Article

A study on the characteristics of azole-metal complexes (II)
– Thermal behaviors of 1H- tetrazole metal complexes –

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Abstract

1H-tetrazole (1HT) -metal complexes were investigated as promising gas generators for airbag inflators. The SC-DSC measurements, sensitivity tests, and deflagration tests were conducted to investigate the influences of the metals on the decomposition characteristics of the complexes. The SC-DSC measurements revealed the 1HT-metal interaction stabilize the complexes. Regarding the sensitivity tests, 1HT-metal complexes were categorized in the same class 6 of friction sensitivity test and class 3 of electrostatic sensitivity test. Besides, drop hammer sensitivity test, those complexes did not explode in this test; they were categorized as class 8 according to JIS. Furthermore, the deflagration test indicated the amount of metals in the substance had a substantial impact on burning rate, which was as verified by the relation of metal percentage and maximum pressure rate.

1. Introduction

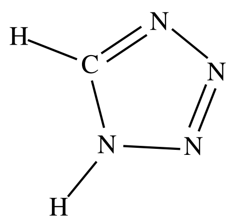
Energetic materials are employed as gas generators in airbags because they easily release a large amount of decomposition gas, inflate an airbag, and protect passengers during life-threatening accidents. Many researchers have been attracted in developing new energetic materials for gas generators because of their practical use.

The important properties for gas generators are as follows [1]: (1) Generate a large amount of decomposition gas in a short period, (2) No gas toxicity, (3) Low residue after decomposition, (4) High thermal stability, (5) Low sensitivity to physical stimulation such as mechanical impact, friction and static electricity, (6) Low cost, (8) No change in properties with time. This research focused on characterization of promising gas generators in terms of thermal stability, sensitivity to friction, impact, and static electricity. Besides, the gas generating performance was examined.

For the promising gas generators, high nitrogen contents are required from the standpoint of gas toxicity. If the substances with 100% nitrogen percentage, Nitrogen-Clusters, were available, they would give clean gases when they decomposed. However, Nitrogen-Clusters only exist in theoretical calculation. Generally, the higher nitrogen percentage it has, the more unstable it is; there are only a few energetic materials whose nitrogen percentage is more than 50%. Among those substances, tetrazole can not only give a large quantity of nitrogen gas but also have satisfactory stability [2)~4)]. Owing to high nitrogen content, they are used as gas generators.

In order to obtain better properties for gas generators, we have applied some chemical modifications to tetrazole; we have designed tetrazole-metal complexes [4]. Transition metals are commonly used to improve reaction rates for propellant because of their catalytic characteristics [5]. As a result, the response to stimuli becomes better.

Among myriad of tetrazole and transition metals, we chose 1H-Tetrazole (1HT) in this report which are the elementary structures of tetrazoles (see Fig. 1). Copper, Cobalt, Nickel and, Silver were selected because of their catalytic characteristics [4].



1H-tetrazole

Fig. 1 The structure of 1H-tetrazole (1HT).

2. Experiments

2.1 Samples

1HT (98% purity), $Cu(NO_3)_2$, $Co(NO_3)_2$, $Ni(NO_3)_2$, and, $AgNO_3$ were purchased from Wako Chemical, Japan. The 1HT-metal complexes were synthesized and analyzed according to the previous studies[6)–8)]: $[Cu(CN_4H)_2]\cdot 1.5H_2O$, $[Co(CN_4H)_3]\cdot 2H_2O$, $[Ni(CN_4H)_3]\cdot 3H_2O$ and, $[Ag(CHN_4)]$ were obtained.

In order to clarify the effects of coordination, the mixtures of each metal nitrate and 1HT were also prepared according to the metal-complex composition[9)].

2.2 SC-DSC

SC-DSC was carried out using DSC20 with the operation system STAR^e System (Mettler Toledo K.K.). In this study, stainless steel cells were selected as the high-pressure sample containers[10)]. The experiments were carried out at a heating rate of 10 Kmin^{-1} under a steady state flow of nitrogen (N_2). An almost constant sample mass of 1.0mg was weighed. They were heated in the scanning mode from 30℃ to 500℃. The temperature and heat flow calibrations were conducted by the recommended procedure using pure indium metal with a melting point of 429.6K and heat of fusion of ΔHf= 287.1 J g^{-1}.

The SC-DSC data on the recording chart were analyzed as follows:

(1) The line connecting the point before the exothermic reaction starts and the point after it ends was used as the baseline.

(2) The temperature at which exothermic reaction starts (T_{DSC}) is determined from the intersection of the tangential line at the inflection point and the baseline.

2.3 Sensitivity test

2.3.1 Electrostatic sensitivity test

An electrostatic sensitivity tester measured the sensitivity to static electricity. The apparatus in this study was designed by Mizushima et al[11)]. It equipped the upper and lower electrodes with fixed distance, which of electrodes connected to a set of condensers at predetermined capacitances. The sample was sandwiched between the two electrodes, and ignited by condenser discharge.

2.3.2 Friction sensitivity test

The Julius Peter friction tester (BAM) was used to determine the friction sensitivity of the metal complexes. The 1/6 explosion point was determined by rubbing the complexes on a moving plate with a fixed pin.

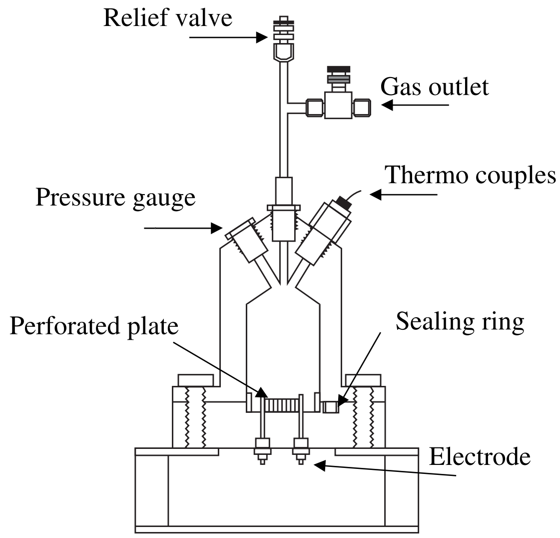


Fig. 2 The 52ml deflagration apparatus.

2.3.3 Drop hammer test

The sensitivity to mechanical impact was measured by the drop hammer test according to Japanese Industrial Standards (JIS). A drop hammer tester was made in Hosoya Firework. Co. Ltd. In the experiments, sample of approximately 0.03 gram was placed in a brass cup. The cup was placed in the device and the weight was dropped from a predetermined height. The tests were repeated following up and down method to determine 50 percent ignition energy.

2.4 Deflagration test

The 52ml deflagration test (see Fig. 2) was carried out to evaluate combustion characters of 1HT metal complexes. The test apparatus is a closed vessel equipped with a pressure transducer (PE-200kws), thermocouples, gas outlet and safety relief valve. The combination igniter of Ti/KNO_3 powder (100mg) as a primary ignition agent, and B/KNO_3 pellet (250mg) as a secondary ignition agent was used to ignite the 1HT-metal complexes. In this work, $KClO_4$ was using as an oxidizing agent.

All of samples in deflagration tests were prepared based on the stoichiometric composition and the zero of oxygen balance as equations (I) and (II):

$$CN_4H_2\ (1HT) + 0.75KClO_4 \rightarrow CO_2 + 2N_2 + H_2O + 0.75KCl \quad (I)$$

$$mMetal\ complex\ ([M(CN_4H_2)n] + nKClO_4 \rightarrow aCO_2 + bN_2 + cH_2O + dKCl + fmetal\ oxide \quad (II)$$

3 Results and discussion

3.1 SC-DSC

Figure 3 shows SC-DSC curves of 1HT-metal complex-

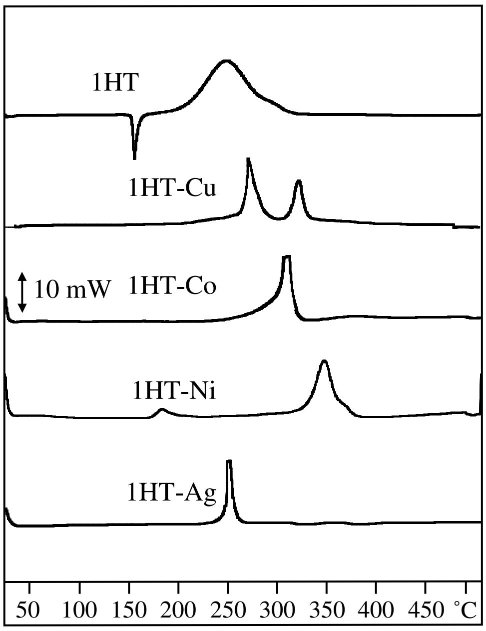


Fig. 3 SC-DSC curves for the 1HT-metal complexes.

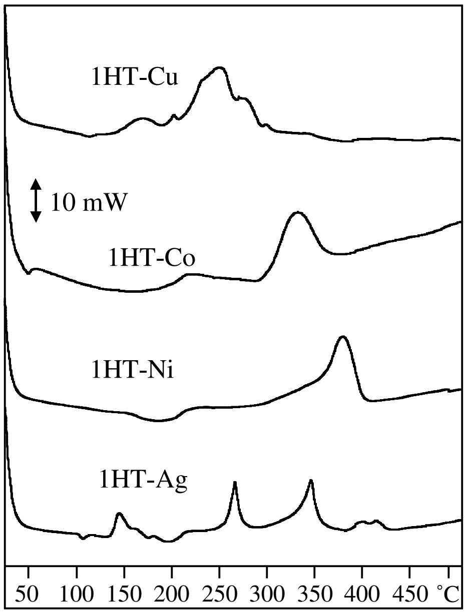


Fig.4 SC-DSC curves for the 1HT mixed with metal nitrates.

Table 1 T_{DSC} and Q_{DSC} of 1HT-metal complexes.

Sample	T_{DSC} (°C)	Q_{DSC} (J/g)	Q_{DSC} (kJ/mole)
1HT	209	3484	246
1HT-Cu	262	1840	186
1HT-Co	299	2094	211
1HT-Ni	329	1602	171
1HT-Ag	248	1130	200

es. The value of T_{DSC} and Q_{DSC} are summarized in Table 1. Before decomposition temperature, 1HT exhibited endothermic peak that corresponded to melting. In case of the complexes, the endothermic peak disappeared. The phenomena might be due to the change of their electronic state[4].

In the metal complexes, 1HT molecules are slightly ionic negatively because neighboring metal cations attract their electrons. Therefore, ionic 1HT molecules and metal link in complex via coulomb force strongly while neutral molecules link together via Van der Waals force in pure azole crystal. Since the Coulomb force is stronger than the Van der Waals force, metal complexes made it difficult to melt compared to 1HT molecular crystals.

Moreover, exothermic peak of complexes became sharp compared to the pure azoles. Figure 4 shows the exothermic behavior of 1HT-metal nitrate mixture. The difference between two types of samples suggested that coordination, i.e. metal-1HT interaction also accelerated exothermic reaction.

The value of acceleration of thermal decomposition (D_{DSC}) was calculated by differentiating the curves with respect to time (Fig. 5). The figure indicated nickel has

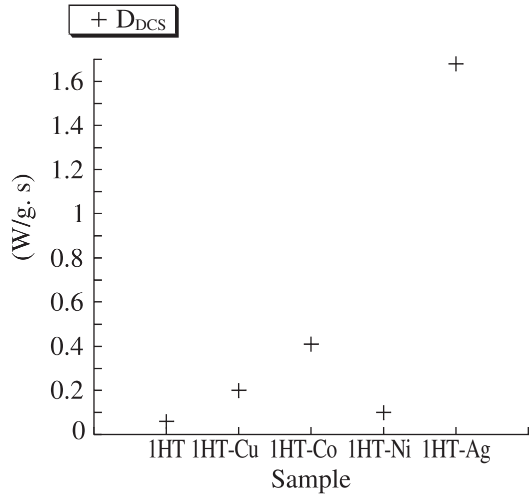


Fig. 5 D_{DSC} of 1HT-metal complexes.

less effect on accelerating reaction than other metals. On the other hand, silver provide good performance.

3.2 Sensitivity test

Table 2 summarized the results of the each sensitivity test. 1HT and 1HT-metal complexes were in the same class in its friction sensitivity and electrostatic sensivity tests, in which every sample explode at load 16-36N, class 6 and class 3, repectively.

The 50% explosion height (E_{50}) was determinded to be 26.92 cm or class 5 for 1HT. In the case of metal complexes, the tests were carried out 6 times at a hammer height setting of 50 cm. It means those complexes did not explode in this test; they were categorized as class 8 according to JIS.

Table 2 The sensitivity test results of 1HT metal complexes.

Sample	Electrostatic sensitivity (E_{50}/J)	Standard deviation (σ)	Drop hammer ($H_{1/6}$/cm)	Friction sensitivity ($M_{1/6}$/N)
1HT	0.14(class 3)	0.12	26.92 (class 5)	16~36 (class 6)
1HT-Cu	0.18(class 3)	0.23	>50 (class 8)	16~36 (class 6)
1HT-Ni	0.22(class 3)	0.37	>50 (class 8)	16~36 (class 6)
1HT-Co	0.21(class 3)	0.03	>50 (class 8)	16~36 (class 6)
1HT-Ag	0.07(class 3)	0.32	14.8(class 3)	16~36 (class 6)

3.3 Deflagration test

The results of the deflagration test of 1HT-metal complexes were shown in Fig. 6 and Table 3. As silver complexes, the sample for deflagration could not be prepared because it could not form the pellet. The deflagration behaviors of 1HT were changed by the coordination of 1HT to metal ions as well as thermal behavior, (dP/dt)max was largely increased; in particular, 1HT-Cu complex showed about twice the (dP/dt)max of 1HT.

It was considered that the burning rate actually improved with the appropriate mixing composition of catalysts and substances [5]. The appropriate amount of metal contains in 1HT-metal complexes allowed to improve burning rate. Since 1HT-Cu and 1HT-Co complexes contained much metal compared with 1HT-Ni complex, both burning rates of 1HT-Cu and 1HT-Co complexes were increased. However, the burning rate of 1HT-Ni decreased even though comparing with 1HT.

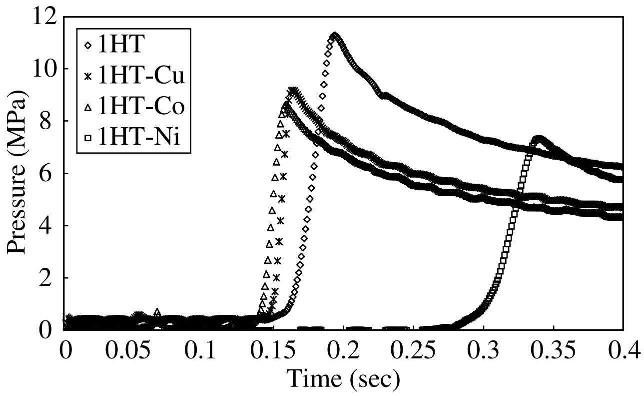


Fig. 6 The 52ml deflagration test result curves.

4. Conclusion

In this work, the experiment on SC-DSC and Deflagration test was conducted in order to investigate the influences of metal in azole complexes on decomposition characteristics. From this experiment, the following results can be concluded.

First, thermal stability of azole metal complexes improved because of 1HT-metal interaction.

Second, catalytic effects on enhancing D_{DSC} were clarified. This can be observed as steep exothermic peaks in SC-DSC graphs.

Third, 1HT-metal complexes were in the same class 6 of its friction sensitivity test and class 3 of its electrostatic test. In drop hammer sensitivity test, those complexes did not explode; they were categorized in class 8 according to JIS.

Finally, it was found that the amount of metal in the substance has a substantial impact on burning rate as verified by the relation of metal percentage and values of maximum pressure rate.

Acknowledgements

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Table 3 The deflagration test results of 1HT metal complexes.

Sample	Chemical formula	Pmax[MPa]	(dP/dT)max[MPa/s]	%metal in complex
1HT		11.3	437.7	
1HT-Cu	$[Cu(CN_4H)_2]\cdot 1.5H_2O$	9.2	729.9	27.8
1HT-Co	$[Co(CN_4H)_3]\cdot 2H_2O$	8.6	583.8	19.5
1HT-Ni	$[Ni(CN_4H)_3]\cdot 3H_2O$	7.3	222.7	18.4