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Role of Additives in the Combustion of Ammonium Dinitramide

Koji Fujisato,*[a] Hiroto Habu,[b] Atsumi Miyake,[c] Keiichi Hori,[b] and Alexander B. Vorozhtsov[d]

Abstract: The thermal decomposition behavior and combustion characteristics of mixtures of ammonium dinitramide (ADN) with additives were studied. Micrometer-sized particles of Al, Fe_2O_3, TiO_2, NiO, $Cu(OH)NO_3$, copper, CuO, and nanometer-sized particles of aluminum (Alex) and CuO (nano-CuO) were employed. The thermal decomposition was measured by TG-DTA and DSC. The copper compounds and NiO lowered the onset temperature of ADN decomposition. The heat value of ADN with Alex was larger than that of pure ADN in closed conditions. The burning rates and temperature of the pure ADN and ADN/additives mixtures were measured. CuO and NiO enhance the burning rate, particularly at pressures lower than 1 MPa, because of the catalyzed decomposition in the condensed phase; the other additives lower the burning rate. This negative effect on the burning rate is explained based on the surface temperature measurements by a physicochemical mechanism, which involves a chemical reaction, a phase change of the ammonium nitrate, and the blown-off droplets of the condensed phase.

Keywords: Ammonium dinitramide · Burning rate · Fine-thermocouple · Nano-CuO · Alex

1 Introduction

The development of environmentally friendly propellants should be encouraged, in addition to the improvement of the propulsion performance. ADN is considered as the most appropriate substitute of AP because it has a high oxygen balance and energy of formation. The manufacturing process of ADN has been improved over the last twenty years, and the cost has become lower. In spite of these advantages, ADN has not been put into practical use as a solid propellant because of its low thermal stability and undesirable combustion characteristics. It is necessary to study the burning rate modifiers of ADN to improve the combustion characteristics of ADN-based propellants. This research summarizes and studies the effects of additives on ADN combustion.

There are several reports on ADN-based propellants. Parr et al. investigated the flame structure of an ADN/binder-sandwich propellant with a PLIF below 1.5 MPa [1]. It was reported that ADN has a weak diffusion flame that is too far from the surface to affect the burning rate. Price and Chakravarthy et al. reported the burning behavior of various compositions [2,3]. They used PBAN and HTPB as the binder and concluded that without the addition of ammonium perchlorate (AP), the compositions are sensitive to the pressure. Korobeinichev et al. studied ADN/polycaprolactone propellants and reported on the influence of the molecular weight of the polycaprolactone on the burning rates [4]. Weiser et al. studied paraffin/ADN mixtures with a mass ratio of 10 : 90 and measured the real-time temperature profiles and characterized the gaseous species during decomposition by UV/Vis and IR spectroscopy [5]. Menke et al. developed a GAP/HMX/ADN propellant [6], and they introduced a new curing system. The GAP/HMX/ADN propellant shows an acceptable pressure exponent ($n = 0.52$), and the burning rate is 2–3 times higher than in conventional AP-based propellant. Wingborg et al. conducted the motor test with a GAP/ADN (30 : 70 mass-%) propellant [7], which is the first report of a firing test of an ADN-based propellant, and the specific impulse (Isp) was 233 s. The ballistic properties of an ADN/Al/HTPB propellant were also reported [8], and the burning rate was $12.8\ mm \cdot s^{-1}$ at 6 MPa, and the pressure exponent was 0.9. These values are almost the same as in our experiment [9] with an ADN/HTPB propellant that does not contain Al. The burning rate of the GAP/ADN propellant is much higher than that of the standard AP-based propellant, and the ADN/HTPB propel-

[a] K. Fujisato
Graduate School of Engineering
The University of Tokyo
7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan
*e-mail: fujisato.kohji@ac.jaxa.jp

[b] H. Habu, K. Hori
Japan Aerospace Exploration Agency
3-1-1 Yoshinodai, Sagamihara, Kanagawa 229-8510, Japan

[c] A. Miyake
Graduate School of Environment and Information Sciences
Yokohama National University
79-7, Tokiwadai, Hodogaya-ku, Yokohama 240–8501, Japan

[d] A. B. Vorozhtsov
Tomsk State University
TLenin Ave., 36, Tomsk, 634034, Russia

lant has high pressure sensitivity; we can conclude that tailoring the burning rate is important for the wide application of ADN-based propellants.

There are several reports on additives for ADN. Price and Chakravarthy et al. reported on the effects of ultra-fine Fe_2O_3, micrometer-sized Al, and Alex as additives; Alex was seen to enhance the burning rate [2]. Sinditskii et al. reported that 0.2% paraffin can extend the pressure deflagration limit (PDL), and 1.5% soot or SiO_2 lowers the burning rate [10]. Korobeinichev et al. studied the effect of CuO on an ADN/polycaprolactone propellant as a burning rate catalyst [11]. A stoichiometric composition was formulated, and 2 mass-% CuO was added. They reported that CuO can suppress the pressure sensitivity and catalytically enhance the condensed phase reaction. Strunin et al. reported on the effects of additives on an ADN pellet, and they added Al, Cu_2O, and $K_2Cr_2O_7$. $K_2Cr_2O_7$ is an effective catalyst for AN; however, it has negative effects on the burning behavior of ADN. They reported that Al (20 mass-%) and Cu_2O (2 mass-%) accelerated the ADN burning rate at low pressures [12].

The effect of CuO is particularly important to develop the ADN propellant. If the pressure sensitivity is kept low, it is possible to conduct the motor firing tests with inert binders. The additives which show negative effects are also attractive because all reported ADN propellants have higher burning rates than conventional ones. However the mechanism of these effects has not been elucidated in detail. The combustion of ADN forms a condensed phase, which controls the burning rate [13,14]. The mechanism of the condensed phase-controlled combustion involves physical phenomena: evaporative dissociation, bubbles, and blown-off liquid droplets on the burning surface, as well as chemical reactions. Therefore, it is difficult to understand the mechanism without temperature measurements of the burning surface. The temperature measurements of pure ADN have been reported [11,13,14], but the effects of additives are still not fully understood.

Nanoparticles of metal and metal oxide have recently attracted attention as burning rate modifiers. In addition to micrometer-sized additives, nano-sized additives are also employed in this report. The thermal decompositions of pure ADN and ADN pellets with additives were measured with TG-DTA and DSC. Further, the burning rates of pure ADN and ADN pellets with additives were also measured, and temperature measurements were conducted with thermocouples whose diameter was 25 μm. This report focuses on Alex and nano-CuO in the temperature measurements, and it is shown that Alex has a negative effect and nano-CuO has a positive effect on the burning surface temperatures. The physiochemical mechanisms of the effects of the additives on the combustion surfaces are described based on the temperature profiles.

2 Experimental

2.1 Samples

The ADN used in this report was synthesized in house with a sulfamic method [15] and purified in acetonitrile and dichloromethane and dried under vacuum. The melting temperature was approximately 362.0 K, as determined by TG-DTA. Using a UV spectrometer, the molar absorptivity was determined to be 42.0 $L \cdot g^{-1} \cdot cm^{-1}$, and thus the purity was estimated to be higher than 98% by a comparison to the reported values [16,17]. The impurity was identified as ammonium nitrate by TG-DTA. The different lot numbers of ADN (lot A and lot B) are used for the combustion studies in this report. First, ADN (lot A) was synthesized and used for the burning rate measurements shown in Section 3.2. A different batch of ADN (lot B) was then synthesized using the same method, and it was used for the measurements of the burning surface temperature (Section 3.3).

Micrometer-sized particles of Al, Fe_2O_3, Al_2O_3, TiO_2, NiO, $Cu(OH)NO_3$ (BCN), Cu and CuO, LiF, Alex, and nano-CuO were selected as additives. The additives and ADN were dispersed and mixed in dichloromethane and dried under vacuum. In the temperature measurements, well-ground ADN was also employed to investigate the effect of the dispersion state of the ADN and additives.

The ratio of additives to ADN was 2 : 100 (2 parts) in the thermal analysis and burning rate measurements. The effects of a 0.5 : 100-ratio (0.5 parts) additive on the burning rate and surface temperature were also studied with Alex and nano-CuO.

2.2 Thermal Analysis and Burning Rate and Temperature Measurements

TG-DTA and DSC measurements were conducted in open and sealed cells. The temperature range was 323–523 K, and the heating rate was 5 $K\,min^{-1}$.

Pressed ADN pellets were used to measure the burning rates. The mixed powder of ADN and additives was pressed under a pressure of 110 MPa, and the density of the resulting pellets was 1.70–1.75 $g\,cm^{-3}$. The diameter of the pellets was 6.0 mm, and the length was 20 mm. The samples were burned in a strand burner purged with nitrogen over a pressure range of 0.5–6 MPa. The burning rate was measured with pictures recorded by a high-speed video camera.

A 25 μm dia-Pt-Pt/Rh13% thermocouple was used for the burning temperature measurements and was embedded inside the sample in parallel with the burning surface, as shown in Figure 1. Both ends were fixed, and the pellet was formulated using a similar method as for the burning rate measurements.

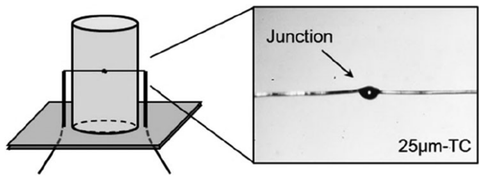

Figure 1. Sample configuration with a 25 μm thermocouple.

3 Results

3.1 Thermal Analysis

Figure 2 shows the TG-DTA results of the ADN and ADN/micro-CuO, nano-CuO, and Alex mixtures. The thermal decomposition of the pure ADN begins at 430 K, and the addition of micro- and nano-CuO lowers the onset temperature by 20 and 40 K, respectively, and increases the heat value to nearly double that of pure ADN.

Figure 3 shows the onset temperatures of the decomposition of the pure ADN and ADN/additive mixtures. The dark rods show the DSC results in closed conditions, and the light rods show the DTA results in open conditions. The decomposition of pure ADN begins at approximately 428 K, and the addition of Al_2O_3, Fe_2O_3, TiO_2, micro-Al, Alex, and LiF have no effect on the onset temperature. The decomposition of the ADN/NiO mixture begins at a slightly lower temperature than pure ADN, and the addition of copper compounds significantly enhances the ADN decomposition. The results are similar under closed and open conditions excepting those obtained with the BCN additive. The ADN/BCN mixture decomposes much faster under open conditions than closed.

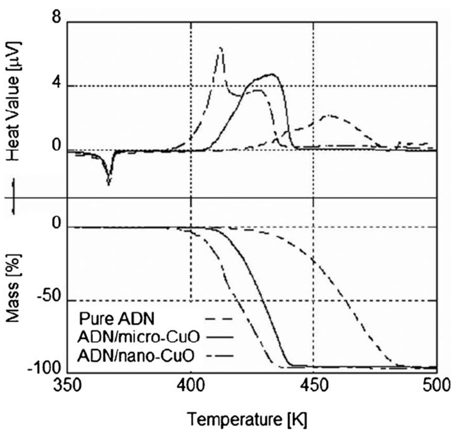

Figure 2. TG-DTA results of pure ADN and ADN/micro-CuO and nano-CuO (2 parts) mixtures.

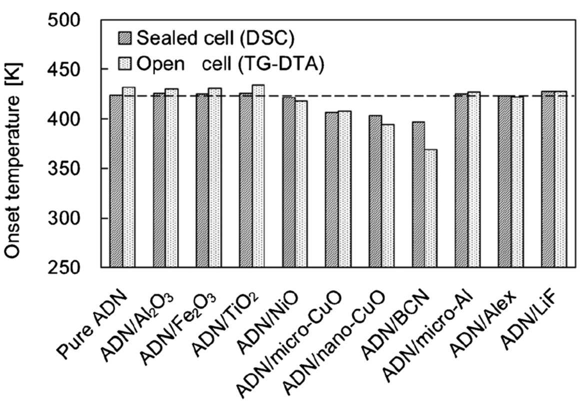

Figure 3. Onset temperatures of pure ADN and ADN/additive (2 parts) mixtures.

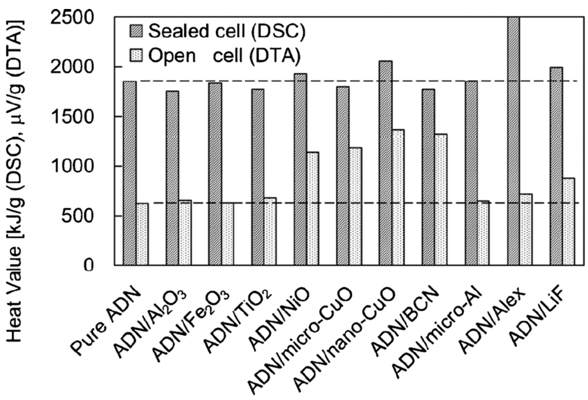

Figure 4. Heat values of pure ADN and ADN/additive (2 parts) mixtures.

ADN shows two exothermic peaks under closed conditions; the initial decomposition of ADN (1st), and the decomposition of AN (2nd), which is the decomposition product of ADN [18,19]. The first exothermic heat values are summarized in Figure 4. The DSC (dark) and DTA (light) measurements were conducted under closed and open conditions, respectively. NiO and Cu additives increase the heat value under open conditions, and Alex increases the heat value under closed conditions. In particular, the heat values of the ADN/nano-CuO and ADN/BCN mixtures reach approximately double that of pure ADN.

3.2 Burning Rate

The burning rates of the samples using ADN of lot A are shown in Figure 5, Figure 6, Figure 7, and Figure 8. In Figure 5, the additives are micrometer-sized Al, Fe_2O_3, TiO_2, NiO, and CuO. The burning rates of the pure ADN increase as the pressure increases, and the pressure exponent, "n" of Vielle's law, $rb = aP^n$, changes at approximately 1 MPa. The pressure exponent is approximately unity below 1 MPa, and no pressure sensitivity is observed at 3 MPa. The burning rate at 3–6 MPa is around 30 $mm \cdot s^{-1}$. Fe_2O_3 has the most negative effect among the different additives, with the burning rate being 5–10 $mm \cdot s^{-1}$ lower than that of pure ADN under all pressures. Micrometer-sized Al also decreases the burning rate. The value at 0.6 MPa is much lower than that of pure ADN, and increases steeply up to a pressure of 1 MPa. At 1 MPa, the burning rate is between

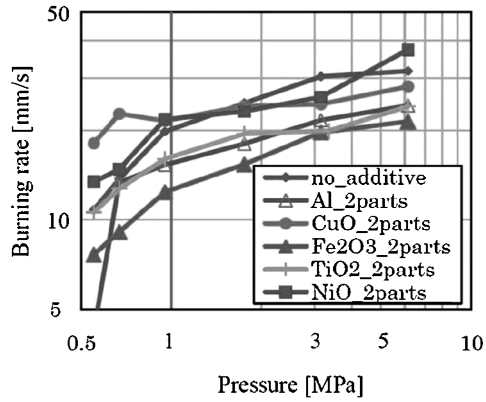

Figure 5. Burning rates of pure ADN and ADN/additive mixtures.

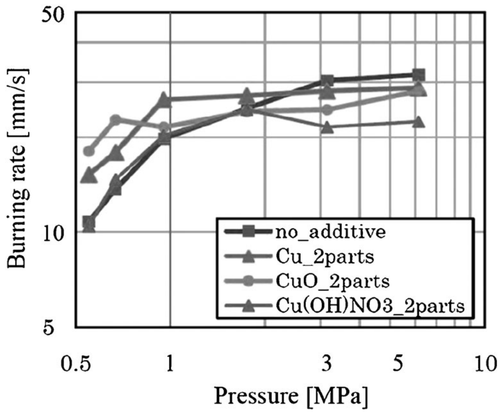

Figure 6. Burning rates of pure ADN and ADN/copper mixtures.

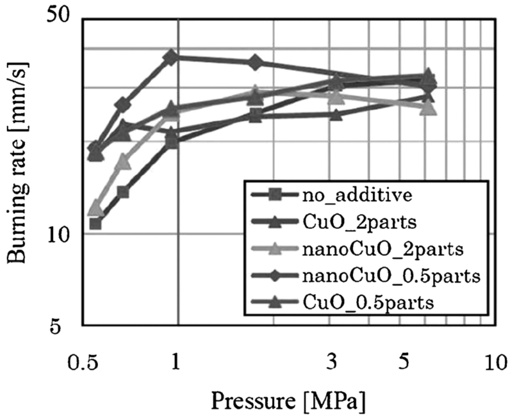

Figure 7. Burning rates of pure ADN and ADN/micro and nano-CuO mixtures.

that of ADN/Fe_2O_3 and pure ADN, and increases up to 6 MPa with $n = 0.2–0.3$. The ADN/TiO_2 mixture burns faster than the ADN/Fe_2O_3 mixture, particularly at low pressures. The burning rate at 0.6 MPa is almost the same as that of pure ADN and increases gradually up to 2 MPa. The burning rate is constant above 2 MPa, around 20 $mm \cdot s^{-1}$, and it

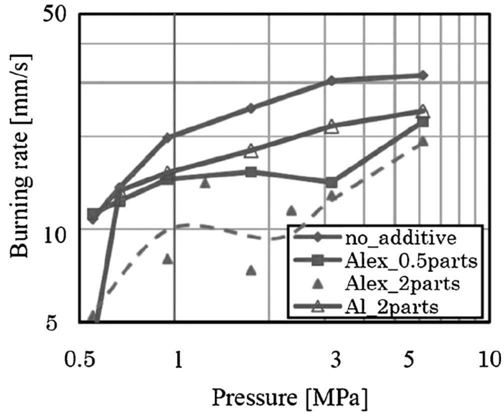

Figure 8. Burning rates of pure ADN and ADN/micro-Al and Alex mixtures.

is almost the same as that of the ADN/Fe_2O_3 and ADN/Al mixtures. The burning rate of the ADN/NiO mixture is close to that of pure ADN at all pressures. At 0.6 MPa, the burning rate is 12 $mm \cdot s^{-1}$, which is slightly higher than that of pure ADN; the pressure sensitivity changes at 1 MPa, as was observed with pure ADN. CuO is the most effective additive as a burning rate catalyst, significantly enhancing the combustion of ADN. The burning rate is around 20 $mm \cdot s^{-1}$ below 1 MPa, twice as high as that of pure ADN. However, CuO is not effective above 1 MPa, and the behavior of the ADN/CuO mixtures is almost the same as that of pure ADN and ADN/NiO.

The effects of the copper compounds on the burning rates are compared in Figure 6. These additives contribute to the generation of more smoke during combustion, and dark zones can be clearly seen above 3 MPa. The ADN/Cu mixture burns faster than ADN/CuO at 1 MPa, but they show similar behavior and enhance the burning rate at low pressures. Copper is easily oxidized by ADN, and the color of the mixed powder before burning turns smoky blue after drying. The burning rates of the ADN/BCN mixture are almost the same as those of pure ADN, and the burning rate decreases to 20 $mm \cdot s^{-1}$ above 2 MPa. These copper-containing compounds remain black residues after combustion.

In Figure 7, the micro- and nano-CuO additives were compared by varying the mass ratios of the additives with ADN; 2.0 and 0.5 parts. The burning rates of the ADN/micro-CuO (0.5 parts) mixture are almost the similar those of the ADN/nano-CuO (2.0 parts) mixture below 1 MPa, and the former is about 5 $mm \cdot s^{-1}$ faster than the latter above 1 MPa. Nano-CuO significantly enhances the burning rate below 2 MPa, and the nano (0.5 parts) pellets also burn faster than the nano (2.0 parts) pellets. Upon addition of CuO, the burning rates increase from 10 $mm \cdot s^{-1}$ to 20 $mm \cdot s^{-1}$ at 0.6 MPa and 20 $mm \cdot s^{-1}$ to 40 $mm \cdot s^{-1}$ at 1.0 MPa. At 6 MPa, the burning rates of all the CuO-containing pellets are close to that of pure ADN.

The burning rates of the ADN/micro-Al and Alex mixtures are shown in Figure 8. The additives have ratios of 0.5 : 100 (0.5 parts) and 2 : 100 (2.0 parts). The ADN/Alex (0.5 parts) mixture showed similar behavior to ADN/micro-Al (2.0 parts), and the burning rates are lower than those of pure ADN. In the case of the ADN/Alex (2.0 parts) mixture, the combustion behavior is unstable; it forms flames intermittently, and the burning rates are scattered between 1 and 3 MPa.

3.3 Temperature Measurements

Lot B of ADN was used in the temperature measurements, and the burning rates were compared with lot A in Figure 9. The burning rate of pure ADN of lot B is almost the same as that of lot A, and the ADN(lot B)/additives mixtures show the same tendencies as the ADN(lot A)/additives mixtures, as shown in Figure 7 and Figure 8: an enhancement by the nano-CuO at low pressures and the negative effect of Alex. The open circle in Figure 10 shows the burning rate of the mixture of well-ground ADN and nano-CuO (0.5 parts) at 0.4 MPa, and it is almost the same as that of pure ADN, though the just-dispersed mixture burns obviously faster than pure ADN.

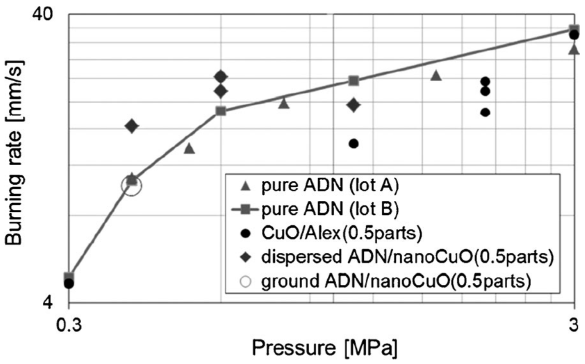

Figure 9. Comparison of the burning behavior of pure ADN and ADN mixtures with Alex (0.5 parts) and nano-CuO.

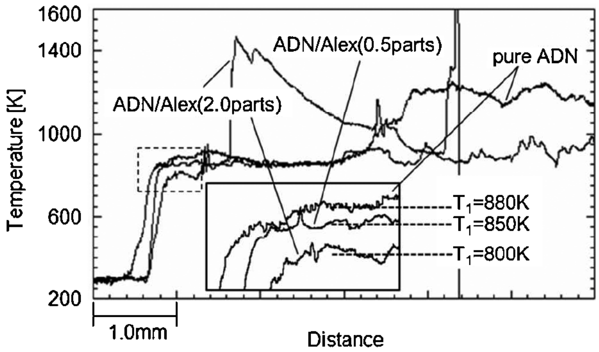

Figure 10. Comparison of the burning behavior of pure ADN and ADN/Alex (0.5 and 2.0 parts) mixtures.

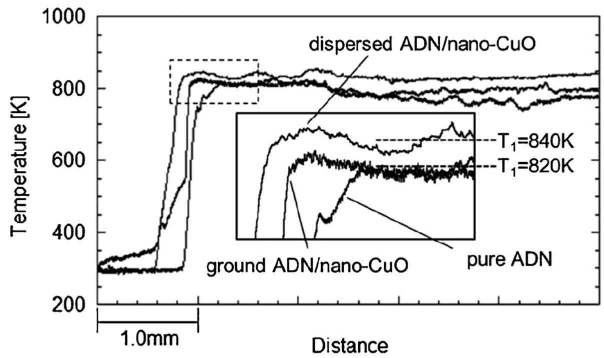

Figure 11. Comparison of the burning behavior of pure ADN and dispersed and ground ADN/nano-CuO (0.5 parts) mixtures.

Figure 10 shows the temperature profile of the pure ADN and ADN/Alex (0.5 and 2.0 parts) mixtures at 1.1 MPa. The temperature profiles have flat zones whose temperatures are shown as T_1 after the first sharp temperature increase. T_1 of pure ADN is approximately 880 K, which is 30 K higher than for ADN/Alex (0.5 parts). The temperature profile of pure ADN has a second temperature increase, which reaches 1200 K at a distance of 3 mm from the first increase. T_1 of ADN/Alex (2.0 parts) is 800 K, and then the profile sharply increases to 1470 K 0.7 mm downstream of the first temperature increase. The profile gradually decreases to 900 K and then sharply increases again to over 1800 K, at which point the thermocouple was broken. The recorded pictures of this intermittent flame are shown in Figure 12. Flames are not observed at $t+0$ ms, and within 1 ms, the flash is observed in the vicinity of the burning surface. The flash becomes small and the gas phase grows red at $t+3$ ms.

Figure 11 shows the temperature profiles of the pure ADN and ADN/nano-CuO (0.5 parts) mixtures. The ADN/nano-CuO (0.5 parts) samples are prepared with just-dispersed and well-ground ADN. T_1 of the pure ADN and well ground-ADN/nano-CuO (0.5 parts) mixture are almost equal (820 K); however, T_1 of the mixture of the just-dispersed ADN and nano-CuO (0.5 parts) is approximately 20 K higher than that of pure ADN.

4 Discussion

4.1 Thermal Analysis

The addition of Cu compounds lowered the onset temperature of the ADN decomposition, which can be speculated from the thermal decomposition of AN and CuO mixtures, because both ADN and AN are salts of ammonia with a strong acid. Kajiyama et al. studied the effects of CuO on the thermal decomposition of AN and mentioned that CuO forms copper complexes such as $[Cu(NH_3)_2](NO_3)_2$, which increases the heat value of the AN decomposition [20]. Therefore, it is considered that CuO forms the intermediate

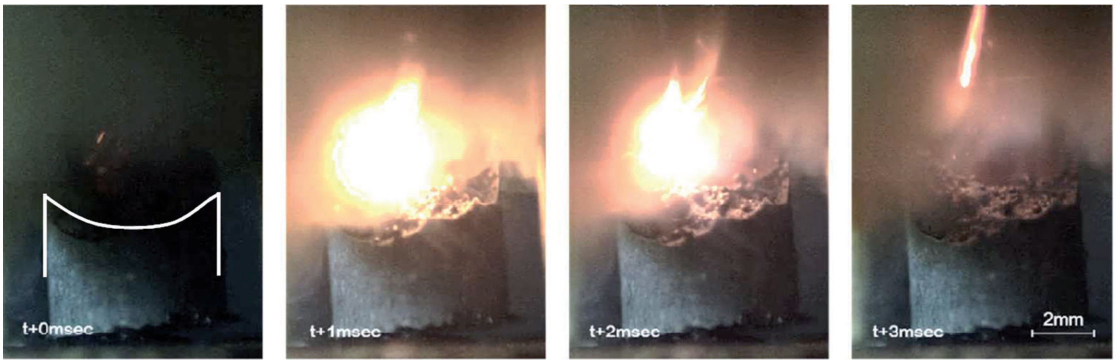

Figure 12. Flash during the combustion of ADN/Alex (2.0 parts) at 1.1 MPa.

compound with ammonia or dinitramide abstracted from the ADN molecules, and then the onset temperatures and the heat values change. It was confirmed that CuO dissolves into the reactants during the ADN decomposition from the recorded pictures, and the color of the reactants turned to blue. Therefore, it is considered that CuO affects the condensed phase reactions and works like a catalyst, because the heat value of the ADN/CuO mixture is almost the same as that of pure ADN under closed conditions, as shown in Figure 4. After the decomposition, the copper intermediates return to CuO, as indicated by the black residues observed on the bottom of the cell after the measurements.

In Figure 4, it is clear that Alex increases the heat value; however, micrometer-sized Al does not increase the heat value under closed conditions. Therefore, the reaction depends on the surface area of the particles. Further, Alex does not react in a condensed phase because no differences are found under open conditions, where the reactions occur in the gas phase.

4.2 Burning Rate and Temperature Measurements

Fe_2O_3, Al, and TiO_2 suppress the burning rate of ADN. Endothermic chemical reactions were not observed in the thermal decompositions of these samples, and the flames observed in the temperature measurements are too far away to affect the condensed phase behavior. Therefore, it is considered that the physical effects of the condensed phase decrease the ADN burning rate. Sinditskii et al. also reported that the physical effects cause such a burning rate decrease because only 1.5% SiO_2, which is inert during ADN decomposition, lowers the burning rate to half that of pure ADN pellets [10]. Further, Manelis et al. reported that the addition of 2% $K_2Cr_2O_7$ decreases the burning rate of ADN at 3–8 MPa by one-third, although $K_2Cr_2O_7$ is a typical decomposition catalyst of AN, which is the decomposition product of ADN and accumulates on the burning surface [12]. These negative effects on the burning rate cannot be explained by the heat absorptions of such small amounts of additives.

It has been reported that the initial ADN decomposition generates a considerable amount of liquid AN. AN accumulates on the burning surface at low pressures, and the condensed phase controls the burning rate [13,14]. Physical effects such as dissociation and boiling, blown-off particles, and the reaction of the condensed phase influence the decomposition temperature; however, it is particularly difficult to estimate the contribution of the physical phenomena. Sinditskii et al. reported that the pressure exponent can be calculated by assuming that the condensed phase temperature is limited to the boiling point of AN at pressures below 2 MPa. However, the negative effects of the additives are caused by another mechanism, and it is considered that the dispersion and reaction also influence the surface temperature, even at low pressures.

Oxley et al. reported that 0.6 mol AN is generated per 1 mol of ADN. The decomposition rate of AN is much slower than that of ADN, and AN remains on the burning surface. AN can have various effects on the surface temperature: exothermic reactions, endothermic dissociations, and no effect on the heat by blown-off particles. The endothermic dissociation energy is 167 $kJ \cdot mol^{-1}$, which is large enough to change the surface temperature by tens of Kelvin because the ADN decomposition heat is 209 $kJ \cdot mol^{-1}$ [18]. Therefore, the small change in the contributions from the dissociation and blown-off particles leads to a change in the surface temperature. If the specific heat of the condensed phase is assumed to be the value of the liquid AN (2.1 $kJ\,g^{-1}\,K^{-1}$), the effects of the AN dissociation can be estimated by a simple calculation; a 1% increase of the AN dissociation decreases the surface temperature by approximately 10 K. The difference in T_1 between pure ADN and ADN/Alex (2.0 parts) is 80 K, as shown in Figure 10, and corresponds to only an 8% increase of the dissociation of AN on the burning surface.

A 2:100 ratio of Alex causes an intermittent combustion, as shown in Figure 12. Alex accumulates on the burning surface, and the ratio of Alex on the surface is increased. When the Alex ratio exceeds a certain value, the heat accumulation caused by the Alex oxidation proceeds much faster than the endothermic phase change of AN, and a thermal explosion occurs in the vicinity of the burning surface. The thermal explosion blows off the accumulated Alex in the condensed phase, and the temperature decreases to the original surface temperature of around 900 K. This cycle of Alex accumulation and thermal explosion causes the intermittent combustion. This accumulation can explain the negative effects of the additives on the burning rates, because the particle accumulation may change the balance of the physical phenomena (evaporative dissociation and the amount of blown droplets of liquid AN). It is considered that the accumulated Alex decreases the amount of blown-off droplets, and the contribution of the endothermic dissociative evaporation increases, which decreases the burning surface temperature and the burning rate. In the other samples of ADN/inert additives; micro-Al, Fe_2O_3, and TiO_2 seem to cause the same physical effects, suppressing the burning rate of ADN.

Only NiO and Cu compounds increase the heat value under open conditions, and they also enhance the burning rate at low pressures; therefore, it is considered that the enhanced condensed phase reaction accelerates the burning rate. It is also suggested that the contribution from the exothermic reactions increases with the addition of CuO and NiO, and when the effect of the exothermic reactions outweighs the negative effects caused by the physical balance change explained above, the burning surface temperature increases along with the burning rate. These competing effects are evidenced by the analysis shown in Figure 11. The surface temperature of the dispersed-ADN/nano-CuO mixture is higher than that of pure ADN. The contribution of the exothermic reaction in the condensed phase seems to exceed the negative physical effects. However, the burning surface temperature and burning rate of the well-ground ADN/nano-CuO mixture are almost the same as those of pure ADN. In this case, the negative effect caused by the physical changes exceeds the positive effect of the exothermic reactions because of the change in homogeneity of the sample.

In summary, the balance of the reaction and the physical phenomena affect the burning surface temperature of ADN; therefore, inert additive particles decrease the burning rate by increasing the endothermic physical contributions. Reactive additives can enhance the burning rate by increasing the contribution from the exothermic reactions. These reactive particles also have some endothermic physical effects, and the total effect is determined by the balance of these physicochemical phenomena.

This report focused on the additives effects to pure ADN, and the results are also helpful to study the ADN propellant. The combustion of ADN propellant includes the other phenomena, the reaction between ADN and the binder in the condensed phase and the heat feedback from the flame. If the condensed phase reaction mainly controls the burning rate, the physicochemical phenomena as shown in this report should occur. In the flame-controlled combustion, the burning rate might be much different from pure ADN. However, if the regression rate of ADN is much faster than the binder, which is likely to occur in inert binders, the binder is left behind the ADN combustion [1]. Then the burning rate should be close to pure ADN, and our results are useful to understand the combustion mechanism.

5 Conclusion

In this report, the effects of additives on ADN combustion were investigated using thermal analysis and burning rate and temperature measurements. Only CuO and NiO increase the heat value of ADN decomposition in the condensed phase; these additives also enhanced the burning rate. The other non-reactive additives showed a negative effect on the burning rate. The burning rate depends on the balance between the chemical reaction, the physical phase change, and the amounts of blown droplets at the burning surface. Alex and inert additives lowered the burning surface temperature because the contribution of the endothermic physical effects was increased, which causes a negative effect on the burning rate. Reactive additives such as nano-CuO increase the burning surface temperature because the contribution of the exothermic reactions exceeds the negative effects from the physical phenomena.

Acknowledgments

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References

[1] T. P. Parr, D. M. Hanson-Parr, Solid Propellant Diffusion Flame Structure, *26th Symposium (International) on Combustion*, Naples, Italy, July 28–August 3, **1996**, p. 1981.
[2] E. W. Price, S. R. Chakravarthy, J. M. Freeman, Combustion of Propellants with Ammonium Dinitramide, *34th AIAA/ASME/SAE/ASEE Joint Propulsion Conference*, Cleveland, OH, USA, July 13–15, **1998**, A98-35220.
[3] S. R. Chakravarthy, J. M. Freeman, E. W. Price, R. K. Sigman, Combustion of Propellants with Ammonium Dinitramide, *Propellants Explos. Pyrotech.* **2004**, *29*, 220.
[4] O. P. Korobeinichev, A. A. Paletsky, A. G. Tereschenko, E. N. Volkov, Combustion of Ammonium Dinitramide/Polycaprolactone Propellants, *Proc. Combust. Inst.* **2002**, *29*, 2955.
[5] V. Weiser, N. Eisenreich, A. Baier, W. Eckl, Burning Behaviour of ADN Formulations, *Propellants Explos. Pyrotech.* **1999**, *24*, 163.
[6] K. Menke, T. Heintz, W. Schweikert, T. Keicher, H. Krause, Formulation and Properties of ADN/GAP Propellants, *Propellants Explos. Pyrotech.* **2004**, *34*, 218.
[7] N. Wingborg, S. Andreasson, J. de Flon, M. Johnsson, M. Liljedahl, C. Oscarsson, Å. Pettersson, M. Wanhatalo, Development of ADN-Based Minimum Smoke Propellants, *46th AIAA/ASME/SAE/ASEE Joint Propulsion Conference*, Nashville, TN, USA, July 25–28, **2010**, AIAA2010–6586.
[8] J. de Flon, S. Andreasson, M. Liljedahl, C. Oscarsson, M. Wanhatalo, N. Wingborg, Solid Propellants Based on ADN and HTPB,

47th AI-AA/ASME/SAE/ASEE Joint Propulsion Conference, San Diego, CA, USA, July 31–August 03, **2011**, AIAA2011–6136.
[9] K. Fujisato, H. Habu, H. Shibamoto, X. Yu, A. Miyake, K. Hori, Combustion Characteristics of ADN-Based Solid Propellants, *Europyro2011*, Reims, France, May 7–19, **2011**, S1c-64.
[10] V. P. Sinditskii, V. Y. Egorshev, A. I. Levshenkov, V. V. Serushkin, Combustion of Ammonium Dinitramide, Part 1: Burning Behavior, *J. Propuls. Power* **2006**, *22*, 769.
[11] O. P. Korobeinichev, A. A. Paletsky, A. G. Tereschenko, E. N. Volkov, Combustion of Ammonium Dinitramide/Polycaprolactone Propellants, *Proc. Combust. Inst.* **2002**, *29*, 2955.
[12] V. A. Strunin, A. P. D'yakov, G. B. Manelis, Combustion of Ammonium Dinitramide, *Combust. Flame* **1999**, *117*, 429.
[13] V. P. Sinditskii, V. Y. Egorshev, A. I. Levshenkov, V. V. Serushkin, Combustion of Ammonium Dinitramide, Part 2: Combustion Mechanism, *J. Propuls. Power* **2006**, *22*, 777.
[14] A. A. Zenin, V. M. Puchkov, S. V. Finjakov, Physics of ADN Combustion, *37th AIAA Aerospace Sciences Meeting and Exhibit*, Reno, NV, USA, January 11–14, **1999**.
[15] A. Langlet, H. Östmark, N. Wingborg, *Method of Preparing Dinitramidic Acid and Salts Thereof*, US Patent 5,976,483, Stockholm, Sweden, **1999**.
[16] S. Venkatachalam, G. Santhosh, K. N. Ninan, An Overview on the Synthetic Routes and Properties of Ammonium Dinitramide (ADN) and Other Dinitramide Salts, *Propellants Explos. Pyrotech.* **2004**, *29*, 178.
[17] V. A. Shlyapochnikov, G. I. Oleneva, N. O. Cherskaya, O. A. Luk'yanov, V. P. Gorelik, O. V. Anikin, V. A. Tartakovsky, Dinitramide and its Salts, *Russ. Chem. Bull.* **1995**, *44*, 1449.
[18] J. C. Oxley, J. L. Smith, W. Zheng, E. Rogers, M. D. Coburn, Thermal Decomposition Studies on Ammonium Dinitramide (ADN) and ^{15}N and ^{2}H Isotopomers, *J. Phys. Chem. A* **1997**, *101*, 5646.
[19] H. Matsunaga, H. Habu, A. Miyake, Influences of Aging on Thermal Decomposition Mechanism of High Performance Oxidizer Ammonium Dinitramide, *J. Therm. Anal. Calorim.* **2013**,*113*,1387.
[20] K. Kajiyama, Y. Izato, A. Miyake, Thermal Characteristics of Ammonium Nitrate, Carbon, and Copper(II) Oxide Mixtures, *J. Therm. Anal. Calorim.* **2013**, *113*, 1475.

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