Research paper

Preparation of reactive thin film consisting of diazodinitrophenol particles and its reaction characteristics ignited by pulse laser ablation

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Abstract

We have prepared reactive thin films by using primary explosive particles with organic material as a binder. Thin films of 20 μm to 750 μm in thickness were prepared by the bar-coater method and also by pour the solution and dry process (PAD method). Diazodinitrophenol (DDNP) particles we have used are 10 μm in size and are fixed by cellulose triacetate (CTA). We chose dichloromethane as the solvent of CTA. By varying the mass ratio of solute to solvent materials in the bar-coater method, DDNP-CTA texture can be controlled.

Ignition tests were performed for reactive thin films prepared in this study. Pulse laser ablation of thin film surface and successive reaction process have been observed by two different high speed cameras with different optics. Reactivity was found to depend on the laser irradiation direction at least in case of films of multi-layered structure manufactured by PAD method with thickness more than 100 μm. No detonation reactions were realized among tested reactive thin films and the experimental conditions.

We have found the following peculiar combustion process. Combustion of the film takes place in three stages: (i) DDNP particles are ejected from both surfaces of the film by pulse laser ablation of the surface, (ii) induced air shock wave leads to the combustion of these particles, and (iii) finally film body starts to react due to residual thermal energy of itself and adjacent high temperature region created by burning particles.

Keywords: Reactive thin film, Primary explosive, Pulse laser ablation, Laser ignition.

1. Introduction

Downsizing of satellites or various space objects are desired. In these applications, very small amount of propellant and / or high energetic materials of less than several tens of mg mass must be used at a time. Reaction control of very small amount of high energetic materials is, to authors' knowledge, not fully established, although some of the authors tried to manufacture thin film made of several kinds of explosive materials. [1)-4)] We have been studying thin layered high explosive as a primary device of initiating high explosive charge. [5)-10)] We are aiming at laser based initiation of high explosive based on the enhancement of laser energy absorption by intentionally roughened surface. [5)-7)] In these studies, pentaerithritoltetranitrate (PETN) powders are sandwiched between a transparent plastic plate and / or a glass plate, one of the surfaces of which is intentionally roughened. Although they can be applied to design the laser detonators, powdered materials are not very convenient compared with solid bulk substances. Furthermore, critical diameter or dimension of any high energetic substances are not well known. In the above case, we have recognized that 500 μm of PETN layer sandwiched by two PMMA (polymethylmetacrylate) plates can be detonated by suitable amount of pulse laser energy deposition.

Tappan of Sandia National Lab. in US have published systematic studies of detonation and / or combustion studies of several high explosives of small size of up to less

Table 1 Prepared reactive thin films consisting of DDNP / CTA with 8 : 2 mass ratio and their ignition properties.

Fabrication procedure	Film thickness μm	Surface of laser irradiation	Fluence J cm^{-2}	Velocity of reacting front m s^{-1}	GO / NOGO
BC	20	bottom	29	0.053	GO
BC	20	bottom	29		NOGO
BC	40	bottom	29	0.127	GO
BC	47	bottom	29	0.063	GO
BC	47	bottom	29		NOGO
BC	57	bottom	29	0.076	GO
BC	74	bottom	29	0.106	GO
BC	74	bottom	29		NOGO
BC	84	bottom	29	0.120	GO
BC	84	bottom	29		NOGO
BC	48	upper	29	0.040	GO
BC	49	upper	29		NOGO
BC	82	upper	29		NOGO
PAD	17	bottom	29	0.060	GO
PAD	17	bottom	29		NOGO
PAD	19	bottom	29	0.050, 0.051	GO
PAD	19	bottom	29		NOGO
PAD	32	bottom	29	0.079, 0.077	GO
PAD	32	bottom	29		NOGO
PAD	40	bottom	29	0.10	GO
PAD	19	upper	29	0.043	GO
PAD	40	upper	29	0.103	GO
PAD	41	upper	29	0.072	GO
multi-PAD	150	upper	40		NOGO
multi-PAD	250	bottom	30	0.027, 0.042, 0.052,	GO
				0.062, 0.069, 0.082,	GO
				0.10, 0.131, 0.17, 0.21	GO
multi-PAD	250	upper	15	Not measured	GO
multi-PAD	250	upper	30		NOGO
multi-PAD	750	bottom	30	0.378, 0.478, 0.806,	GO
				1.072, 1.172, 1.133	GO
multi-PAD	750	upper	30		NOGO

than 1 mm. [11), 12)] His future scope is to establish manufacturing and controlling method of high explosive material in small size and shape processed by micro electro mechanical system (MEMS) techniques.

In the patents in US and Canada [1), 2)], manufacturing method of reactive thin films containing primary explosive substance were published, although we don't know whether this patent is widely used or not. At least one may safely say that use of the azides is not very easy while keeping safety during the film manufacturing process.

In this study, reactive thin film consisting of primary explosive material has been prepared. [13)] In a form of a thin film, it is natural that the sensitivity of reaction decreases due to size effect. Therefore, larger energy input is required to ignite these forms of energetic materials. By the same reason, reactive films prepared in this study are limited to air-standing films. Purposes of the present study are twofold. (i) To establish a safe method to fabricate thin film of primary explosive with appropriate binder, and (ii) to study the reaction characteristics induced by pulse laser ablation.

2. Preparation of reactive thin film containing primary explosive material

2.1 Concept

It is inevitable to establish a reliable and reproducible procedure of preparing thin film containing high energetic materials. Steele et al [1)] obtained a patent on creating reactive thin film containing a sensitive primary explosive lead azide. They showed that the thin film can be detonated by suitable thermal energy deposit, and measured the dependence of detonation velocity on the film thickness. Simply for safety, we abandoned to use azides as an energetic material for the reactive thin film. Instead, we adopted diazodinitrophenol (DDNP) and lead stephnate (LS) as a reactive medium. These energetic materials are provided by Asahi Kasei Chemicals Corporation as micron sized particles.

Today, various methods of creating thin film have been known and established. Among them, we chose the bar-coater method (BC method) and the pour-and-dry method (PAD method). Strategy to adopt these methods is as follows; (i) the method must be flexible enough to control and change the fabrication conditions of the film of

desired thickness, (ii) it is desirable to limit the energetic materials spreading to some confined area during and after the treatment of film making process, and finally (iii) it should be safe enough to the operator(s). By considering these requirements, several methods such as spin coater and/or processes inside metal chambers are ruled out in this study. Both methods we have adopted satisfy the conditions described above.

In the present study, we adopted DDNP, and lead stephnate (LS) and also nitrocellulose (NC) as energetic component and cellulosetriacetate (CTA) and also nitrocellulose (NC) as a binder material with dichloromethane as a solvent. Since specific gravity of DDNP and lead stephnate particles is larger than that of dichloromethane solution, explosive particles are sinking to bottom surface. Energetic materials whose specific gravity is smaller than solution cannot be used to form a film with smooth surface. Materials chosen in the present scheme as a solvent and solute are chosen by the following reason: solvent is chosen so that explosive particles have little solubility and therefore, explosive particles are suspending in the solution and sinking to bottom.

Preliminary experiments showed that films created on substrates can hardly be ignited even by direct heating. This result demonstrates that thermal energy due to the decomposition of reactive thin film is not large enough to maintain reaction process. That is, faster rate of the production of heat of decomposition is required to burn out of the whole film. According to this result, present study is focused on the manufacture and test of air-standing films. In the reaction of air-standing films, it is expected that very little heat is lost into air within short times.

Films created on some substrate surface must, therefore, be peeled off as an air-standing film. Teflon sheet is appropriate for the substrate, otherwise dried films cannot be peeled off completely. Sometimes a commercial teflon tape with glue paste is convenient.

As described later in detail, we have prepared mono-layer films and multi-layered films due to difference in the manufacturing process. Ignition characteristics depends on the various aspects of film properties such as film texture and film thickness as a result of chosen methods of film preparation.

2.2 Solution preparation

Before applying BC method or PAD method, solution containing explosive particles is prepared. At first, CTA powders are completely solved into dichloromethane. Next, explosive particles are mixed carefully into the solution. In order to obtain fully mixed homogeneous solution by dispersing explosive particles, samples are sonicated and sometimes submerged to warm bath. Mass ratio of explosive to CTA is desired to be as large as possible. Maximum mass ratio of them realized in the present study is 9 : 1 for the film whose thickness is thicker than 100 μm. In the case of thinner films, ratio is limited to 8 : 2. Due to this reason, a series of experiments has been conducted for the film with mass ratio of 8 : 2. For the purpose of comparison, films with 1 : 1, 7 : 3 and 9 : 1 mass ratio were prepared in limited experimental conditions.

Specifications of the created thin films are summarized in Table 1. Thin films of thickness smaller than 100 μm were prepared by two different procedures described below, while thicker films were prepared only by the PAD method. Most of the films were prepared by PAD method whose thickness ranges from 20 to 750 μm. Thin films with thickness less than 100 μm have also been prepared by BC method in order to control the film properties. These two procedures are explained separately in the next section. Upper surface of thin films manufactured by the following two methods is not smooth basically due to the particle size of high energetic materials.

2.3 PAD (pour-and-dry) method

We have adopted a very simple procedure of making films. A simple dip-shaped structure was made by using teflon sheets and tapes. Bottom smooth surface and low height wall are made of teflon sheets in order to ensure that the manufactured film can be removed off from the structure after the process. Solution of CTA in dichloromethane with suspending DDNP particles are first prepared with desired mass ratio of CTA to DDNP and then it is poured into teflon structure. Films with thickness thicker than 100 μm, however, can be realized only by repeating the "pour-the-solution-and-dry-out" process. Multiple processes are necessary for thicker film preparation by the following reason. Amount of the solution of CTA-dichloromethane-DDNP is basically determined by that of dichloromethane, since the mass ratio of CTA to dichloromethane is set to 0.5 wt% in the present case, and most of the volume will be dried out. We cannot obtain flat and very thick film applying the process only once.

Due to the necessity of multiple dry processes, the resultant film could be a laminated structure. Even so, DDNP particles remain at the bottom surface which makes the bottom face sensitive to the other surface. Furthermore, as explained in a later section, DDNP particles at the bottom surface can easily be scabbed away from the surface by the instantaneous energy deposition at the surface by pulse laser irradiation. This feature is one of the important factors of the reaction characteristics of the present films.

Figure 1 shows the typical microscopic photographs of prepared thin film at the upper and bottom surface. Two surface images of Fig. 1 (a) correspond to thin film with 19 μm thickness by single PAD process, while those of Fig. 1 (b) correspond to thin film with 372 μm by multiple PAD processes. One may note clearly that the bottom surface is covered with many DDNP columnar particles at bottom surfaces of both films, while upper surface of multi-layered film contain DDNP particles of lesser number density, and is seen to be covered with CTA material. For monolayer thin film, number density of DDNP particles at upper surface seems no appreciable difference from that at bottom surface.

2.4 BC (bar coater) method

Bar coater method has been one of the established methods of making films by using liquids with some viscosity. By using a metal bar wound with a thin metal wire, it is possible to spread the viscous liquid sample into some designated area. Since the area of spread sample material

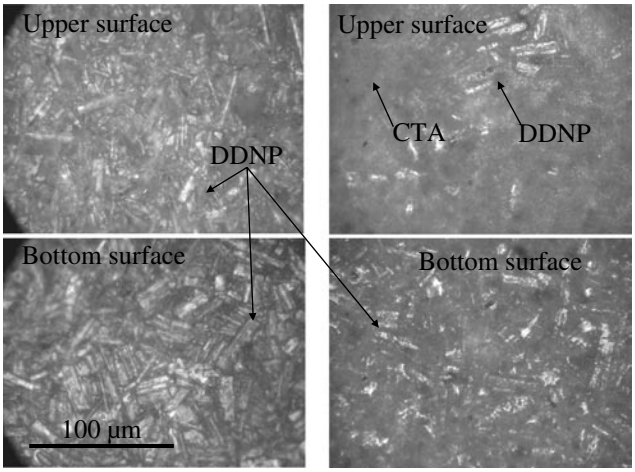

Fig. 1 Microscope pictures of upper and bottom surface of DDNP / CTA reactive thin film prepared by PAD method. Mass ratio of DDNP / CTA is 8 : 2. (a) Monolayer film with 19 μm thickness, and (b) multi-layered film with 370 μm thickness, respectively.

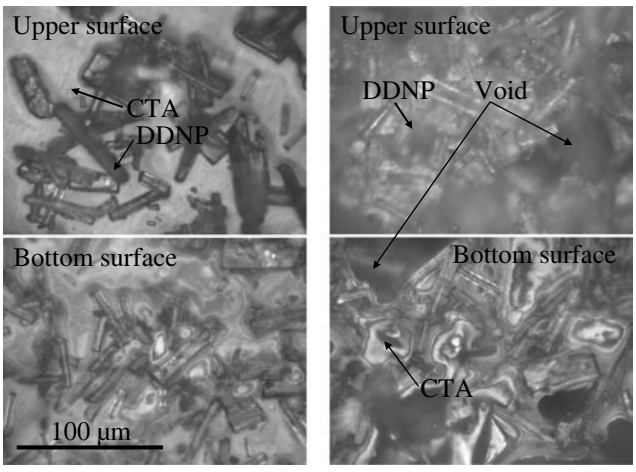

Fig. 2 Microscope pictures of upper and bottom surface of DDNP / CTA reactive thin film prepared by BC method. Mass ratio of DDNP / CTA is 8 : 2. (a) Monolayer film with 21 μm thickness, and (b) monolayer film with 84 μm thickness, respectively.

can be easily limited to that of our own convenience, this is suitable for treating materials requiring the careful handling. In the present experiment, BC method was used to prepare thin film with thickness thinner than 100 μm. As noted, in order to make this method sense for film preparation, some viscosity of the liquid is required to spread the solution to limited area. In the present study, we have made several tens of μm thick films by this method with the mass ratio of CTA to dichloromethane of 2 wt. percent. Although the value of mass ratio is only four times larger than that used in PAD method, it seems that slower dry-out process during film formation prevents agglomeration of DDNP particles at the bottom surface. For films manufactured by BC method, only monolayer film can be prepared, and the film properties and ignition characteristics depend on the film thickness. Film surface structure changes with increasing film thickness.

Figure 2 compares upper and bottom surface micrographs of films with 21 μm and 84 μm thickness. As seen in Fig. 2, DDNP particles do not seem to expose even at the bottom surface for both films. For the thinner film, it is seen from Fig. 2 (a) that upper and bottom surfaces have different surface structure. Observation of the bottom surface of thinner film shows that DDNP particles seem to be confined by CTA material. For thicker film of Fig. 2 (b), clear exposure of DDNP particles is not observed for both upper and bottom surfaces. It is plausible that thicker CTA layer is expected even at bottom surface. These differences in film properties by BC method are attributed to the concentration of CTA in the solution and also to finite size of DDNP particles of about 10 μm. We will later see that difference in film properties leads to the difference in ignition characteristics of these films.

3. High speed framing shadowgraph observation

One of our aims is to find experimental condition for the manufactured reactive thin film to burn at very fast rate. For this purpose, we have tried to ignite it by pulse laser ablation. By the instantaneous energy deposition on a small amount of reactive material, we will expect to control the combustion (deflagration) process except for the case of possible detonation reaction.

We have made extensive experiments of high-speed camera observation on the reaction process of thin films initiated by direct pulse laser ablation of the sample surface. As explained later, most of the entire reaction process is rather a long time process of *ms* time range, although the energy deposition has *ns* time scale. By this reason, we adopted two different high-speed cameras. One for the fast events and the other one for the whole process observation.

For fast events observation, high-speed camera of Cordin 220 was used, which can record six frames by image-intensified CCD cameras with 10 ns exposure time and arbitrary delay time. Near parallel light source by using a small flash lamp was used as an illumination. Phantom V4.2 high-speed video camera was also used to observe the relatively slow burning process. Experimental conditions by using high-speed video camera are set to 2 μs exposure time and 123 μs frame interval.

Figure 3 shows the schematic illustration of the optical layout. For high speed photography of the events by the Cordin camera, we have used two observation conditions by inserting or removing aperture 2 in Fig. 3. By doing so, we can observe the heated gas flow field without light emission from burning film material, and the high-temperature emitting region indicating temperature distribution of the flow field. These two kinds of recordings cannot be realized simultaneously in an experiment, and we made experiments of the same conditions with and without aperture 2. Combustion of the film proceeds in a relatively slow velocity, velocity of the reaction front was measured by the high-speed video record.

We have used an Nd : YAG laser of fundamental frequency and of 10 ns duration for igniting the film by pulse laser

ablation of the film surface. Laser energy of 100-500 mJ per pulse was used.

Specimen was a ribbon cut out from the prepared reactive thin film sheet. As an air-standing film, specimen was supported by a paper-made holder as depicted in the figure in Fig. 3.

4. Results and discussion

As is explained later, combustion process depends on the film thickness, film texture and laser irradiation direction. Properties of the films used in the experiments and experimental results are also summarized in Table 1. It is found that the ignition properties depends on the layered structure of the film, i.e., films of multi-layered structure or those of monolayer. Since the films thicker than about 100 μm can be prepared only by PAD method, change in ignition properties were observed for the films with thickness of around 100 μm. Due to the differences described above, results and discussion will be divided into sections for monolayer and multi-layer films.

The most striking finding is that for multi-layered films, reaction depends on the laser irradiation direction. If the laser irradiates from the upper surface of the film, pulse laser ablation results in making holes of the film, but no further reaction was noticed. Pulse laser ablation on the bottom surface of the film, on the other hand, leads to the total combustion of the film.

On the contrary, for monolayer film, pulse laser irradiation to both surfaces of the film leads to combustion with some probability, otherwise no continuous reaction. In case of monolayer films, further complication arises since they are prepared by both PAD and BC method which give different film structure for these monolayer thinner films.

Discussions of the results are basically limited to the DDNP : CTA films with mass ratio of 8 : 2, since most of the measurements are focused on these samples. Other samples and experimental conditions are summarized in later sections.

4.1 DDNP / CTA films with multi-layered structure (thickness larger than 100 μm)

The most striking findings of the high-speed photographic observation of the film combustion process is that the ignition and combustion process of the film prepared in this study takes appreciably long time compared with the instantaneous energy deposition by 10 ns pulse laser. It is found that the whole combustion process can be divided into three stages. Typical high-speed photographs of DDNP : CTA multi-layered thin film by laser irradiation from bottom surface at several selected delay times are shown in Fig. 4.

As seen in Fig. 4 (a), at the earliest stage of the process, pulse laser irradiation produces strong air shock waves emanated from the ablated region. This figure clearly shows that a group of small fragments are produced for both sides of the film by the pulse laser ablation. From the figure, it is seen that amount and size of the fragments are different in the direction of motion. Reaction takes place for the particles blown to the laser irradiation direction. More energy deposition by laser ablation direction causes faster or stronger

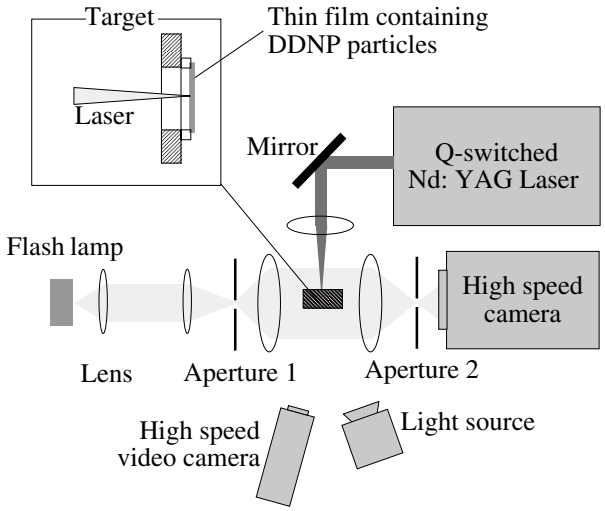

Fig. 3 Optical setup for high-speed photography with high-speed camera and video camera. Both camera systems can be used simultaneously for selected experimental conditions.

shock wave due to plasma plume absorption of laser beam, and this effect will be responsible for the ignition of particles only in the half space of laser irradiation.

When the laser beam was irradiated from the upper surface of the film, no combustion takes place, while laser irradiation from the bottom surface leads to ignition. Shock wave may be responsible at least partly for the combustion of the fragments. Since stronger shock wave and larger amount of DDNP fragment generation are produced when the laser is irradiated onto the bottom surface of the film, particle combustion is observed only in these cases. As seen in Fig. 1 (b), CTA covers DDNP particles at upper surface of the multi-layered films, laser irradiation onto upper surface does not lead to combustion of the DDNP particles.

Figure 4 (b) and (c) shows typical pictures of particle combustion stage, i.e., the 2nd stage at 100 μs delay time after laser ablation. It is found that intense emission of particles lasting more than 200 μs shows intense reaction of particles. Figure 4(c) shows pictures observing emission of burning DDNP particles by removing aperture 2 in Fig. 3, while Fig. 4 (b) shows picture of the same delay time with aperture 2. By doing so, Fig. 4 (b) shows density modulations or the high temperature low density region near the film surface created by particle combustion. From Fig. 4 (c), one may notice that particle emission has modular spatial distribution, and this is caused by the process of particle production by laser ablation of multi-layered films. Emission of particles near the film surface lasts longer than that of particles separated from the film surface, and this is considered to be responsible for the ignition of film body.

Figure 4 (d) shows the picture at further delay time. This figure clearly shows combustion reaction front in the film body. The delay time of this figure is 7 ms after ablation. It is found that ignition of the film itself takes place at very late delay time of *ms*. Ignition mechanism of the process can be explained by the residual heat in the film body by pulse laser ablation as well as the heating by particle-burning high temperature region adjacent to the film.

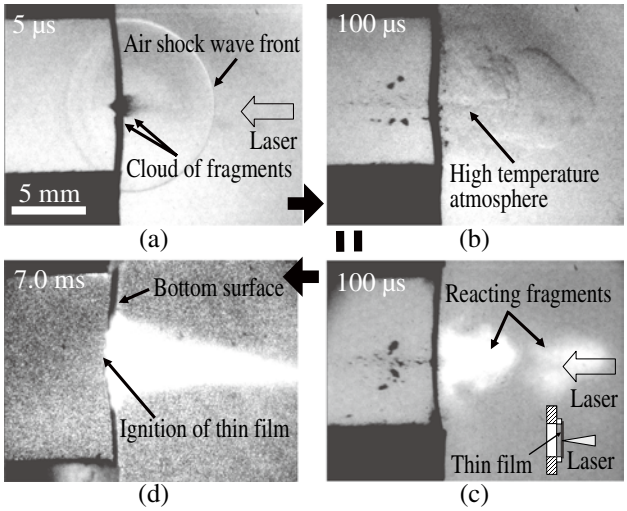

Fig. 4 High speed photographic records of multi-layered DDNP / CTA reactive film combustion process. Film specifications are as follows: DDNP / CTA = 8 / 2, and have 250 μm in thickness prepared by PAD method. Pulse laser fluence is 15 J cm^{-2}. Delay time of each frame is (a) 5 μs, (b) 100 μs, (c) 100 μs and (d) 7ms, respectively. These pictures are taken at separate experiments, and photos (b) and (c) are taken with and without aperture 2 in optical setup of Fig. 3.

Consequently, high speed photographic observation of the multi-layered reactive thin film combustion process can be summarized as follows: (i) laser ablation at the upper surface leads to no ignition of the film, (ii) within tested experimental conditions, no detonation reaction was observed, (iii) laser ablation at the bottom surface leads to the following three stage ignition process, i.e.,

(1) at early delay time of less than 10 μs after ablation, stronger air shock wave followed by clouds of DDNP particles is produced,
(2) combustion of DDNP particles adjacent to the film takes place at around 100 μs after ablation and lasts for more than 100 μs, which also creates very hot region above the film surface, and
(3) finally, at several ms after ablation, ignition of film body takes place due to the residual heat and heating by hot region adjacent to the film surface.

4.2 DDNP / CTA monolayer films (thickness less than 100 μm)

For monolayer films or films thinner than 100 μm prepared by both PAD method and by BC method, it is found that the ignition criterion is independent of laser irradiation direction. As shown in Fig. 1(a) and Fig. 2(a), no appreciable difference in the surface structure of the film by PAD or BC method. It is found that either ignition or no ignition of the film could occur by pulse laser ablation at both upper and bottom surfaces. The appreciable differences of monolayer film ablation from multi-layered film ablation are ; (i) process has no dependence on the laser irradiation direction, (ii) more DDNP fragments are produced in the rear side of the film unlike multi-layered film cases, and (iii) burning of the particles occurs at the rear side of the film.

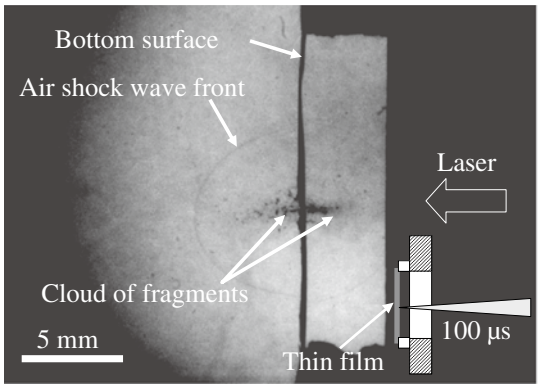

Fig. 5 High speed photographic records of monolayer DDNP / CTA reactive film combustion process. Film specifications are as follows: DDNP / CTA = 8 / 2, and have 33 μm in thickness prepared by PAD method. Pulse laser fluence is 29 J cm^{-2}. Delay time is 10 μs.

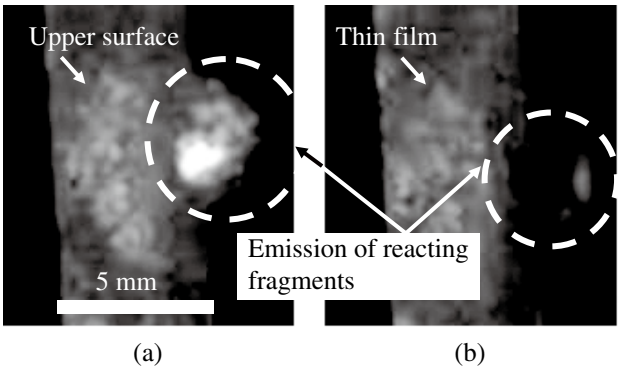

Fig. 6 High speed video camera record of monolayer DDNP / CTA reactive thin film combustion process. Film specifications are as follows: DDNP / CTA = 8 / 2, and have 32 μm in thickness prepared by PAD method. Pulse laser fluence is 29 J cm^{-2}. Delay time is (a) 50 μs and (b) 174 μs with gate time of 2 μs.

Typical high-speed photograph of DDNP / CTA thin film is shown in Fig. 5 at short delay time corresponding to Fig. 4 (a) for multi-layered film. Due to the smaller thickness of the film, shock front can be clearly observed in both sides of the film. This figure clearly shows that a group of small fragments are produced by the pulse laser ablation especially in the direction of laser irradiation in the rear side of the film. This may be explained as follows; (i) pulse laser ablation induces high stress compression wave in the film, (ii) and at the reflection of the wave at the rear free surface, tension will be induced near the rear surface which leads to scabbing of the surface. This tension wave will be less effective for thicker and multi-layered films, since stress wave will attenuate with the propagation to the film thickness direction. As a result, larger tension will be induced in case of thinner film which produces more particles at the rear surface.

In case of multi-layered films, particle combustion does not take place for the particles at the rear side of the film, since heating of them by shock wave in the rear side may not be very large. On the contrary, DDNP particles produced in the rear side from monolayer film, are heated up

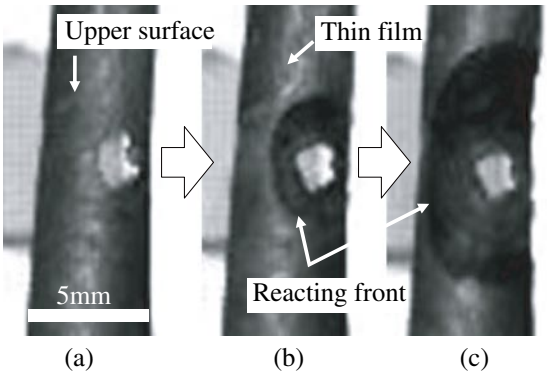

Fig. 7 High speed video camera record of monolayer DDNP / CTA reactive thin film combustion process. Film specifications are as follows: DDNP / CTA = 8 / 2, and have 32 μm in thickness prepared by PAD method. Pulse laser fluence is 29 J cm^{-2}. Delay time is (a) 1ms and (b) 21 ms, 35 ms with gate time of 2 μs.

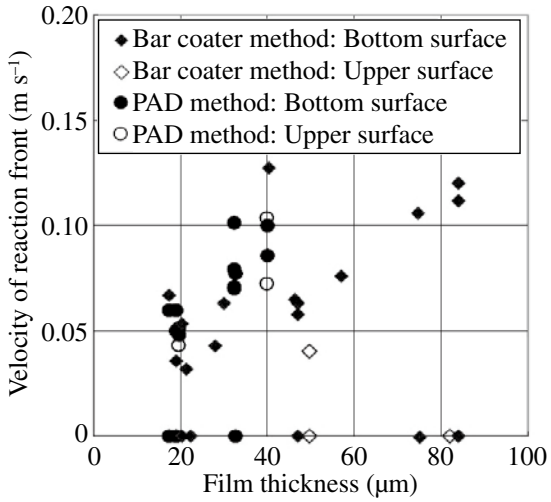

Fig. 9 Reaction front velocity of monolayer DDNP / CTA reactive thin film whose thickness is less than 100 μm. Mass ratio DDNP / CTA is 8 : 2. Laser fluence for all the data is 29-30 J cm^{-2}. Data of zero velocity stands for no combustion.

by strong air shock wave. Consequently, ignition of the film body takes place at the rear surface.

In the photographic observation of the emission of particle combustion, flash lamp intensity should be controlled to the brightness level comparable to that of particle emission intensity. Due to the small amount of particle production at the rear surface of monolayer film, and their low emission intensity, emission photograph like Fig. 4 (c) in case of multi-layered film cannot be obtained for monolayer films. Some features of the monolayer combustion process therefore were observed by high speed video camera especially for long time observation.

Figure 6 and 7 show several frames of combustion process of monolayer film recorded by video camera. These pictures are taken in the same experimental conditions as that in Fig. 5. Emission by the combustion of particles produced at rear side of the film can be seen in the left picture of Fig. 6. Slight emission can be observed also at the next

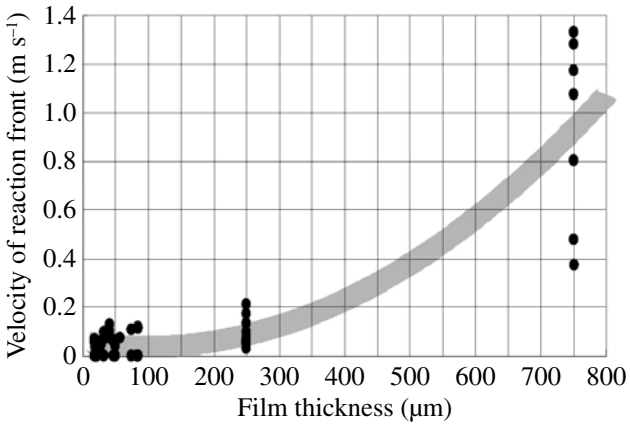

Fig. 8 Reaction front velocity of DDNP / CTA reactive thin film as a function of film thickness. Mass ratio DDNP / CTA is 8 : 2. Laser fluence for all the data is 29-30 J cm^{-2}.

frame (right picture of Fig. 6 which is 123 μs from the left frame) but not further frames. Ignition of the film body occurred after several ms from these frames.

Figure 7 clearly shows the burning front on the film indicating that combustion starts from the punching hole created by pulse laser ablation.

4.3 Reaction front velocity of DDNP / CTA films

Velocity of reaction front of DDNP / CTA films were measured by the observation of high-speed video or by ICCD camera. Figure 8 and 9 shows the thickness dependence of reaction front velocity. Figure 8 includes all the data for DDNP / CTA films with mass ratio 8 : 2. While reaction velocity for monolayer films is separately plotted again in Fig. 9.

It is clearly shown in Fig. 8 and 9 that the reaction front velocity increases with increasing film thickness. Data scatter will also increase with thickness. For thicker films, faster reaction is realized by the larger heat content produced by the combustion of DDNP fragment particles. It is plausible that random nature of the reaction velocity for thicker films stems from the spatial modulation of particle combustion due to the laminated structure. It is apparent that combustion of particles near the film will give larger effects on the ignition of the film.

For thinner films, on the contrary, they are consisting of monolayer and ejected particle cloud is considered to be more reproducible compared with films with layered structure. Relatively small scatter of the reaction velocity may be due to the relatively reproducible heat release by ejected particles. In Fig. 9, one may see the reaction velocity of thinner films with different manufacturing process. It is shown that no appreciable difference in reaction front velocity can be observed for films by two prepared methods. No appreciable differences are seen also in the reaction front velocity by pulse laser irradiation onto bottom and upper surface as shown in Fig. 9. Ignition probability of the film, however, is lower for films by BC method. It is plausible that the present result is attributed to the properties of relatively thicker monolayer film that DDNP par-

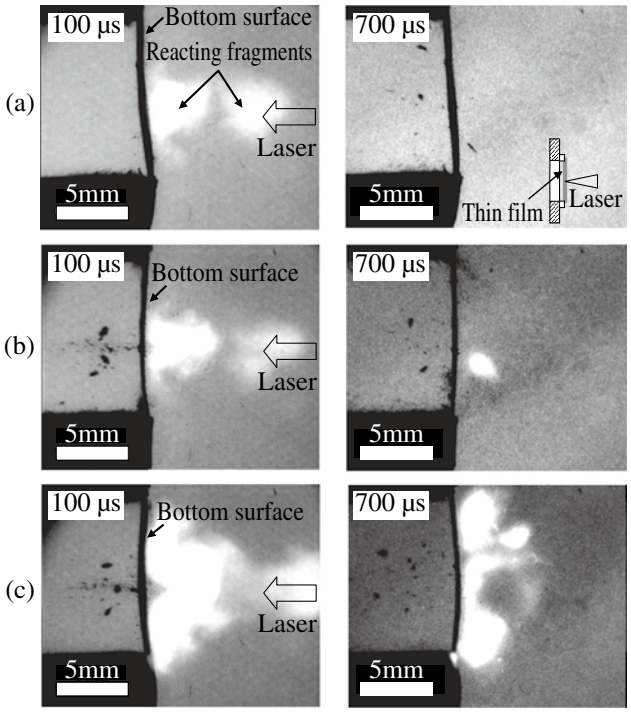

Fig. 10 High speed photographic records of the combustion process of multi-layered DDNP / CTA reactive film with different mass ratios. Film thickness for all cases is 250 μm. Mass ratio DDNP / CTA is 8 : 2 for cases (a), and 9 : 1 for cases (b) and (c), respectively. Laser fluence is 15 J cm^{-2} for cases (a) and (b), and 30 J cm^{-2} for case (c), respectively.

ticles is covered with CTA layer, as is recognized from the figure of Fig. 2 (b). It is also seen in Fig. 9 that the ignition probability for monolayer films is lower than that for multi-layered films.

4.4 Dependence of DDNP mass ratio and laser fluence on the film ignition process

Figure 10 compares the difference in combustion process for films with different mass ratio of DDNP and CTA. Pictures, Fig. 10 (a) or (b) and (c) correspond to the combustion of 8 : 2 film and 9 : 1 films, respectively. It is found that with decreasing CTA content and increasing DDNP content, reaction velocity increases. From Fig. 10 (b), combustion of DDNP particles for 9 : 1 film continues longer than that for 8 : 2 film. Ignition probability decreases with decreasing DDNP content, namely, for multi-layered film of 350 μm thickness, it is 100 % at least for films with 70 % DDNP content, while 36 % for that with 50 % DDNP content. This result is reasonably explained by the content of the inert material CTA. Although increase in DDNP content leads to higher reaction velocity, but film quality or surface smoothness is getting worse. It seems also natural that ignition probability decreases with decreasing DDNP content.

By the comparison of Fig. 10 (a), or Fig. 10 (b) with (c), one may see the change in ignition property of the film by the change in laser fluence. More intense combustion of DDNP particles is observed for higher fluence experiments. Ignition probability also increases with laser fluence.

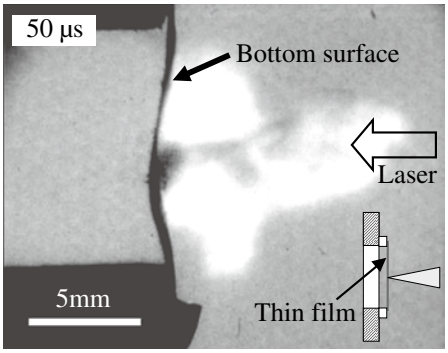

Fig. 11 High speed photographic records of the combustion process of multi-layered LS / CTA reactive film. Mass ratio LS / CTA is 8 : 2 with 200 μm in thickness. Laser fluence is 30 J cm^{-2}.

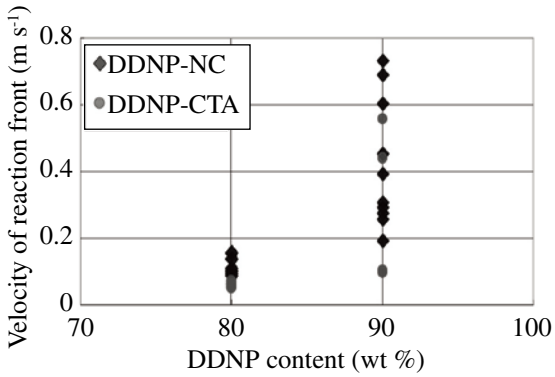

Fig. 12 Reaction front velocity of DDNP / CTA and DDNP / NC reactive thin films. Laser fluence for DDNP / CTA films is 30 J cm^{-2}, while that for DDNP / NC films is 15 J cm^{-2}, respectively.

4.5 Lead stephnate / CTA and DDNP / NC films

We have also tested material dependence of the resultant film properties. The following two cases are investigated; (i) DDNP is replaced by lead stephnate (LS), i.e., LS/CTA film, and (ii) CTA is replaced by nitro cellulose (NC), i.e., DDNP/NC film.

Since the sensitivity of LS is higher than DDNP, combustion process is found to be shorter than that for DDNP / CTA films. Figure 11 shows high speed photograph of LS/CTA combustion process. Ignition of film body takes place during fragment particle combustion. As seen in Fig. 11, emission by the reaction of LS / CTA film is more intense than that for DDNP / CTA films, and reaction is faster. Compared with the three stage combustion found for DDNP / CTA multi-layered films, particle combustion at the second stage and film body ignition of the third stage merges for LS / CTA film combustion. Bright emission from particle combustion masks the emission from film body reaction. Reaction front velocity estimated by the propagation of the film deformation is several tens of meter per second.

It is expected that DDNP / NC films may be more combustible than DDNP / CTA films due to the heat release by both DDNP and NC reaction. For these films, it is found that fragment by laser ablation with high fluence

have wide spatial distribution, and ignition of film surface area at various points ahead of the reaction front, and this behavior prevents from measuring the reaction front velocity. By this reason, reaction velocity data for this film is performed for lower laser fluence of 15 J cm^{-2}. Reaction front velocity for DDNP / NC films is faster than that for DDNP / CTA films, and they are compared in Fig. 12.

5. Summary

High energetic materials are fixed to air-standing thin film by the use of inert binder material, and the prepared films are ignited by pulse laser ablation. By the use of two different preparation methods, monolayer films with thickness less than 100 μm and multi-layered films with thickness more than 100 μm have been manufactured in this study. Film textures and surface structures are different for films with different preparation methods.

Multi-layered structure leads to the large scatter in the reaction front velocity, while difference in the properties of monolayer film by two preparation method leads to the difference in the ignition probability.

Ignition and combustion process of the present films are observed by high speed camera and video camera. It is found from these observations that ignition and combustion of all the films can be described as

(i) Some amount of fragments is produced from film surface by pulse laser ablation, then
(ii) combustion of moving fragments takes place, and finally
(iii) combustion of the film body starts long after ablation by the residual heat by ablation and heating by burning particles.

Even if the film does not combust, laser ablation of the film surface leads to the punching hole.

Reaction front velocity of the film is strongly influenced by the burning particles produced by laser ablation. Fragment particle production depends on surface structure of the film, film thickness, DDNP content, laser energy, high energetic material and binder.

References

1) T.G. Steele, H. Township, M. County, *Primary Explosive Composition for Explosive Bonding or Forming*, US patent 03704186, November 28, 1972.
2) G. W. C. Taylor and S. E. Napier, *Preparation of Explosive Substances*, Canadian Patent 687, 341, May 26, 1964.
3) K. L. Erickson, R. D. Skocypec, W. M. Trott, and A. M. Renlund, *Development of Thin-Film Samples for Examining Condensed-Phase Chemical Mechanisms Affecting Combustion of Energetic Materials*, Proc. 15th IPS, 239-260 (1990).
4) J. W. Shaffer, B. W. Cranston, G. Krass, *Explosive Bonding of Metal Foils to High Alumina Ceramic Substrates*, Proc. 4th Symposium on Combustion, 28 (1973)
5) M. Nakahara, and K. Nagayama, Proc. 21st Shock Wave Symp. 1997, vol. **2**, pp. 801-804 (1998).
6) M. Nakahara, and K. Nagayama, J. Mat. Proc. Tech., **85**, 20 (1999).
7) K. Nagayama, K. Inou, and M. Nakahara, Shock Compression of Condensed Matter-2001, pp. 995-998 (2002).
8) K. Murakami, K. Inou, M. Nakahara, S. Kubota and K. Nagayama, J. of the Japan Explosives Society, **63**, pp. 275-278 (2002).
9) K. Nagayama, K. Inou, K. Murakami, S. Kubota and M. Nakahara, Proc. 29th Int. Pyrotechnics Seminar, pp. 363-368 (2002).
10) K. Nagayama, Y. Kotsuka, M. Nakahara and S. Kubota, Sci. Tech. Energetic Materials, **66**, 416 (2005).
11) A. S. Tappan, A. L. Brundage, G. T. Long, A. M. Renlund, S. H. Kravitz, J. J. Nogan, B. Wroblewski, J. A. Palmer, and M. R. Baer, Proc. 13th Int. Detonation Symp., 138.
12) A. S. Tappan, R. J. Pahl, A. M. Renlund, J. J. Nogan, W. C. Sweatt and F. M. McCormick, Proc. 33th Int. Pyrotechnics Seminar, p.129.
13) K. Nagayama, K. Takahashi, K. Nishiyama and S. Kubota, final report of national fund from Min. Education, Culture and Science, Japan, 2006.

ジアゾジニトロフェノール粒子による反応性薄膜の製作とパルスレーザーアブレーションによる燃焼特性

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有機物質をバインダーとして起爆薬粒子を用いた反応性薄膜を製作した。厚さ 20-750 ミクロンの薄膜をバーコーター法および溶液を型に注いで乾燥させる方法で製作した。用いたジアゾジニトロフェノール（DDNP）粒子の大きさは 10 ミクロンであり , それをセルロースストリアセテート（CTA）で固定した。製作において溶媒 - **溶質質量比を変えることにより** DDNP-CTA の組織を制御できる。

製作した反応性薄膜の点火試験をおこなった。薄膜表面のパルスレーザーアブレーションと引き続く反応過程は２つの異なる高速度カメラと光学系により観測した。反応性はレーザー照射方向に依存する。試験した反応性薄膜と実験条件の範囲では爆轟反応は生じなかった。

以下の特異な燃焼過程があきらかになった。薄膜の燃焼は３段階で生じる。(i)DDNP粒子は表面のパルスレーザーアブレーションによって両表面から射出される , 次に (ii) 誘起される空中衝撃波がこれらの粒子を燃焼へ導き , 最後に (iii) 自分自身の残留熱量と燃焼粒子の発熱により薄膜自身の反応が始まる。

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