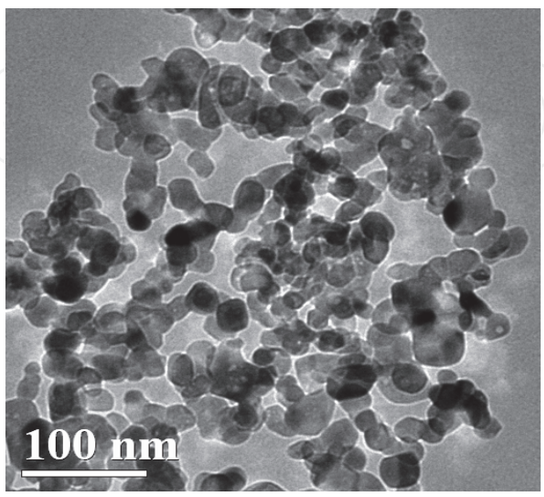


Fig. 8. TEM image of nano Al_5O_6N powder obtained by calcining the precursor at 600°C

Fig.8 shows the TEM image of the sample prepared in the optimum technology. It is concluded that the sample is particle-like with a uniform diameter from 30~40 nm and has no obvious accumulation.

1.2.4.7 XPS analysis of the sample

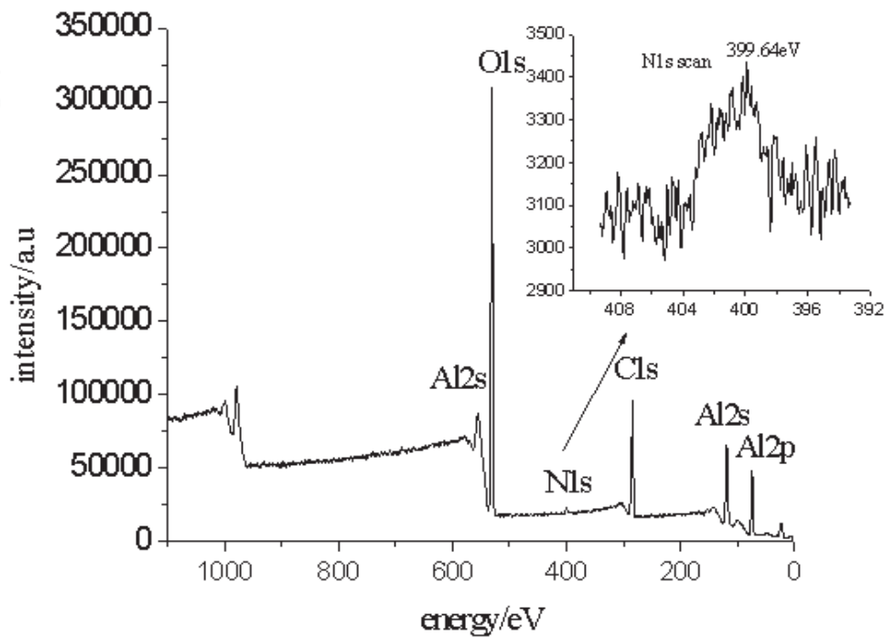


Fig. 9. XPS analysis of the nano Al_5O_6N powder

Fig.9 displays the XPS profile for the as-synthesized Al_5O_6N sample. The analysis results for the XPS spectrum areas show that the N1s region is near 400 eV, the Al2s region is near 119 eV and 582 eV, and the O1s region is near 530 eV. The binding energy peak for the N is broad, extending from 395.4 eV to 405.7 eV, which can be indexed to Al–N binding energy. Although the N1s peak in the XPS spectrum is weak, the peak position and its broaden are clear in the inset.

1.3 Discussion of mechanism for Al_5O_6N nano-powder

1.3.1 Mechanism for preparation of Al_5O_6N

1.3.1.1 Theoretical analysis

It is well known that the explosion is a very complex and rapid chemistry process. The strong hit and huge pressure produced in a split second become the largest barriers to analyze the reaction detailedly. An improved theory from the classic one about the detonation of the explosive compound contained Al insists that the first step of composite detonation of explosive is the detonate reaction of the energy-contained material:

$$C_7H_5N_3O_6 \longrightarrow 2.06CO + 1.03CO_2 + 1.88H_2O + 0.62\ H_2 + 1.5N_2 + 3.91C \qquad (1\text{-}2)$$

Then the metal reacted with the product of the detonation at the high temperature and high pressure:

$$1.03CO_2+0.6\ Al \longrightarrow 0.34Al_2O_3+1.03CO \quad (1\text{-}3)$$

$$1.88\ H_2O+1.26Al \longrightarrow 0.63\ Al_2O_3+1.88H_2 \quad (1\text{-}4)$$

The overall reaction is :

$$C_7H_5N_3O_6+1.94Al \longrightarrow 0.97Al_2O_3+3.09CO+2.5H_2+1.5N_2+3.91C \quad (1\text{-}5)$$

However, our experiment indicates that the product gained from the detonation of TNT/Al explosive under the protection of water is Al_5O_6N but not Al_2O_3.The possible mechanism of the formation of Al_5O_6N may be as follows:
In process [1], the reaction goes by the classic theory. Firstly, Al_2O_3 forms, and then Al_5O_6N is obtained followed by the replace reaction of N_2 at the high temperature.

$$TNT / Al \longrightarrow Al_2O_3 \longrightarrow Al_5O_6N$$

In process [2], Al_5O_6N forms after the detonate reaction immediately.

$$TNT / Al \longrightarrow Al_5O_6N$$

And if the process [2] comes into existence, is there a conflict with the classic theory of the detonation of explosive that has been approved?
The preparation of Al_2O_3 by detonation of explosive has been proved by the classic experiment and that Al_5O_6N gained under the protection of water has been proved by this experiment. The results look like opposite, unless there is a process [3].
In process [3], Al_2O_3 is obtained by the detonate reaction of TNT/Al without water. At the beginning, Al_5O_6N may produce. Then the reactions of oxygenation and denitrify at the high temperature occurred. Finally, Al_2O_3 is obtained.

$$TNT / Al \longrightarrow Al_5O_6N \longrightarrow Al_2O_3$$

In order to prove the process [1], we should testify whether Al_2O_3 could react with C or N_2 to form Al_5O_6N at the high temperature. This step will be tested by the proving experiment (1).
If process [1] doesn't come into existence, which means the Al_5O_6N could be formed directly without forming the intermediate Al_2O_3, then process [2] worked.
For process [3], we only need to check whether the final product of the oxidation reaction of Al_5O_6N is Al_2O_3 or not,which react without any protections at the high temperature. This step will be tested by the proving experiment (2).
The proving experiment (1): the negative-oxygen explosive TNT and the common Al_2O_3 were mixed uniformly with a mass ratio of 4:1 and the mixture was loaded into a mould and pressed into a column shape with a density of 1.60g/cm^3. Then the sample was produced for characterization by repeating the operation of the synthesis process of nano Al_5O_6N.
The proving experiment (2): The synthesized Al_5O_6N was calcined at 1300°C with oxygen existing. Then, the gained sample was characterized by XRD.

1.3.1.2 The comparison of XRD of two detonations' products

Fig.11(a) and Fig.11(b) show the XRD patterns of the detonated products of TNT/Al and TNT/Al_2O_3.

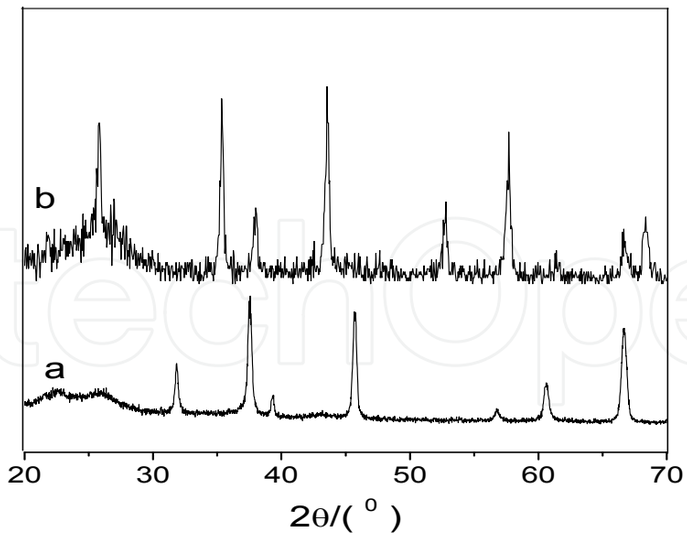


Fig. 11. XRD patterns of two different detonated products (a): TNT/Al (80/20); (b) TNT/ Al_2O_3 (80/20)

The position of the major diffraction peaks in Fig.4(a) has a strong inosculation with the standard JCPDS 48-0686, which confirms that the powder is mainly composed of Al_5O_6N. The main peak has an obvious broad band and the strongest diffraction appeared at 37.54^0 with the half band width of 0.440 can be indexed to (311) plane. According to Scherer equation, the average size of the particles is 28 nm, which matches the result of the electron microscope image. The whole spectrum has a higher diffraction mount and in $20\sim30^0$ exits some low and broad peaks, which indicates the product contains ultrafine imperfectly crystallized carbon in the detonate process, especially in the diffraction position at 25.5^0 where exists a low and broad graphite diffraction.

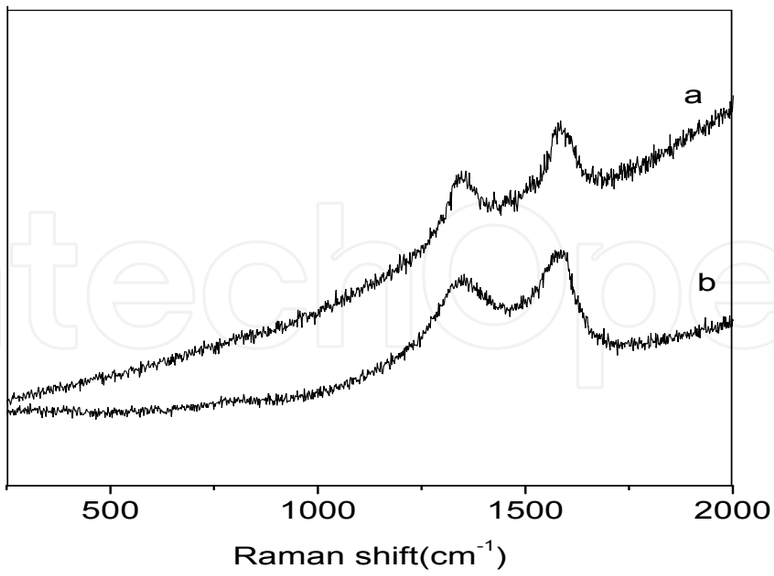
The position and intensity of the diffraction showed in fig.4 (b) match the standard JCPDS 46-1212 well, which confirms that the powder is α-Al_2O_3. The main peaks also have an obvious broad phenomena and the strongest diffraction for (311) plane located at 43.28^0, with the half band width is 0.440. According to Scherer equation, α-Al_2O_3 has a size of about 25 nm.

It is concluded that under the protection of water, the products are Al_5O_6N and Al_2O_3, which obtained from the detonation of explosive of TNT/Al and TNT/Al_2O_3 respectively.

1.3.1.3 The comparison of Raman spectra of two detonations' products

Fig.12 (a) and (b) show the laser of the detonate products from TNT/Al and TNT/Al_2O_3.

There is no obvious difference between the two Raman spectra of the products. Two wide peaks are located at 1344.81 cm^{-1} and 1575.94 cm^{-1}, and at the lower wave number side exists tailing. The whole spectra are unsymmetrical. The peak at 1344.81cm^{-1} is related to graphite's D-peak, formed from the A_{1g} vibration of aberrant carbon atoms induced by graphite micro-crystal border effect. The peak at 1575.94cm^{-1} is related to graphite's G-peak, formed from E_{2g} mold vibration of atom plane layer in the graphite's lattice, which suggested that the carbon in the mixture powder is graphite phase. According to the analysis of XRD, we can conclude that the micro-size carbon is not crystallized perfectly, but genus-graphite phase.



(a) TNT/Al (80/20) (b) TNT/ Al_2O_3 (80/20)

Fig. 12. Raman spectrum of two detonate products

Conclusion from the XRD and Raman analysis of the two detonate products is that in the explosion, Al_2O_3 could not react with N_2 to form Al_5O_6N at the high temperature with the coexistence of C.

1.3.1.4 The IR spectra of two detonations

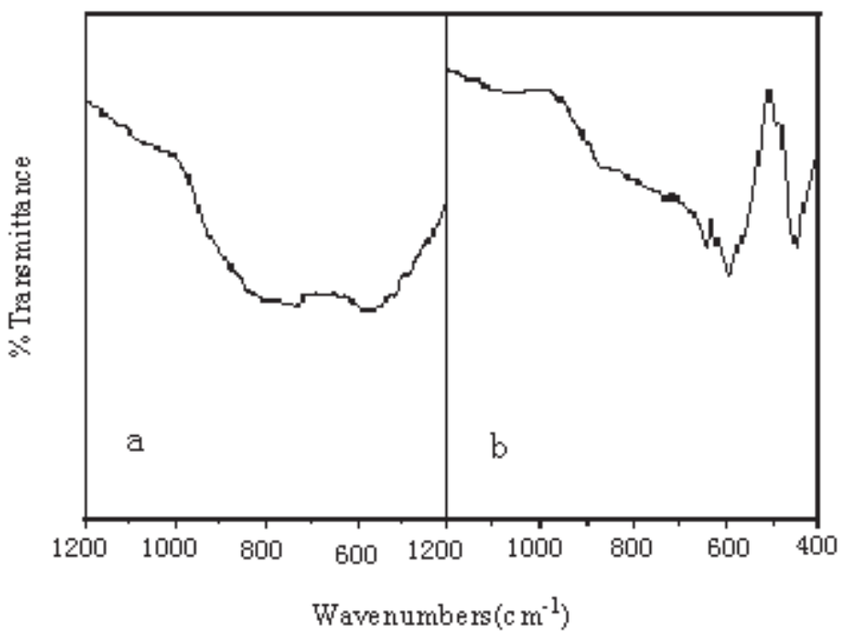


Fig. 13. The infrared spectra of two different detonations (a): TNT/Al(80/20) ; (b) TNT/ Al_2O_3(80/20)

In the Fig.13 (a), Al_5O_6N has a broad and messy absorption band in the area 400 cm^{-1} to 1200 cm^{-1}, which are the characteristic absorbing peaks of Al_5O_6N. Its board frequency band and strong absorption spectrum is induced by the nano-powder's huge specific surface area. Compared with the pure Al_2O_3, the specific surface area increases with the atom O replaced by N. Which induces the decrease of average coordination number of Al^{3+} and increase of unsaturated bonds. As a result, the nano Al_5O_6N would not have a single and merit bond vibration mode, but a rather broad distribution of vibration mode, and the vibration frequency also has a broad distribution under the infrared light field. Thence, the infrared spectrum of Al_5O_6N has a characteristic of peak broaden (Fig.13 (a)). The Fig.13 shows that Al_2O_3 exists obvious fine structures at 455.3 cm^{-1}, 598.7 cm^{-1} and 639.3 cm^{-1}, as Al^{3+} has a higher average coordination number and it is easier to generate a single and merit bond vibration mode which leads to the present of fine structure in the infrared spectrum. In the precondition of the similar size, the obvious differences between the two powders' capacity for infrared absorption makes a further proof of the different composition of the two powders.

Integrated on the comparative analysis of the XRD、Raman、IR, it is known that under the protection of water, the detonation product of TNT/Al（80/20）is made up of Al_5O_6N and type-graphite ultrafine carbon. It suggests that in the explosion, Al_2O_3 could not react with N_2 to form Al_5O_6N at the high temperature with the coexistence of C and N_2, and Al_5O_6N could only be produced by one step.

1.3.1.5 The discussion of the TNT/Al detonation reaction mechanism

According to the results of the two detonations, Al_2O_3 could not be replaced by N_2 at the high temperature and pressure. It is concluded that TNT/Al explosive detonation product, Al_5O_6N, is directly generated. The possible reaction mechanism is like this:

The explosive reaction forms a detonation field with ultrahigh temperature and pressure in a flash. All the materials that TNT contained exist in the form of fragment "atom". Aluminum is dissociated into gaseous ions in a moment and all of the fragments diffuse and mix under the disturbance of strong charge in the shock wave plasma space. Different atoms splash after being mixed in the effect of rapid cooling. The splash is selective and the splash ability is closely related to the electro-negativity of the element. The electro-negativity of different elements in the plasma space is showed in table 1[31, 32].

element	Al	H	C	N	O
$\mathbf{X_P}$	1.61	2.18	2.55	3.04	3.44

Table 1. the electro-negativity(X_p) of different elements in the shock wave plasma space

Table 1 shows that the electro-negativity of O and N is larger than Al. When different Ions react in a splash, Al^{3+} with the smallest electro-negativity has priority to splash with O, N and generates Al_5O_6N. The excessive N atoms will form N_2 through a covalent bond in the splash process, in spite of its higher electro-negativity. Because the excessive N atoms are stable and could not attract electrons easily due to its half-full state P orbit. In addition, the

diameter of N atom is small, which will lead to a large repulsion force among the electrons. Empathy, C and H elements formed C and H_2, and the total reaction equation of the mixed detonation of TNT and Al is:

$$C_7H_5N_3O_6+5Al \longrightarrow Al_5O_6N+2.5H_2+N_2+7C \quad (1\text{-}6)$$

The excessive TNT reacts according to type (1-2).
The prepared Al_5O_6N powder was calcined at 1300°C for 2h with aerobic condition, and the Fig.14 shows the XRD spectrum of the generated powder.

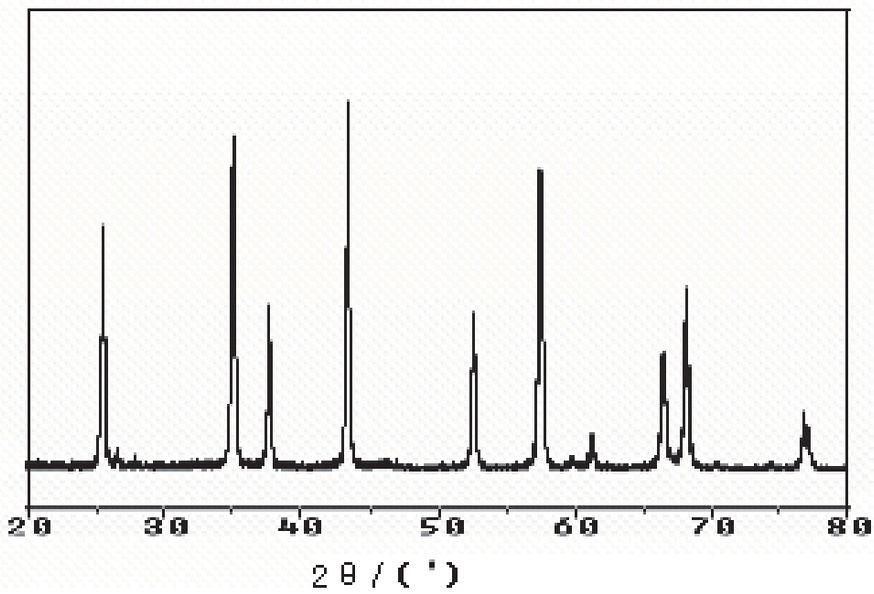


Fig. 14. XRD of the sample got from the calcined nano-Al_5O_6N

Test results from the samples show that Al_5O_6N powders calcined at high temperature can remove N and generate Alumina. Thence, it is entirely possible to rapidly oxidize and remove nitrogen at a higher temperature. When the rapid cooling occurs under the protection of water and C, the detonation stops by (1-6). However, in the absence of the protection of water and under aerobic condition, the solid-phase C is completely oxidized, and the Al_5O_6N is transformed to Al_2O_3 by oxidation and denitrification losing the protection of C.

$$4Al_5O_6N+3O_2 \longrightarrow 10Al_2O_3+2N_2 \quad (1\text{-}7)$$

1.3.1.6 Verification of the mechanism

The crucial point to judge an analysis of a reaction mechanism is whether it can accurately predict the composition of the final product. According to the above mechanism analysis, 20g Al reacting with 33.6 g TNT due to the formula 1-6 would generate 36.3g Al_5O_6N and 12.4g C.
According to the explosion reaction formula 1-2, superfluous 46.6 g TNT would generate 9.6 g C, the explosion reaction of TNT with Al (80:20) could produce 58.3 g solid materials consist of 37.7% C and 62.3% Al_5O_6N.

Take advantage of the removal of carbon in the mixed-products in oxygen, we carry on TGA tests to the TNT/Al detonation product, and the results are showed in Fig.6.
The DTA-TG curves of the mixture show that there are two obvious exothermic peaks at 23~800°C . The mass loss of 38% at 672°C is attributed to the oxidation of nano-graphite. After the heat released, the curve goes to a platform, which indicates the nano-graphite is completely released, and Al_5O_6N is 62%. The contrast of the theoretical calculation and the actual detection is showed in table 2.

Composition	Carbon content (Wt%)	Al_5O_6N content (Wt%)
Theoretical calculation	37.7	62.3
Actual detection	38	62

Table 2. The contrast of theoretical prediction and actual detection to the TNT/Al detonation product's component

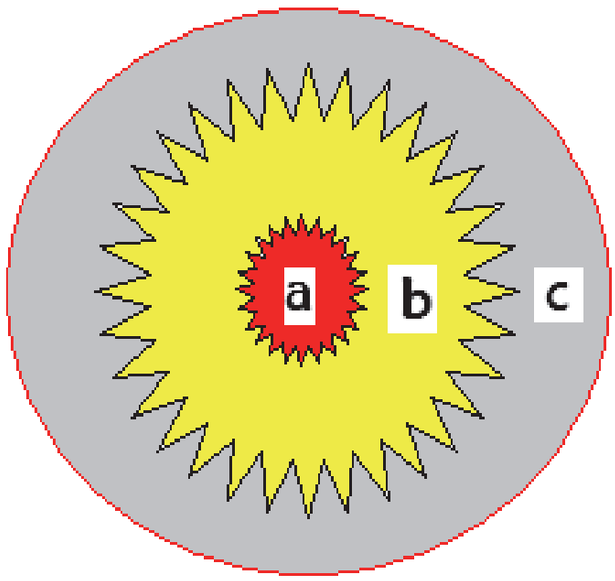
The theoretical analysis is basically consistent with the actual detection, and the analysis of the process of preparation of Al_5O_6N under water protection is further confirmed.
In a word, TNT/Al could directly generate Al_5O_6N by detonation reaction. In the classical theory, Al_5O_6N is transformed to Al_2O_3 by oxidation and denitrification at the high temperature without water protection as follows:

$$TNT/Al \longrightarrow Al_5O_6N \longrightarrow Al_2O_3$$

In this sense, the result does not contradict with the classical theory, but a further complement to it.

1.3.2 Discussion of mechanism of controlling agglomeration during the preparation of Al_5O_6N nanoparticles by shock wave plasma technics

The key point of preparation of nano-materials is to control the agglomeration, which is an integral process of the micro-particles' growth speed with time. As the speed or the time tends to 0, the agglomeration would be over. So, there are two ways to control the agglomeration, one is slow down the particles' growth speed; and the other is to reduce the growth time.
From the traditional compose techniques, high temperature is a necessary condition for preparation of Al_5O_6N, which is also the main driving force of agglomeration. Therefore, it is very difficult to control the growth speed of micro-particles under high temperature, which is the reason why Al_5O_6N nano-powder could not be prepared by conventional method. So, control the growth time is the only path to reduce agglomeration. Shock wave plasmas technique is chosen to prepare Al_5O_6N nano-powder because it could control the growth time during the composition at high temperature and further control of the agglomeration of the micro-particles.
Shock wave plasmas are obtained by instant compress of the gaseity substance by strong shock wave engendered from the explosion of materials with high energy. With the speed emission of the explosion products, shock wave plasmas field will orderly evolve as shown in Fig.15:



(a) plasmas field (b) splash field (c) crystal field

Fig. 15. Sketch map of orderly evolvement of shock wave plasmas field

The main body of TNT/Al detonator column explodes instantly under the shock wave of starting detonator, with the early pressure of 18～25GPa and temperature of 3000～3500K . The explosive detonation reaction forms a mass of gaseity matters and powerful shock waves.

In the exiguity area of the explosion, under the cooperation of super high pressure and strong shock wave, gaseity molecules absorb energy and bring on high temperature, which makes the atoms vibrate more acutely. Then the bonds among atoms break and form various lively free radicals in plasma state called plasma as showed in Fig.15 (a). In this area, fragments of C、H、O、N and Al irons radiate forth. Along with the expander of bulk, attenuation of shock wave energy and rapid decline of plasma temperature, products of explosion come into spatter area which is showed in Fig.15(b).

In spatter area, fragments of C, H, O, N and Al irons spatter and react selectively. O, N and Al form Al_6O_5N. H combines with O to compose H_2O. C combines with O to compose CO and CO_2. Some dissociate carbon atoms or radicals in the reaction area diffuse, collide and finally agglomerate. The products continue to radiate forth and come into crystal area with the further decline of temperature as showed in Fig.15(c).

Liquid matters diffused into crystal area crystal rapidly to form millions of nucleus due to sharp decline of temperature. The crystal nucleus is highly dispersed because of strong shock waves. At the same time, the forced soon cooling of water protection results in very short crystal time of goal production, which controls the growth time of crystal nucleus effectively. The powder keeps on diffusing and come into normal temperature area, where growth will stop immediately without heat drive of agglomeration.

From the rapid and orderly evolvement of shock wave plasma field, products of explosion existed as gaseity or liquid state in plasma and spatter area could not reunite under strong shock waves, and the agglomeration only happens in crystal area. However, the forced soon

cooling of water protection make the process of temperature decline from crystal temperature to normal temperature finish in a second. This is a typical rapid quencher process, which makes the crystal area very narrow and crystal time very short. All these would control growth time of crystal nucleus effectively, and further control of the agglomeration. In addition, super-micro-carbon produced by explosion of detonator in balance of negative oxygen are highly dispersed under strong shock waves, which has some obstruct effects on coagulation of crystal nucleus during the crystal process and management later. It is proved by the phenomenon that the size of nano-particles has no obvious changes before and after calcining

In a word, strong concussion, ultra-high temperature and pressure and rapid forced cooling are the distinct virtues of shock wave plasmas technique. Products of explosion advance orderly along with plasma, spatter and crystal area instantly by rapid diffusion, which controls the growth time of micro-particles and further control their agglomeration under high temperature.

1.4 Thermal stability of Al_5O_6N nano-particles

1.4.1 TG/DTA curves of Al_5O_6N nanoparticles

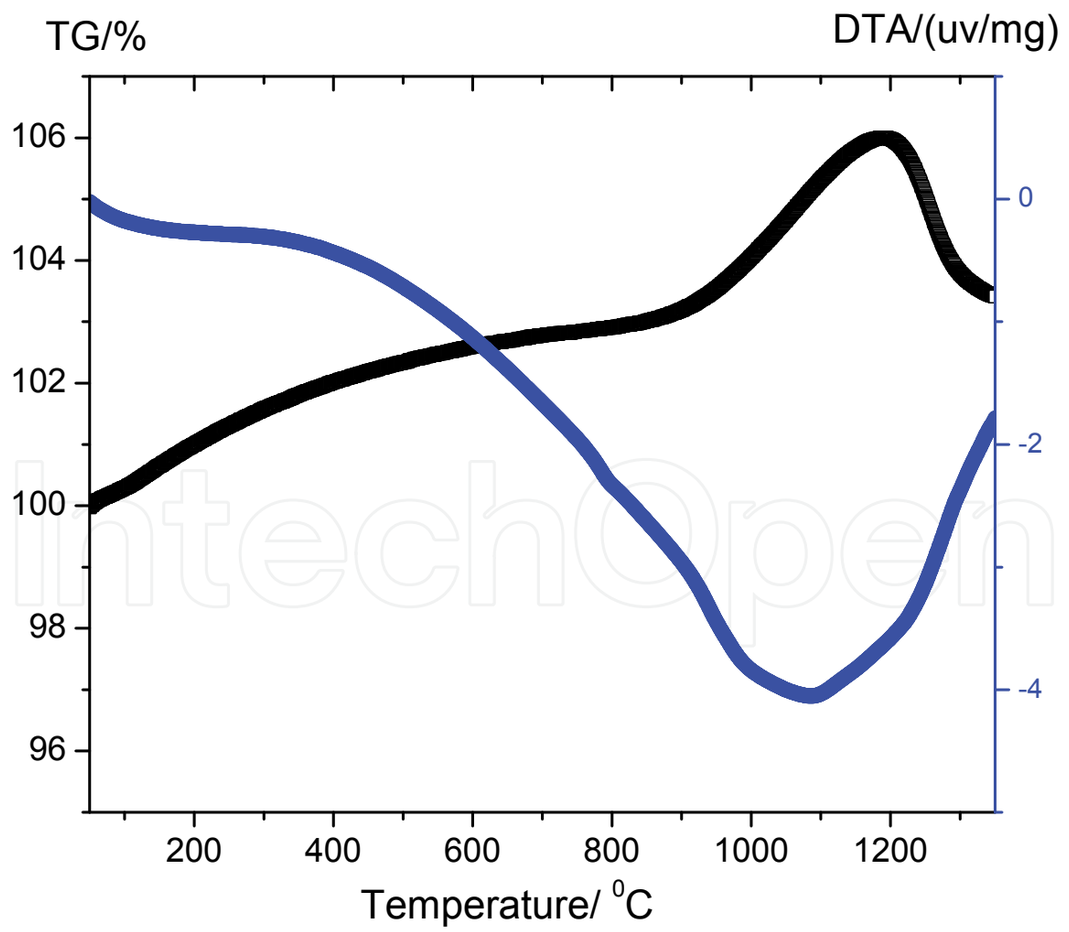
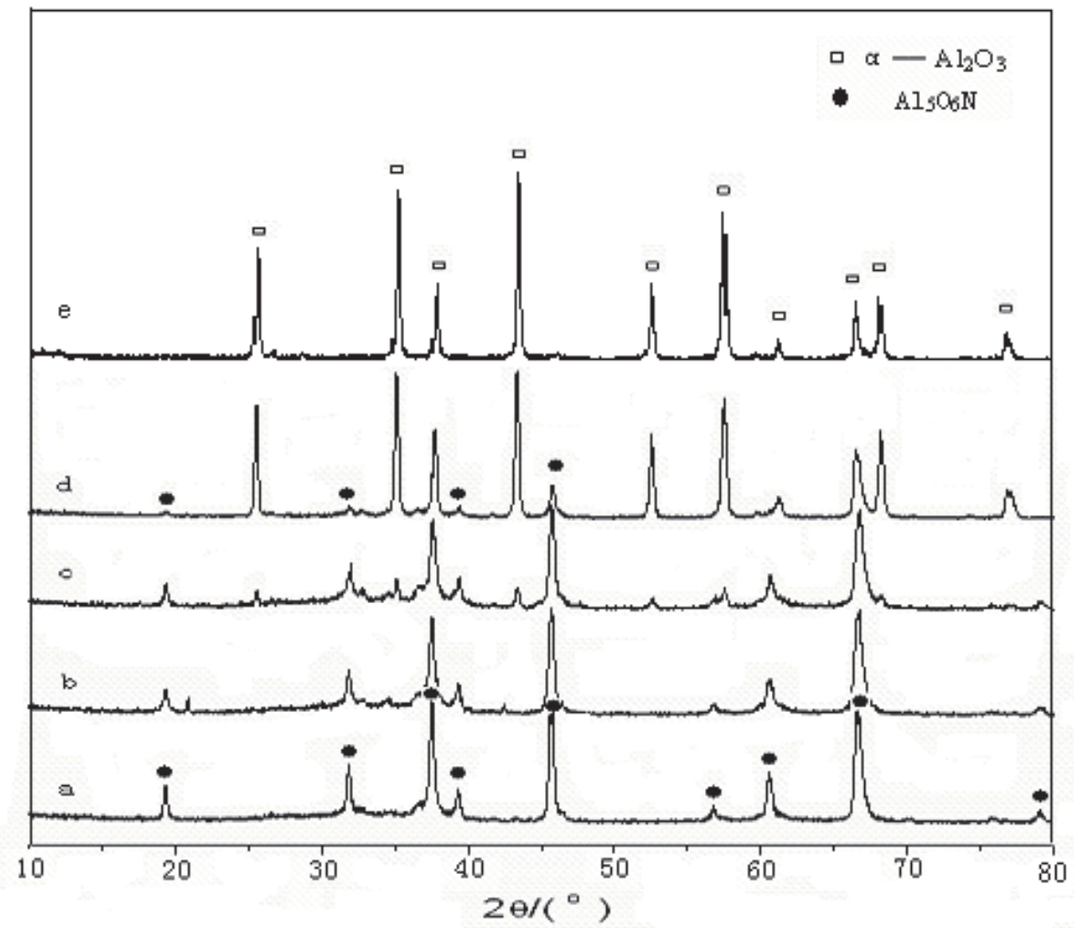


Fig. 16. DTA/TG curves of the nano- Al_5O_6N

DTA tests were performed to lucubrate the oxidation process of Al_5O_6N, and the results were showed in Fig.16.

The DTA-TG curves of the mixture show an obvious broad peak under the temperature from 23 to 1360°C .. There is only a little weight gain from room temperature to 950°C , which maybe have relation with N-doped effect. The effect results in many O holes in nano-powders and makes it possible for O to enter the inside of the powders. The nano-powder can absorb oxygen at low temperature, but atom O has a weak ability to enter the lattice. With the increase of the temperature, the powder's weight increases quickly until 1200°C . Then, the quality of the powder declines as the temperature rises, which may be due to the reaction of denitrify. The whole trend of the process is entirety similar to the DTA-TG curves of existing Al_5O_6N. The major difference is the denitrify temperature of Al_5O_6N bring forward 85°C than that of Al_5O_6N's 1285°C . Meanwhile, the DTA curves exist a visible endothermic peak in the heating process, which indicates the denitrify process of Al_5O_6N is an obvious endothermic process.

1.4.2 XRD patterns of the samples calcined at different temperature



(a) Al_5O_6N (b) 1000°C 3h (c) 1100°C 3h (d) 1200°C 3h (e)1200°C 5h

Fig. 17. XRD patterns of different samples

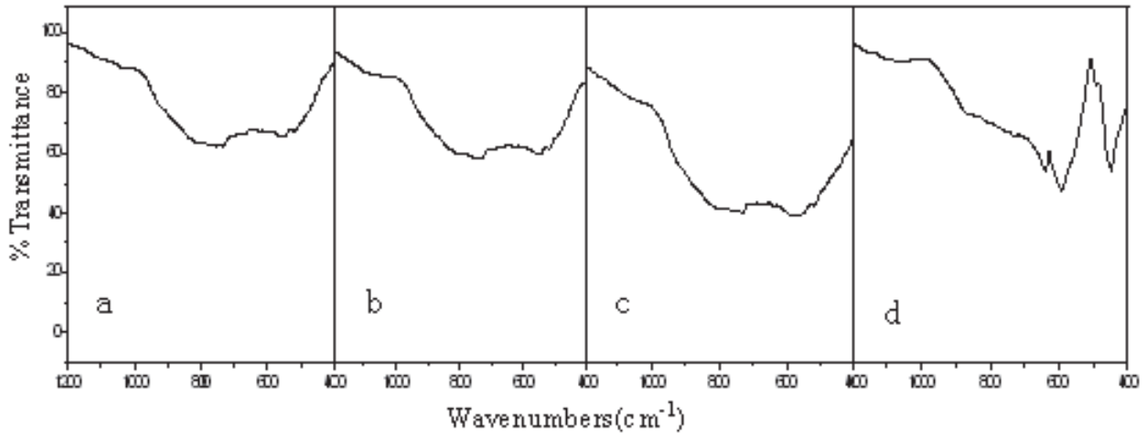
The influence of different calcining temperature on crystal phase of the samples was studied by XRD, and the results are showed in Fig.17.

From Fig.17, we can see that the crystalline phase of nano- Al_5O_6N powder keep well in the condition of 1000°C for 3h,which indicates that in low temperature Al_5O_6N has certain antioxidant capacity. As the temperature rises to 1100°C , the peaks of Al_5O_6N still exist, but some low peaks of γ-Al_2O_3 appear at the same time. Integrate with TG, the reason could be that the enriched oxygen causes Al_2O_3 separate out and γ-Al_2O_3 is stable at low temperature. When the sample is calcined at 1200°C for 3h, the diffraction of γ-Al_2O_3 has a boost up and the peaks belongs to Al_5O_6N die out gradually, which suggests that most of the Al_5O_6N has been oxidated and trasformed into α-Al_2O_3. If the temperature keeps at 1200°C and calcination time prolongs to 5h, the peaks belong to Al_5O_6N disappear and all the powders change into α-Al_2O_3. So, we can conclude that when the temperature is below 1000°C , Al_5O_6N has certain stability, and the reactions of oxygenation and denitrify will occur when it comes to 1200 °C . The denitrify needs a few time, because the denitrify reaction in crystal is a diffuse process. According to the existing researches [33,34] to the dynamics of nitrogen oxides, the oxidation of nitrogen oxides can be divided into three stages; the control of reaction speed, mixed speed and diffusion speed. The advance of α-Al_2O_3 interface in the process of thermal oxidation above 1200°C is the main restrict step to the continuance of oxidation. The final result of thermal oxidation is the genaration of α-Al_2O_3. The reaction equation is:

$$4Al_5O_6N + 3\,O_2 = 10\,Al_2O_3 + 2N_2 \tag{1-8}$$

1.4.3 IR spectra of the samples calcined at different temperature

Fig.18 shows the results of IR characterization of the samples calcined in different conditions.



(a) nano-Al_5O_6N (b) 1000°C 3h (c) 1100 °C 3h (d) 1200°C 5h

Fig. 18. The infrared spectra of different samples

In Fig.18 (a), there is a broad and messy absorption band in the area 400 cm^{-1} to 1200 cm^{-1}, which belongs to Al_5O_6N. The nano-powder's huge BET surface area induces Al_5O_6N's broad frequency band and strong absorption spectra. Compared with the pure Al_2O_3, as the

atom O is replaced by the atom N, the BET surface area increases, which induces the decrease of average coordination number of Al^{3+} and increase of its unsaturated bonds. As a result, the nano Al_5O_6N would not have a single and priority bond vibration mode, but a rather broad distribution of vibration mode, and so the vibration frequency also has a broad distribution under infrared irradiation. Thence, the infrared spectrum of Al_5O_6N has a width characteristic.

Related to XRD results, the main phase of the samples in Fig.18(b) and (c) is still Al_5O_6N with only a little γ- Al_2O_3, and there is no obvious change to the shape of the characteristic absorbing peaks of the mixture. Pure Al_2O_3 (Fig.18(d)) can be obtained after being calcined at 1200°C for 5h. The characteristic absorbing peaks completely disappeared, and the spectrum is obviously different from Al_5O_6N. Al_5O_6N has a broad and messy absorption band and doesn't have obvious fine structures. While Al_2O_3 in the similar size has obvious fine structures at 455.3 cm^{-1}, 598.7 cm^{-1} and 639.3 cm^{-1}, as Al^{3+} has a higher average coordination number and it is easier to generate a single and priority bond vibration mode which leads to the present of fine structure in the infrared spectrum. In the precondition of the similar size, the obvious difference between the two powders' composition makes a further difference in the capacity for infrared absorption.

1.5 The dynamics research of thermal oxidation to Al_5O_6N

According to the thermal analysis of the high-temperature oxidation process of Al_5O_6N, we can see that there is an obvious nitrogen and oxygen reaction during the process. To learn more about the nano- Al_5O_6N's activation energy of the nitrogen occurred in the thermal oxidation, we use Kissingrer [35] to solve the apparent activation energy (E) and pre-exponential factor (Z) of the Al_5O_6N's thermal oxidation:

$$\ln\frac{\beta}{T_r^2} = \ln\frac{R\cdot Z}{E} - \frac{E}{R}\cdot\frac{1}{T_r} \tag{1-9}$$

In the formula, β, Tr, E, R and Z represents the heating rate, the temperature of the peak, the activation energy, the gas constant and the pre-exponential factor, respectively. The Value of R equals to 8.314J/ (mol·K).

Tr can be learned from the thermal decompositon curve of different heating rate(β), mapping of $\frac{1}{T_r}$ to $\ln\frac{\beta}{T_r^2}$,we can obtain the activation energy(E) from the curve's slope and the pre-exponential factor(Z) from the intercept of the line.

We can also calculate the reactive rate constant(K) in the thermal oxidation process by Arrenius equation

$$K = Z\exp(-\frac{E}{T\cdot R}) \tag{1-10}$$

Use DTA analysis to research the effect of different heating rate to the decompound process of Al_5O_6N's denitrify. The calefactive rates are 5°C /min, 10°C /min, 20°C /min, 30°C /min and Fig.19 shows the results.

The curves indecate that as the increase of the heating rate the decomposition peaks of nano-Al_5O_6N offset to the pyrorigion. According to Kissingrer method equation to solve the

apparent activation energy(E) and pre-exponential factor(Z) of the Al_5O_6N's thermal oxidation are showed in table 2.

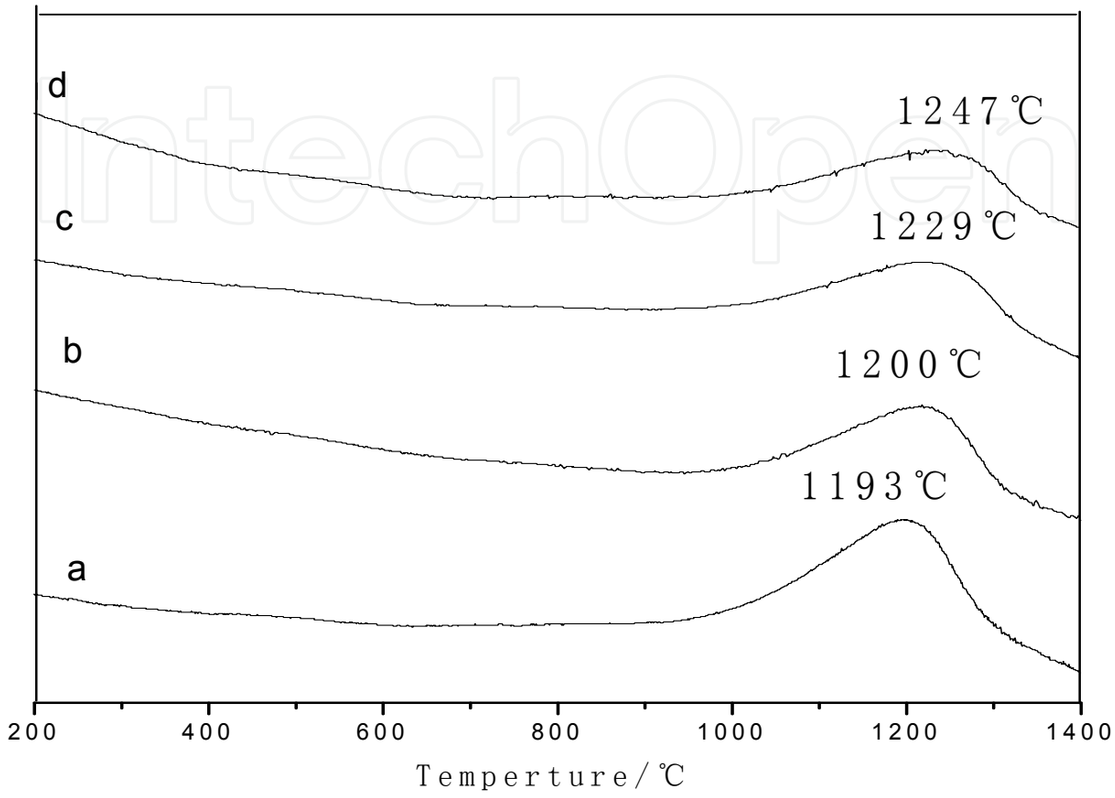


Fig. 19. The TG curves of different heating rate (a):5°C /min; (b):10°C /min; (c):20°C /min; (d): 30°C /min

Sample	t (°C)	E (KJ/mol)	ln Z_H
5	1193	60.25	38.49
10	1200		
20	1229		
30	1247		

Table 2. The data of DSC and dynamics constants of nano- Al_5O_6N's thermal oxidation

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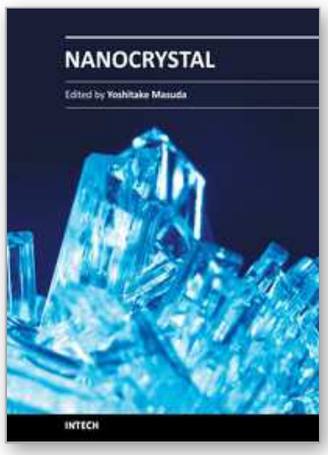
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