Letter

Burning characteristics of some azodicarbonamide / ammonium nitrate / additive mixtures

Ken Ikeda*†, Yuji Shiraishi*, and Shingo Date*

*Department of Applied Chemistry, National Defense Academy, Yokosuka, Kanagawa 239-8686, Japan
Phone : +81-46-841-3810
†Corresponding author : em51043 @nda.ac.jp

Received : July 26, 2013 Accepted : November 7, 2013

Abstract

The burning characteristics of stoichiometric ratio azodicarbonamide (ADCA)/ammonium nitrate (AN) mixture, together with those of ADCA/AN/CuO mixtures, were studied. From chemical equilibrium calculation, the linear burning rate test, the rate-of-pressure-rise test, and the temperature history test, the following conclusions were obtained : (1) the calculated values of adiabatic flame temperature and heat of explosion decreased with an increase in CuO content ; (2) ADCA / AN mixture burned readily under 0.1 MPa N_2 atmosphere, showing relatively good ignitability ; (3) the addition of CuO accelerated the linear burning rate and also generally decreased the pressure exponent of Vieille's equation as compared to ADCA/AN mixture, while it also accelerated the rate-of-pressure-rise. Its CuO 10 % and 20 % mixtures were higher in the rate-of-pressure-rise as compared to guanidinium nitrate (GN) / strontium nitrate (SrN) / basic copper nitrate (BCN) mixture that is put into practical use ; (4) increasing the amount of CuO reduced the thickness of the condensed phase and lowered the burning surface temperature. In the condensed phase reaction layer, it is suggested that CuO accelerates the thermal decomposition reaction.

Keywords : azodicarbonamide, copper (Ⅱ) oxide, rate-of-pressure-rise, temperature profile, condensed phase

1. Introduction

Automotive airbag system, one of the automobile occupant safety restraint systems, is a standard safety system in the automobile that comes with the seat belt restraint. It is an aux-iliary restraint system that complements the effect of the seat belt, and it has a role to alleviate the impact applied to the head and chest. The system consists of sensor collision detection, diagnostic unit and an air bag module. Upon collision, collision sensors sense the shock, and after the diagnostic unit determines that the collision took place, it sends an electrical signal to ignite the inflator, which burns and produces large amount of gas in a short period of time to inflate the airbag. In principle, the inflation of the airbag must be faster than the movement of the occupant at the time of collision.

Recently, a number of researches and developments of new gas generating agent, using ammonium nitrate (AN) as an oxidizing agent, have been carried out[1)2)]. The advantages of using AN as an oxidizer, are its low cost and high gas yield, but it is difficult to ignite, and the burning rates of its mixtures are generally slow. In order to solve the problem of low combustion characteristics, we selected a foaming agent, azodicarbonamide (ADCA) as a fuel, and copper (Ⅱ) oxide CuO as an additive for improving combustion characteristics. In this study, the burning characteristics of ADCA/AN/CuO mixtures were investigated.

2. Experimental

2.1 Samples

Figure 1 gives the structural formula of ADCA. After drying ADCA (75-150 μm particle size) and AN (75-149 μm particle size) separately, they were mixed in stoichiometric ratio (ADCA : AN= 26.6 % : 73.4 %). Then, with the addition of 5, 10 or 20 % by weight of CuO to 100 % of ADCA/AN mixture, ADCA / AN / CuO mixtures were prepared by mixing with a rotational mixer. Meanwhile, prepared as to compare guanidine nitrate (GN) / strontium nitrate (SrN) / basic copper nitrate (BCN) mixture, which has been put to practical use.

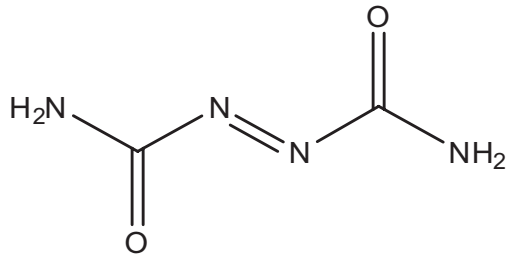

Figure 1 Chemical structure of azodicarbonamide (ADCA)

2.2 Chemical equilibrium calculation

Chemical equilibrium calculation was conducted to estimate adiabatic flame temperature and heat of explosion of the mixtures tested. For the calculation, chemical equilibrium calculation software (ICT-Thermodynamic code, Institut fr Chemische Technologie)[3] was used.

2.3 Linear burning rates test

About 4 g sample mixture was pressed at 190 MPa by a hydraulic press to prepare a pellet of approximately 14.7 mm in diameter. In addition, the surface of the pellet was coated with TSE 3941 silicone adhesive sealant (Momentive Performance Material), which was then dried, to achieve end-burning.

Placed in a closed chimney-type strand burner, the pellet, whose coated sealant at its top surface was peeled off beforehand, was tested at an initial temperature of 298 K under nitrogen, with an initial gauge pressure between 0.1-10 MPa. The mixture was ignited through heated nichrome wire, and based on the time taken to reach peak pressure from the onset of pressure-rise inside the burner, the linear burning rate was determined.

2.4 Rate-of-pressure-rise test

About 4 g pellet was set up in a closed chimney type strand burner under pressurized nitrogen with an initial gauge pressure of 2 MPa, and at an initial temperature of 298 K, the sample was ignited through heated nichrome wire. From the amount of pressure-rise in the vessel and the combustion duration, the rate of pressure rise ($\Delta P/\Delta t$) was determined.

2.5 Temperature history of the combustion wave

Each pellet (diameter : about 10.3 mm) was prepared by compressing about 1.0 g mixture at 400 MPa while embedding K-type (alumel-chromel) thermocouple (diameter : 50 μm). In addition, the surface of the pellet was coated with the above silicone adhesive sealant to achieve end-burning. The sample, set up in a closed chimney type strand burner, was tested under pressurized nitrogen at an initial gauge pressure of 2 MPa, and at an initial temperature of 298 K.

3. Results and Discussion

3.1 Chemical equilibrium calculation

Table 1 shows the results of chemical equilibrium calculation using the ICT program[3]. The result for GN/SrN/BCN mixture was also compared.

Table 1 Adiabatic flame temperature and heat of explosion.

Sample	Adiabatic flame temperature [K]	Heat of explosion [J·g^{-1}]
ADCA/AN	2543.7	3295.6
ADCA/AN/CuO 5%	2466.3	3096.0
ADCA/AN/CuO 10%	2405.9	2914.5
ADCA/AN/CuO 20%	2265.2	2596.8
GN/SrN/BCN	2366.0	2552.4

Increasing the amount of CuO, the adiabatic flame temperature was lowered but it was not possible to fulfill the 2200 K[4] under a desired value for CuO 20 % mixture.

As for the calculated heat of explosions for all mixtures, they have shown higher values than GN/SrN/BCN mixture. Furthermore, since they were lower than 3300 J·g^{-1} [4] that was suggested as a desired value as a gas generating agent, it is suggested that there is no problem with mixtures with regard to the heat of explosion.

3.2 Influence of CuO on the burning rate

3.2.1 Linear burning rates test

Figure 2 shows the results of log-log plot of P vs r for ADCA/AN based mixtures. Sustained burning was observed for stoichiometric ratio ADCA/AN mixture from a gauge pressure of 0.1 MPa. It was also shown that while the addition of CuO increased r, as compared to ADCA/AN mixture there was little difference in r with the change in the amount of CuO added. It was also shown that r increased with P in the closed chimney-type burner, obeying the Vieille's law, which is expressed with the following Equation (1).

$$r = aP^n \tag{1}$$

where r is the linear burning rate, P is the ambient pressure, a is the pre-exponential factor, and n is the pressure exponent of the burning rate. Table 2 gives the values of a and n determined from Figure 2. It was found that the addition of CuO increased the values of a while it generally decreased the values of n. This indicates also that r of the addition CuO by 10 % was higher than that of

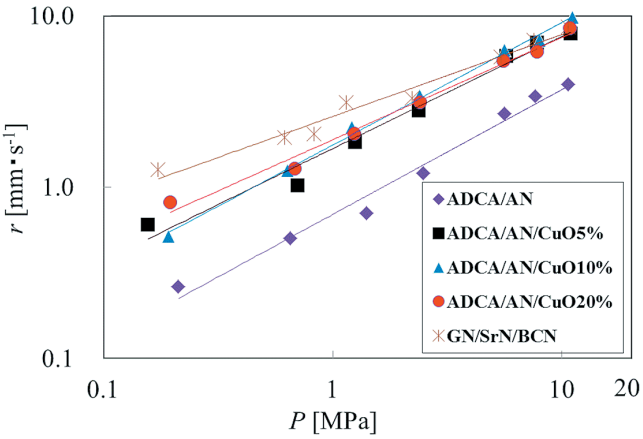

Figure 2 Linear burning rates for ADCA/AN based mixtures.

Table 2 Values of a and n of the Vieille's law for ADCA/AN based mixtures.

Sample	a [mm·s^{-1}·MPa^{-1}]	n [−]
ADCA/AN	0.70	0.73
ADCA/AN/CuO 5%	1.69	0.65
ADCA/AN/CuO 10%	1.78	0.72
ADCA/AN/CuO 20%	1.90	0.60
GN/SrN/BCN	2.59	0.48

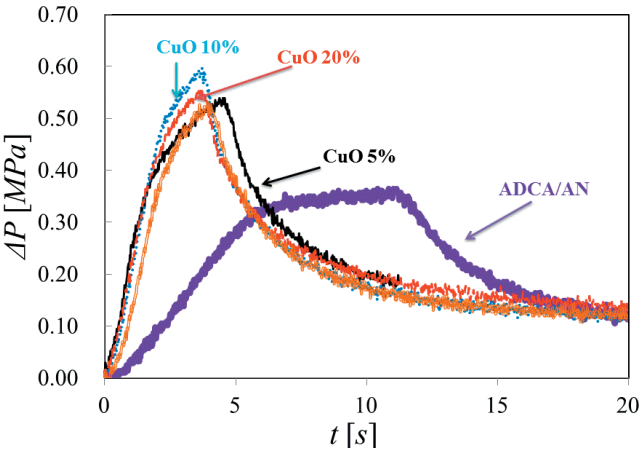

Figure 3 Pressure-time history of ADCA/AN based mixtures from rate-of-pressure-rise test.

Table 3 ΔP, Δt and $\Delta P/\Delta t$ of *ADCA/AN* based mixtures.

Sample	ΔP [MPa]	Δt [s]	$\Delta P/\Delta t$ [MPa·s^{-1}]
ADCA/AN	0.36	11.06	0.033
ADCA/AN/CuO 5%	0.54	4.38	0.123
ADCA/AN/CuO 10%	0.59	3.52	0.168
ADCA/AN/CuO 20%	0.56	3.68	0.152
GN/SrN/BCN	0.53	4.19	0.126

GN/SrN/BCN in high pressure.

3.2.2 Rate-of-pressure-rise test

Typical pressure history during rate-of-pressure-rise test is shown in Figure 3. ΔP, Δt and $\Delta P/\Delta t$ for each mixture is shown in Table 3. The data were compared with GN/SrN/BCN mixture. It was shown that $\Delta P/\Delta t$ of ADCA/AN/CuO 10 % and 20 % mixtures were higher than that of GN/SrN/BCN mixture, showing that ADCA/AN/CuO mixtures have the potential as gas generating agents.

3.2.3 Temperature history of the combustion wave

In order to investigate how the addition of CuO affects the combustion mechanism of ADCA/AN mixture, temperature history in the vicinity of the burning surface was measured, and the surface temperature (T_s) was determined through the temperature inflection point method by Sabadell et al[5]. The following Equation(2)[5] represents the temperature history at the solid phase.

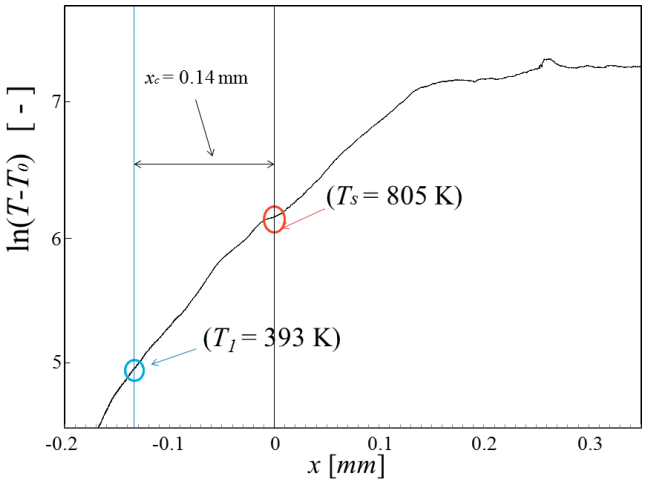

Figure 4 An example of ln(T-T_0)vs x curve for ADCA/AN mixture at 2 MPa.

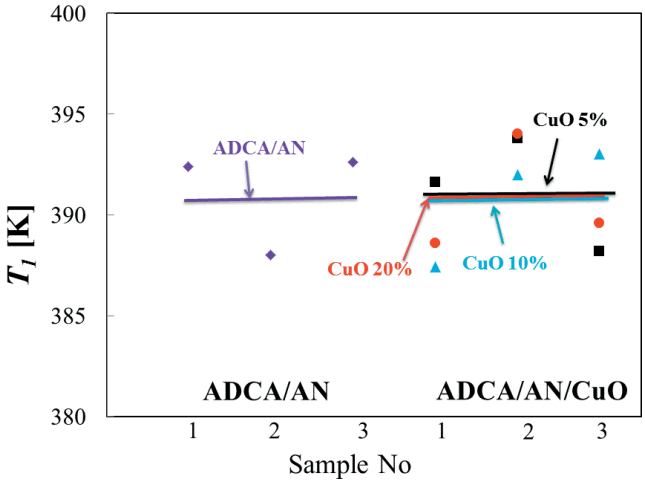

Figure 5 Onset temperature of the condensed phase for ADCA/AN based mixtures.

$$T - T_0 = (T_s - T_0)\, exp\left(\frac{c\rho r x}{\lambda}\right) \quad (2)$$

where T_0 is the initial temperature, λ is the thermal conductivity of the solid phase, ρ is the sample density, c is the specific heat of the solid phase, r is the burning rate, and x is the distance in the direction of the combustion. Figure 4 shows an example of the relationship between ln ($T-T_0$) and x, and Figure 5, 6 and 7 are the results of three types of measurements for each mixtures, where T_1 is of onset the temperature of the condensed phase, and x_c is the thickness of the condensed phase.

As shown in Figure 5, the onset of temperature of the condensed phase did not change. However, burning surface temperatures were lowered with the addition of CuO as compared to ADCA/AN mixture, as shown in Figure 6. In addition, burning surface temperature also became lower by increasing the amount of CuO.

Meanwhile, as shown in Figure 7, the thicknesses of the condensed phase for ADCA/AN/CuO mixtures were also smaller than those of ADCA/AN mixture. It is suggested that the addition of CuO accelerates the thermal decomposition reaction in the condensed phase reaction layer[1].

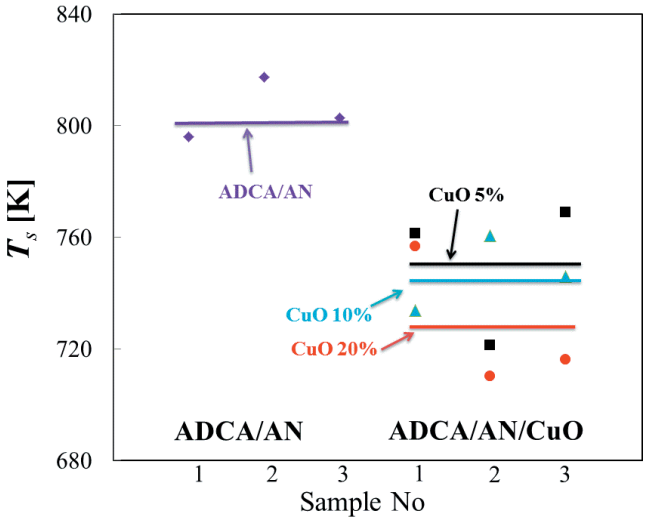

Figure 6 Burning surface temperature for ADCA/AN based mixtures.

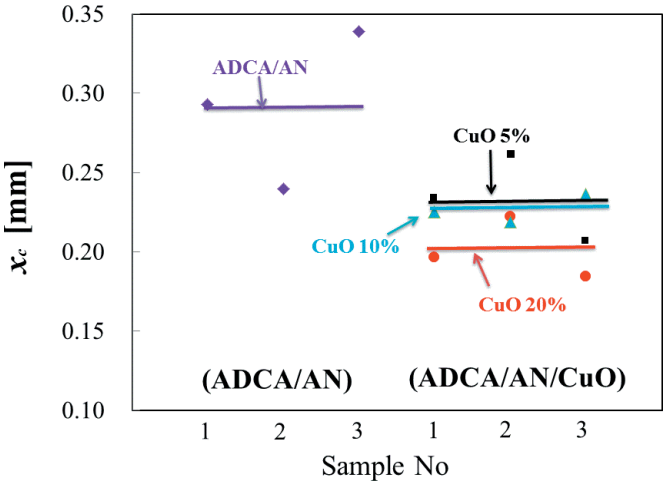

Figure 7 Thickness of condensed phase for ADCA/AN based mixtures.

4. Conclusions

From the above experimental studies, the conclusions were obtained as follows :

(1) Calculated adiabatic flame temperature for ADCA/AN /CuO 20% mixture was below that of GN/SrN/BCN mixture, indicating that it is a desired value, as well as the calculated heat of explosion, for ADCA/AN based mixtures.

(2) Stoichiometric ratio ADCA/AN mixture burned readily under gauge pressure of 0.1 MPa nitrogen atmosphere. Meanwhile, the addition of CuO increased the linear burning rate and reduced the pressure exponent of ADCA /AN mixture.

(3) ADCA/AN/CuO 10 parts and 20 parts mixtures has shown higher rate of pressure-rise than GN/SrN/BCN mixture.

(4) By adding CuO, the measured burning surface temperature became lower while the measured thicknesses of the condensed phase became smaller.

5. References

1) Y. Miyata, M. Abe, S. Date, M. Kohga, and K. Hasue, Sci. Tech. Energetic Materials, 69, 117−122 (2008).
2) Y. Wada, K. Hori, and M. Arai, Sci. Tech. Energetic Materials, 71, 83−86 (2010).
3) F. Volk and H. Bathlet, User's manual for the ICT-Thermodynamic Code (1988)
4) US Patent, US 69,58,100, Gas generating agent composition and gas generator employing the same (2005).
5) A. J. Sabadell, J. Wenograd, and M. Summerfield, AIAA Journal, 3, 1580−1584 (1965).

アゾジカルボンアミド／硝酸アンモニウム系混合物の燃焼特性について

池田謙*†，白石雄二*，伊達新吾*

硝酸アンモニウム（AN）は自動車エアバッグ用ガス発生剤の酸化剤として注目されている。本研究では，燃料として，工業的に発泡剤として多く使われているアゾジカルボンアミド（ADCA）を用いた。化学量論比でADCA / AN混合物を調整し，また，燃焼特性を高めるために，ANの分解触媒として知られている酸化銅（Ⅱ）（CuO）を加えた。化学平衡計算，線燃焼速度試験，圧力上昇速度試験，温度履歴試験を行い，実験結果から(1)～(4)の結論が得られた。(1)化学平衡計算から，CuO添加量の増加に伴い，断熱火炎温度は低下していき，爆発熱も同様の結果が得られた。(2)ADCA / AN混合物は1.0 MPa, N_2の雰囲気下でニクロム線の通電により，着火は容易であった。(3)CuOを添加することにより，線燃焼速度は増加し，圧力指数は減少した。また，CuO 10%及び20%添加の混合物においては，実用化されている硝酸グアニジン（GN）/硝酸ストロンチウム（SrN）/塩基性硝酸銅（BCN）混合物よりも圧力上昇速度が高くなった。(4)CuOの添加量を多くするに従い，燃焼表面温度が低下して凝縮相の厚さが減少し，凝縮相反応層において，CuOが反応を促進させていることが考えられた。

*防衛大学校応用科学群応用化学科　〒239-8686　神奈川県横須賀市走水1-10-20
Phone : 046-841-3810
†Corresponding author : em51043 @nda.ac.jp