

Influence of the physical properties of carbon on the thermal decomposition behavior of ammonium nitrate and carbon mixtures

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Abstract

To understand the influence of the physical properties of carbon on the thermal decomposition behavior of ammonium nitrate (AN) and carbon mixtures, Raman spectroscopic analysis, differential scanning calorimetry (DSC), thermogravimetry–differential thermal analysis with infrared spectrometry (TG–DTA–IR), thermogravimetry–mass spectrometry (TG–MS), and flash pyrolysis mass spectrometry (Py–MS) were carried out. From DSC scanning analysis, AN mixed with activated carbon or carbon nanotubes exhibited violent reactions after the melting of AN, while AN mixed with graphite or fullerene showed mild exothermic peaks, the same as for pure AN. From the TG–IR results, the formation of carbon dioxide was more pronounced for AN and activated carbon and AN and carbon nanotube mixtures than other mixtures. Mass spectra of decomposition gases for AN and activated carbon and AN and graphite mixtures showed different patterns at a heating rate of 100 K min^{-1} with TG–MS, but they showed similar spectra when instantaneous heating with a flash pyrolyzer was performed. It is concluded that AN mixed with carbon of low crystallinity showed violent reactions after melting, while AN mixed with carbon of high crystallinity showed the same behavior as pure AN. The thermal decomposition behavior of AN/carbon mixtures was not influenced by the crystallinity of carbon when heated instantaneously.

Keywords : Ammonium nitrate, Carbon, Thermal decomposition, Evolved gas analysis

1. Introduction

Ammonium nitrate (AN) has been widely used as a fertilizer and as an ingredient of industrial explosives or oxidizing chemicals because it is relatively cheap, releases almost 100% gaseous products when it reacts and has a positive oxygen balance (+20.0 g/g). Recently, compositions of AN mixed with suitable combustibles have been proposed for gas generants or halogen-free propellants of the next generation¹⁾²⁾. For the safe development and use of such devices, understanding of the physical and chemical influence of mixed materials and the reaction mechanisms of AN mixtures are needed.

The purpose of this study is to examine the influence of the physical properties of carbon on the thermal decomposition behavior of AN and carbon mixtures. By employing several experimental techniques such as Raman spectro-

scopic analysis, differential scanning calorimetry (DSC), thermogravimetry–differential thermal analysis connected with infrared spectrometry (TG–DTA–IR), thermogravimetry–differential thermal analysis connected with mass spectrometry (TG–DTA–MS), and flash pyrolysis–mass spectrometry analysis (Py–MS), the thermal behavior of AN and AN/carbon mixtures were investigated and the influence of physical properties such as crystallinity on the thermal decomposition behavior of AN and carbon mixtures was explored.

2. Materials

Commercially available powdered explosive grade AN was used in this study. Four types of carbon [activated carbon (AC), graphite (GC), carbon nanotube (CNT) and fullerene (C₆₀)] were used. The physical properties of AN

Table 1 physical properties of AN

Type of AN	Density [kgm ⁻³]	Ave. particle diameter [mm]	Purity [%]	Moisture content [%]
Powdered	260	0.14	> 99	0.1

Table 2 Physical properties of carbons

	Ave. particle diameter [μm]	Purity [%]	Specific surface area [m ² g ⁻¹]
AC	20	>99.9	1433
GC	10	>98.0	5.3
CNT	0.023	>95.0	—*
C ₆₀	—*	>99.9	—*

* not available

and the carbon materials used in this study are listed in Tables 1 and 2. AN was carefully prepared by hand mixing with each type of carbon to obtain desired compositions. The stoichiometric composition of AN/AC, AN/GC, AN/CNT and AN/C₆₀ mixtures was 93.0/7.0 wt%, in accordance with the following equation.



3. Experimental

3.1 Raman spectroscopic analysis of carbons

The crystallinity of the carbon materials was determined by Raman spectroscopic analysis. The analysis was performed using a computerized Raman spectroscopy system, a Kaiser Raman RXN System equipped with a semiconductor laser, operating at 780 nm for excitation. A laser power of 50 mW was applied.

3.2 Differential scanning calorimetry of AN/carbon mixtures

Thermal characteristics of AN/carbon mixtures were measured on a Mettler Toledo HP DSC827e. The mixtures loaded in a stainless sealed cell under 0.1 MPa air atmosphere were heated from 303 up to 723 K at a heating rate of 5K min⁻¹ and the onset temperature of the exothermic endothermic peaks and the heat of reaction were determined.

3.3 Thermogravimetry–infrared spectroscopic measurements (TG–DTA–IR)

Weight loss and decomposition gases during the heating of AN/carbon mixtures were determined by a Shimadzu simultaneous thermogravimetry/differential thermal analysis DTG-50 connected with a Shimadzu infrared spectrometer IR Prestige-21/FTIR 8400S. Sample amounts ranging from 2 to 5 mg were placed in open aluminum cells and heated from 303 to 673 K at a heating rate of 100 K min⁻¹ in 0.1 MPa argon. Decomposition gases produced in the DTG-50 were directed through a heated stainless tube and injected into a pre-heated gas cell placed in an infrared spectrophotometer.

3.4 Thermogravimetry–differential thermal analysis with mass spectrometry (TG–DTA–MS)

Thermal characteristics and decomposition gases of AN/AC and AN/GC mixtures were determined by thermogravimetry–differential thermal analysis with mass spectrometry (TG–DTA–MS) using a Rigaku TG/DTA-8120 connected to a Shimadzu GC/MS-2010 mass spectrometer. A number of 5 mg samples were heated from 303 to 723 K at a heating rate of 100 K min⁻¹ under helium gas flow (200 mL min⁻¹) with the TG/DTA-8120, and the evolved gases were directed to the GC/MS-2010 to identify decomposition gas products of each sample. The mass spectrometer was operated in electron impact ionization mode and the mass range of m/z 10–100 was scanned.

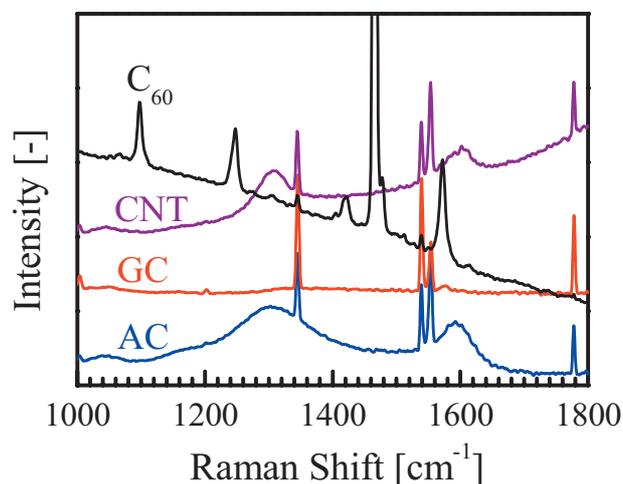
3.5 Flash pyrolysis mass spectrometry (Py–MS)

Decomposition gases of AN/AC and AN/GC mixtures during instantaneous heating were determined with flash pyrolysis mass spectrometry. Approximately 0.5 mg samples were pyrolyzed at 1073 K under helium gas using a Frontier lab PY-202iD pyrolyzer interfaced to an Agilent JEOLMS-600Y gas chromatograph/mass spectrometer. The flow rate of the carrier gas was 2mL min⁻¹ and the split ratio was 50 : 1. The pyrolysis interface and the GC injector were kept at 473 K. The mass spectrometer was operated in the electron impact mode. The mass range of m/z 10–100 was scanned.

4. Results and discussion

Figure 1 shows the Raman spectra of the four types of carbon used in this study. Since both the D-band (1360 cm⁻¹) and D'-band (1620 cm⁻¹) were observed in the Raman spectra of AC and CNT, they were determined to have low crystalline amorphous structures with rigid crystal arrangements³⁾.

The sealed cell DSC profiles of AN and AN/carbon mixtures are shown in Fig. 2 and the onset temperature, maximum heat flow and heat of reaction are summarized in Table 3. The onset temperature of the exothermic peak of AN/AC was found at around 450 K, just after melting of AN, and at about 500 K for AN/CNT followed by a violent reaction. AN/GC and AN/C₆₀ showed moderate exother-

**Fig. 1** Raman spectra of carbons

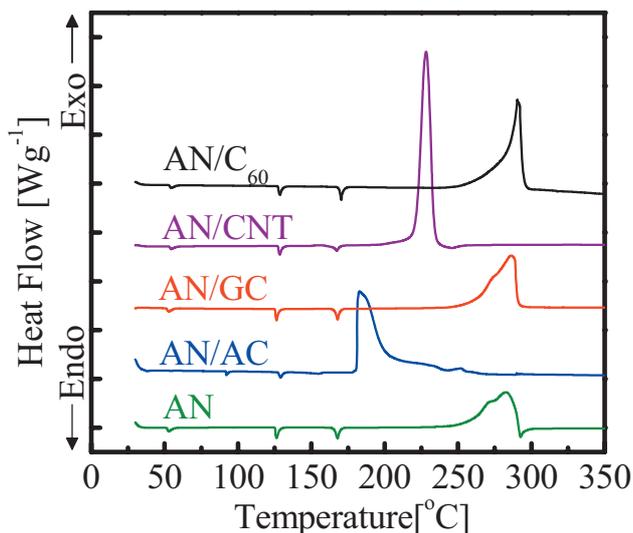


Fig. 2 DSC results of AN and carbon mixtures

Table 3 DSC results of AN and carbon mixtures

	Onset temperature [K]	Max heat flow [Wg^{-1}]	Heat of reaction [kJg^{-1}]
AN	538	6.8	1.5
AN/AC	453	16.3	3.5
AN/GC	533	10.7	2.5
AN/CNT	469	40.0	3.9
AN/C ₆₀	537	17.5	3.0

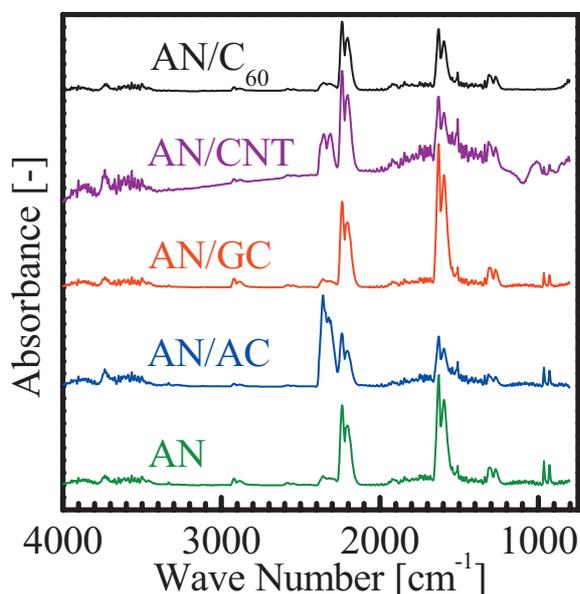


Fig. 3 IR spectra of AN and carbon mixtures

mic peaks starting at about 535 K and ending at 565 K, similar to that of pure AN. Although the heats of reaction of AN/GC and AN/C₆₀ were smaller than those of AN/AC and AN/CNT, they were still larger than that of pure AN. It is considered that a mild reaction occurred between carbon and nitric oxides in the gaseous phase for AN/GC and AN/C₆₀ mixtures.

Results of TG-IR measurements are shown in Fig. 3. A strong peak at 2349 cm^{-1} , which is derived from carbon di-

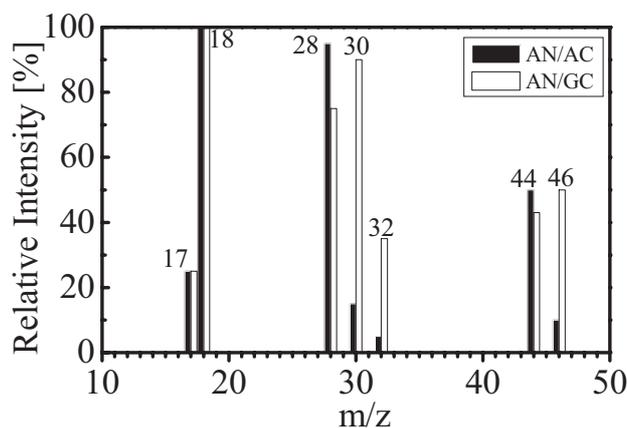


Fig. 4 TG-MS results of AN/AC and AN/GC mixtures

oxide (CO_2), was observed in the spectra for AN/AC and AN/CNT. This indicates that decomposition gases from AN/AC and AN/CNT mixtures contained a large amount of CO_2 . Since CO_2 gas evolution suggests a redox reaction between AN and carbon, it is considered that AC and CNT are oxidized by AN during heating. A weak peak for CO_2 is observed in the spectra for AN/GC and AN/C₆₀, suggesting that GC and C₆₀ are not oxidized by AN but by NO_x gases.

Ammonium nitrate generally dissociates into ammonia and nitric acid after melting according to Eq. (2)⁹.



In general, low crystallinity carbon is oxidized by nitric acid, while high crystallinity carbon is not oxidized by nitric acid but by NO_x gases⁵⁻¹². In the decomposition process of AN/AC and AN/CNT mixtures, nitric acid forms by dissociation of AN, and it oxidizes AC and CNT. A large amount of heat is released by the reaction between AN and the carbon materials, promoting decomposition of AN. Therefore, AN/AC and AN/CNT mixtures showed violent reaction after melting. Since GC and C₆₀ have high crystallinity, they are not fully oxidized by nitric acid, but oxidized mainly by NO_x . Therefore, the IR spectra of the thermal decomposition of AN/GC and AN/C₆₀ showed the same behavior as that of pure AN powder. As AN/GC and AN/C₆₀ mixtures were oxidized by NO_x produced from the decomposition of AN during heating in sealed cells, they showed a higher heat release than pure AN.

The results of TG-MS and Py-MS are shown in Figs. 4 and 5. The TG-MS spectrum of AN/AC exhibited a different shape from that of AN/GC at a heating rate of 100 K min^{-1} but exhibited a similar spectrum when heated instantaneously with a flash pyrolyzer. Mass-to-charge ratio (m/z) showed that AN decomposes without accumulation of nitric acid when heated instantaneously, so that both AN/AC and AN/GC showed a similar reaction. It is concluded that the thermal decomposition behavior of AN/carbon mixtures is not influenced by physical properties of carbon when heated instantaneously.

5. Conclusions

The thermal characteristics of AN and mixtures of AN and four types of carbon, e.g., AC, GC, CNT and C₆₀, were

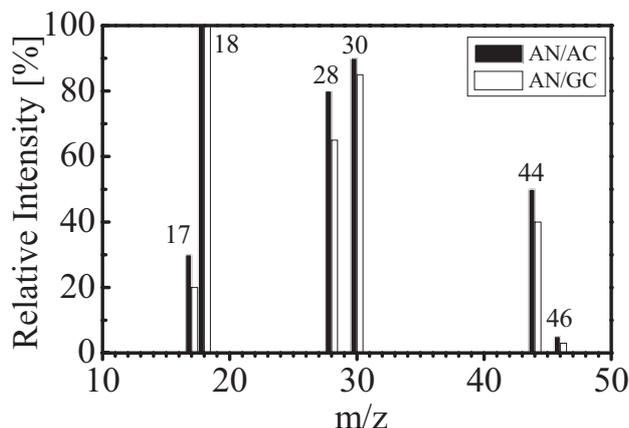


Fig. 5 Py-MS results of AN/AC and AN/GC mixtures

measured by DSC and evolved gas analysis was performed by TG-IR, TG-MS and Py-MS. The following conclusions can be drawn:

- (1) The crystallinity of carbon has a strong influence on the thermal decomposition behavior of AN/carbon mixtures. AN mixed with low crystallinity carbon such as AC and CNT showed violent reaction after melting. AN mixed with high crystallinity carbon such as GC and C₆₀ showed relatively mild decomposition above 530 K, which coincides with that of pure AN.
- (2) From evolved gas analyses of AN/carbon mixtures performed by TG-IR and TG-MS, nitric acid forms by the melting of AN, which then oxidizes AC and CNT. AN/GC and AN/C₆₀ mixtures are oxidized by NO_x formed from the decomposition of AN and they

show a higher heat release than pure AN.

- (3) The thermal decomposition behavior of AN/carbon mixtures with instantaneous heating is not influenced by the difference in type of carbon.

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硝酸アンモニウム／炭素混合系の熱分解に及ぼす炭素物性の影響

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硝酸アンモニウム (硝安)／炭素混合系の熱分解に及ぼす炭素物性の影響を検討するため、ラマン分光分析、示差走査熱量測定 (DSC)、熱重量-示差熱分析熱-赤外分光分析 (TG-DTA-IR)、熱重量-質量分析 (TG-MS)、瞬間熱分解質量分析 (Py-MS) の各測定を行った。DSC昇温測定より、硝安に活性炭またはカーボンナノチューブを加えた混合系では硝安の融解後に激しい発熱を観測したが、黒鉛またはフラーレンとの混合系では硝安単体同様の穏やかな発熱であった。TG-IR結果より、硝安と活性炭またはカーボンナノチューブとの混合系では他の組成に比べ二酸化炭素の発生が顕著であった。硝安／活性炭および硝安／黒鉛の熱分解ガスは、昇温速度が100 K min⁻¹時の発生ガスは異なるものの、瞬間熱分解時には同様の組成を示した。以上より、硝安と低結晶化度炭素との混合系の熱分解は硝安の融解後に激しい発熱を示すのに対し、高結晶化度炭素との混合系では硝安単体と同様の分解挙動を示すこと、および瞬間加熱時には、炭素の結晶化度は硝安／炭素混合系の熱分解特性にほとんど影響を及ぼさないことが明らかとなった。

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