Letter

Burning characteristics of some azodicarbonamide / ammonium nitrate / additive mixtures (II)

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Abstract

As a sequel to the previous study, the burning characteristics of azodicarbonamide (ADCA)/ammonium nitrate (AN) based mixtures were studied, where either MnO_2, Cu or basic copper nitrate (BCN) was selected as an additive in this study. From chemical equilibrium calculations, linear burning rate tests, and rate-of-pressure-rise tests, the following conclusions were obtained : (1) the calculated values of adiabatic flame temperature and heat of explosion of all ADCA/AN based mixtures were higher than those of guanidinium nitrate (GN)/strontium nitrate (SrN) /basic copper nitrate (BCN) mixture ; (2) ADCA/AN /MnO_2 mixture did not burn readily at or below 0.5 MPa N_2 atmosphere, showing relatively poor ignitability ; (3) the addition of Cu 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, exceeding that of GN/SrN/BCN mixture that used commercially, while in the case in which BCN was added, its rate-of-pressure-rise showed a close value.

Keywords : azodicarbonamide, ammonium nitrate, chemical equilibrium calculation, linear burning rate, rate-of-pressure-rise

1. Introduction

Recently, a number of researches and developments of new gas generating agents, using ammonium nitrate (AN) as an oxidizing agent, have been carried out[1)−4)]. 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) was used as an additive in the previous study[4)]. In this study, manganese dioxide (MnO_2), copper (Cu) or basic copper nitrate (BCN) was selected as an additive for improving combustion characteristics, and their burning characteristics were compared.

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 10% by weight of MnO_2, Cu or BCN to 100% of ADCA/AN mixture, the mixtures were prepared by mixing with a rotational mixer.

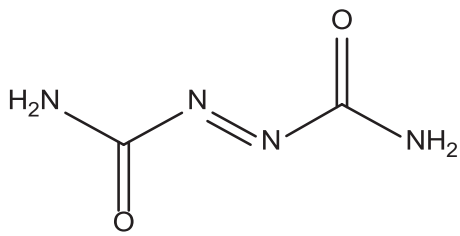

Figure 1 Chemical structure of azodicarbonamide (ADCA)

2.2 Chemical equilibrium calculation

The details of the procedures of the chemical equilibrium calculation could be found elsewhere[4)]. The results of calculated adiabatic flame temperature and heat of explosion of the mixtures were compared with those of

Table 1 Adiabatic flame temperature and heat of explosion for ADCA/AN based mixtures.

Sample	Adiabatic flame temperature [K]	Heat of explosion [J·g^{-1}]
ADCA/AN[4]	2543.7	3295.6
ADCA/AN/CuO[4]	2405.9	2914.5
ADCA/AN/MnO_2	2403.0	2933.9
ADCA/AN/Cu	2467.1	2996.5
ADCA/AN/BCN	2385.1	2868.9
GN/SrN/BCN[4]	2366.0	2552.4

ADCA/AN mixture, ADCA/AN/CuO 10% mixture and guanidine nitrate (GN)/strontium nitrate (SrN)/BCN mixture in the previous study[4].

2.3 Linear burning rates test

The details of the procedures of the linear burning rates test could be found elsewhere[4]. The results of linear burning rates (r) of the mixtures were compared with those of ADCA/AN mixture, ADCA/AN/CuO 10% mixture and GN/SrN/BCN mixture in the previous study[4].

2.4 Rate-of-pressure-rise test

The details of the procedures of the rate-of-pressure-rise test could be found elsewhere[4]. The results of rate-of-pressure-rise ($\Delta P/\Delta t$) of the mixtures were compared with those of ADCA/AN mixtures, ADCA/AN/CuO 10% mixture and GN/SrN/BCN mixture in the previous study[4].

3. Results and discussion

3.1 Chemical equilibrium calculation

Table 1 shows the results of chemical equilibrium calculation using the ICT Thermodynamic Code[5]. The results[4] for ADCA/AN mixture, ADCA/AN/CuO 10% mixture and GN/SrN/BCN mixture were also compared. The adiabatic flame temperature of all ADCA/AN/additive mixtures tested in this study were lower than ADCA/AN mixture, but they were higher than that of GN/SrN/BCN mixture, and it was not possible to reach below 2200 K[6] that was recommended as a desirable value. As for the calculated heat of explosions for all mixtures, they were lower than 3300 J·g^{-1} [4] that was suggested for a desired value as a gas generating agent, hence it is suggested that there is no problem with the ADCA/AN based mixtures with regard to the heat of explosion.

3.2 Influence of additives on the burning rate

3.2.1 Linear burning rates test

Figure 2 shows the results of log-log plot of P (the average absolute pressure) vs r for ADCA/AN based mixtures. Sustained burning was observed for almost all mixtures from an initial gauge pressure of 0.1 MPa, except for ADCA/AN/MnO_2 mixture which could not be ignited by heated nichrome wire at or below 0.5 MPa. It was also shown that while the addition of Cu, CuO or BCN increased r, as compared to ADCA/AN mixture there was a little difference in r with the other additives. 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).

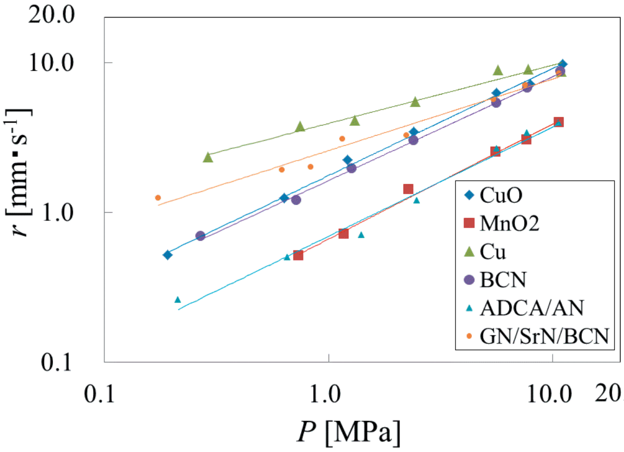

Figure 2 Linear burning rates for ADCA/AN based mixtures.

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[4]	0.70	0.73
ADCA/AN/CuO[4]	1.77	0.72
ADCA/AN/MnO_2	0.67	0.77
ADCA/AN/Cu	3.93	0.39
ADCA/AN/BCN	1.64	0.69
GN/SrN/BCN[4]	2.59	0.48

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

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 Cu and BCN increased the values of a while it generally reduced the values of n. This indicates also that r of the Cu-added mixture was higher than that of GN/SrN/BCN mixture.

3.2.2 Rate-of-pressure-rise test

Typical pressure history during the 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 those of GN/SrN/BCN mixture. It was shown that $\Delta P/\Delta t$ of ADCA/AN/CuO mixture and ADCA/AN/Cu mixture were higher than that of GN/SrN/BCN mixture, showing that both mixtures have the potential as gas generating agents. In the case of BCN-added mixture, $\Delta P/\Delta t$ was close to that of GN/SrN/BCN mixture.

4. Conclusions

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

(1) Calculated adiabatic flame temperature as well as the

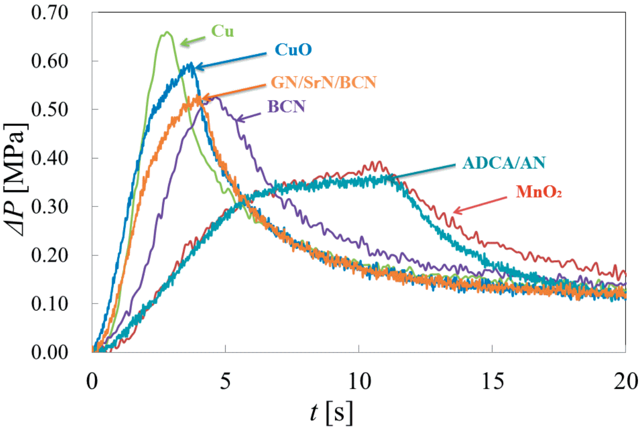

Figure 3 Pressure–time histories of ADCA/AN based mixtures from rate-of-pressure-rise tests.

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[4)]	0.36	11.06	0.033
ADCA/AN/CuO[4)]	0.59	3.52	0.168
ADCA/AN/MnO_2	0.40	11.27	0.035
ADCA/AN/Cu	0.67	2.80	0.239
ADCA/AN/BCN	0.54	4.60	0.118
GN/SrN/BCN[4)]	0.53	4.19	0.126

calculated heat of explosion for all ADCA/AN based mixtures were higher than those of GN/SrN/BCN mixture.

(2) Except for ADCA/AN/MnO_2mixture, all ADCA/AN based mixtures burned readily under 0.1 MPa nitrogen atmosphere. Meanwhile, the addition of Cu increased the linear burning rate and reduced the pressure exponent of ADCA/AN mixture.

(3) ADCA/AN/CuO mixture and ADCA/AN/Cu mixture have shown higher rate-of-pressure-rise than GN/SrN/BCN mixture.

5. References

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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（Ⅱ）

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本研究では，前回の続編として，アゾジカルボンアミド（ADCA）／硝酸アンモニウム（AN）混合物に，燃焼特性を高めるために，二酸化マンガン（MnO_2），銅（Cu），又は塩基性硝酸銅（BCN）を加えて，添加物の影響について検討した。化学平衡計算，線燃焼速度試験及び圧力上昇速度試験を行い，実験結果から（１）～（３）の結論が得られた。（１）化学平衡計算から，いずれのADCA/AN系混合物もGN/SrN/BCN混合物よりも断熱火炎温度が高くなり，爆発熱についても同様の結果が得られた。（２）ADCA/AN/MnO_2混合物は，0.5 MPa以下のN_2雰囲気下で着火ができず，比較的低い着火性であった。（３）Cu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，また，圧力上昇速度も高くなり，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一方，BCN添加の場合は近い値を示した。

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