Thermal behavior of various metal complex nitrates (IV)

−Ni complex nitrates−

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As a new gas generant, the thermal behavior of the Ni complex nitrates of carbohydrazide and aminoguanidine (hereafter, NiCDH and NiAG, respectively) was investigated when mixed with $Sr(NO_3)_2$ of the oxidizing agent.

The thermal stability of NiAG was higher than that of NiCDH based on the results in DTA. In both complexes, there was a slight difference in the heat of combustion and the burning temperature in a tube at the stoichiometric composition with $Sr(NO_3)_2$. However, for the burning rate in a tube, the NiCDH system was two times as fast as the NiAG system. The burning rate for the NiAG system was almost equal to one for the MgCDH system[7] when the CDH was coordinated to Mg. A non-stoichiometric NiO ($Ni^{2+}_{1-x}Ni^{3+}_{2x}O$) produced during the decomposition of the Ni complex was assumed to be the catalyst in the oxidation-reduction reaction during the combustion.

For the evolved gases, N_2 and CO_2 account for about 99 percent of all evolved gases in both complex mixtures. In the NiAG system, the evolution amount of HCN gas was very slight (10^{-1} mol /mol-complex), and the amount of CO gas was also slight (10^{-2} mol /mol-complex).

1. Introduction

Recently, automobiles sold in Japan are equipped with an airbag system for safer driving. A non-azide gas generant as a substitute for sodium azide has been studied, and tetrazole derivatives[1], urazole[2] and azodicarboamide[3] were the subjects of this study.

The authors evaluated the metal complexes of organic compounds, which are composed of many nitrogen atoms, as the new gas generant. In previous reports[1]-[12], the thermal decomposition behavior of metal complexes of carbohydrazide was investigated.

In this report, the Ni complex nitrate of carbohydrazide and aminoguanidine ($Ni(NH_2NHCONHNH_2)_3(NO_3)_2$, $Ni(NHCNNH_2)_2(NO_3)_2$:

hereafter, NiCDH and NiAG, respectively) was synthesized, and the thermal behavior was investigated when mixed with $Sr(NO_3)_2$.

2. Experiment

2. 1 Reagents

NiCDH was synthesized based on the method by Ivanov et. al.[13]. NiAG was synthesized based on the synthesis method of CuAG previously reported. The Ni complex nitrate of amine[14] was slowly added to the AG nitrate in water in a 1 to 2 molar ratio at 65°C in a water bath. The solution was concentrated by evaporation. The obtained complexes were identified by elemental analysis and polarized light zeman atomic absorption spectrometry due to their insolubility in water.

The Sr nitrate oxidizing agent was Wako pure chemical reagent grade. Reagents screened to under 63 μ m were mixed for sixty minutes using splittable chopsticks on parchment paper. Five kinds of samples were prepared by mixing: a stoichiometric composition and two compositions each

Table 1 Compositions of mixtures (Ni complex/Sr(NO₃)₂

	Ni complex/Sr(NO₃)₂ (mol/mol)	(wt./wt.)	Oxygen balance (g/100 g)
	0.57/0.43	0.74/0.26	-10
	0.49/0.51	0.67/0.33	- 5
NiCDH	0.42/0.58	0.60/0.40	0
	0.35/0.65	0.54/0.46	+ 5
	0.29/0.71	0.47/0.53	+10
	0.65/0.35	0.74/0.26	-10
	0.57/0.43	0.68/0.32	- 5
NiAG	0.50/0.50	0.61/0.39	0
	0.43/0.57	0.54/0.46	+ 5
	0.37/0.63	0.48/0.52	+10

with positive and negative oxygen balances based on eq. 1. Table 1 shows these compositions.

$$5\,NiCDH + 7\,Sr(NO_3)_2$$
$$\rightarrow 5\,NiO + 7\,SrO + 42\,N_2 + 15\,CO_2 + 45\,H_2O \quad (1)$$
$$NiAG + Sr(NO_3)_2$$
$$\rightarrow NiO + SrO + 6\,N_2 + 2\,CO_2 + 6\,H_2O \quad (2)$$
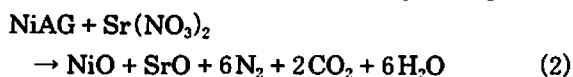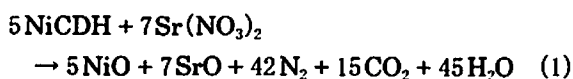
2. 2 Apparatus and method
2. 2. 1 Thermal analysis

The differential thermal analysis and the gravimetric analysis were carried out using a Rigaku TAS-200 Thermal Analyzer. The sample container was an alumina cell and the sample amount was 3 mg. The sample was heated to 800℃ at a heating rate of 20℃/min under Ar.

2. 2. 2 Combustion reactivity

The heat of the reaction was measured using a Shimadzu CA-4 Type Automatic Bomb Calorimeter in argon. The results of the investigation at ambient pressure showed a variation in the measured values of 3% to 4% over the pressure range of 1. 1 MPa to 3. 1 MPa. Also, there was no combustion at 0. 1 Mpa; therefore, the measurement was carried out at 1. 1 MPa.

The measurement of the burning rate was carried out under the following conditions. A preliminary investigation showed that the linear burning rate in the theoretical density range of 0. 65 to 0. 70 became small as the theoretical density became large, while the weight burning rate was independent of it. Also, when the diameter of the burning tube was 6 mm, the burning rate had a maximum value. Consequently, the sample was loaded at 0. 6 of the theoretical density in a 6 mm i.d. aluminum tube. The pressure dependence was measured over the pressure range of 0. 1 to 4. 1 MPa and the influence of the composition on the burning rate was investigated at 1. 1 MPa. The burning rate was determined by the time that was needed for the combustion wave to proceed 10 mm.

The burning temperature was also measured using the same theoretical density and tube diameter used for the measurement of the burning rate. A 0. 25 mm diameter W/Re thermocouple was vertically inserted into the burning tube against the combustion direction and was connected to a Yokogawahokusinn Analyzing Recorder.

The combustion residue was analyzed by X-ray diffraction using a Rigaku rotaflex RU-200.

2. 2. 3 The evolved gas

The evolved gases, produced when the heat of reaction was measured, were collected in a collection bag (Tedlar bag, 350 ml capacity). The amounts of N₂, CO, CO₂ and N₂O gases evolved were quantified using a Shimadzu GC-4C Gas Chromatograph (hereafter, GC). Table 2 shows the measurement conditions for the GC. The NO and NO₂ gases were

Table 2 Gas chromatograph conditions

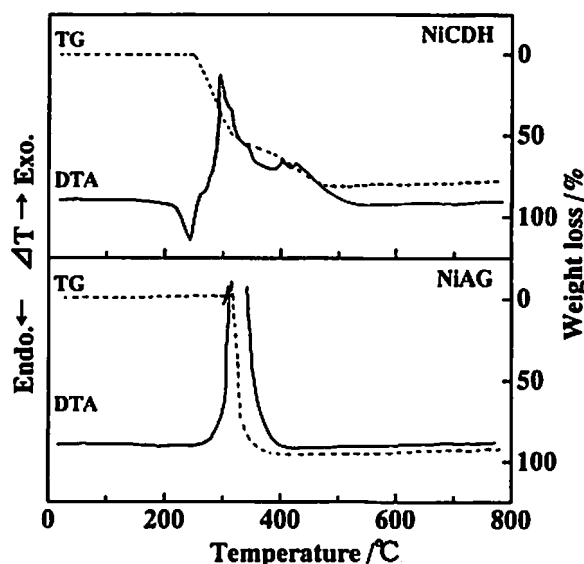| Gases	N₂, CO	N₂O, CO₂
Column	Molecular sieves 5A	Activated charcoal
Particle size	60～80 mesh	60～80 mesh
Length	2 m	1 m
Temp.	40℃	40℃
Carrier gas	He, 20 ml/min.	He, 60 ml/min.

Fig. 1 DTA-TG curves for the Ni complex nitrates

Fig. 2 DTA-TG curves for Ni complex mixtures

quantitatively analyzed using a Gastec gas detector tube. The NH_3 and N_2H_4 gases were quantified by the indophenol method[15] ($\lambda = 630$ nm) and the p-aminobenzaldehyde method[16] ($\lambda = 458$ nm), respectively.

3. Results and discussion

3. 1 Thermal analysis

Fig. 1 shows the results of the thermal analysis for NiCDH and NiAG. For NiCDH, the endothermic peak for melting was confirmed at 230℃; immediately after melting the NiCDH started to exothermally decompose. The decomposition reaction was complicated over a wide temperature range. The final residue was NiO, which was confirmed by powder X-ray diffraction and the final weight loss (83.5%, theoretical value: 84%). On the other hand, NiAG started to exothermally decompose at 270℃. The final weight loss was 95%, which was inconsistent with the calculated value for the NiO formation (83%). The sample was scattered due to the vigorous reaction. Comparing two Ni complex nitrates, the thermal stability of NiAG was larger than that of NiCDH based on the initial temperature of the exothermic decomposition. This might be caused by the fact[17] that the complex stability of the NiAG was higher than that of NiCDH: the NiAG is a four-coordinated planear structure, while NiCDH is a six-coordinated octahedron complex. For NiAG, however, the decomposition reaction
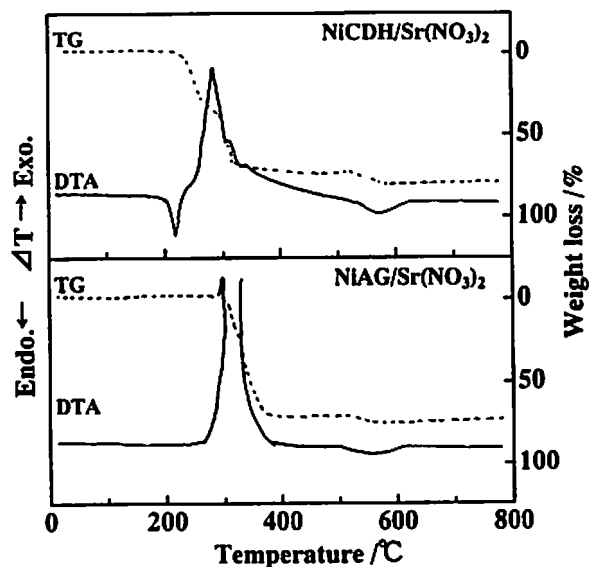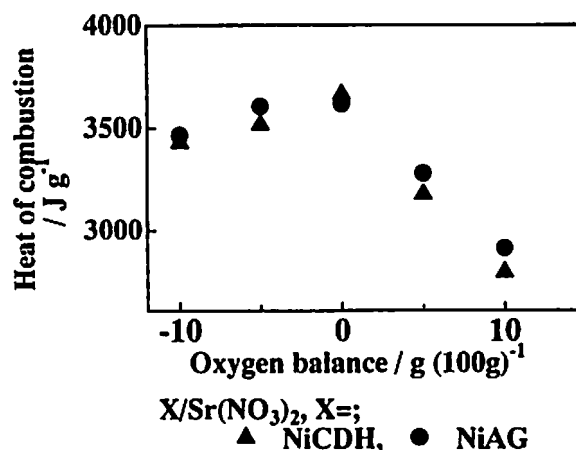

$X/Sr(NO_3)_2$, X=;
▲ NiCDH, ● NiAG

Fig. 3 Heat of combustion for mixtures

progressed acceleratedly, once started.

Fig. 2 shows the results of the thermal analysis for the mixtures with $Sr(NO_3)_2$ at the stoichiometric composition for both Ni complexes. There was a little difference in the apparent thermal behavior compared with that of only the complex (as seen in Fig. 1). The unreactive $Sr(NO_3)_2$ oxidizing agent was found to decompose at 560℃ in both systems. The unreacted $Sr(NO_3)_2$ for the NiAG system was a small amount compared to that for the NiCDH system, and the reactivity of NiAG with $Sr(NO_3)_2$ was expected to be higher than that of NiCDH with $Sr(NO_3)_2$

3. 2 Combustion reactivity

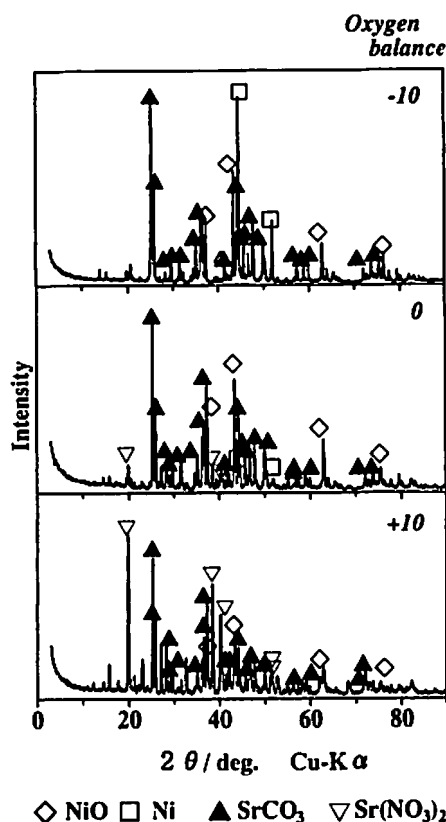Fig. 3 shows the composition dependence of the heat of reaction. The heat of combustion had a maxi-

Fig. 4 XRD patterns of the combustion residue for the NiCDH/Sr(NO₃)₂ mixtures

$\Diamond$ NiO $\Box$ Ni $\blacktriangle$ SrCO₃ $\triangledown$ Sr(NO₃)₂

$\blacktriangle$ SrCO₃, $\triangle$ Sr(NO₃)₂, $\Diamond$ NiO, $\Box$ Ni

Fig. 5 XRD pattern of the combustion residue at the for NiAG/Sr(NO₃)₂ mixtures (oxygen balance = 0)

X / Sr(NO₃)₂ X=,
$\blacktriangle$ NiCDH, $\bullet$ NiAG
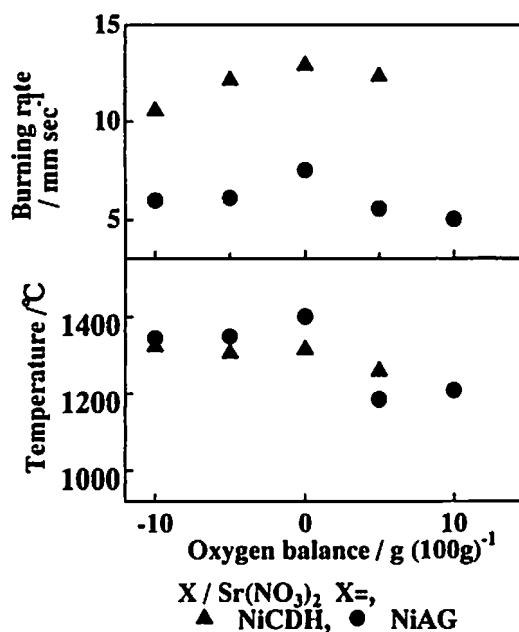
Fig. 6 Combustion characteristics for Ni complex/ Sr(NO₃)₂ mixtures

mum value at the stoichiometric composition in both systems, and their values were approximately equal. For the NiAG system, there was a slight difference in the calorific amounts at the stoichiometric composition and at -5 g/100 g of the oxygen balance.

Fig. 4 shows the XRD patterns of the combustion residue for the NiCDH systems. The XRD pattern of unreactive Sr(NO₃)₂ was confirmed at the stoichiometric composition. The XRD pattern of Ni was also confirmed in addition to that of NiO. A part of NiO, which was produced by the decomposition of NiCDH, was thought to act as an oxidizing agent. SrCO₃ was produced by the reaction of SrO and CO₂. Fig. 5 shows the XRD pattern of the combustion residue at the stoichiometric composition for the NiAG system. Unreactive Sr(NO₃)₂ was not confirmed in this system. However, the XRD pattern of Ni was also confirmed in addition to that of NiO, so the composition seemed to be not a stoichiometric but one at a slight positive oxygen balance.

Fig. 6 shows the composition dependence of the burning rate and the burning temperature. For the burning temperature, there was a slight difference
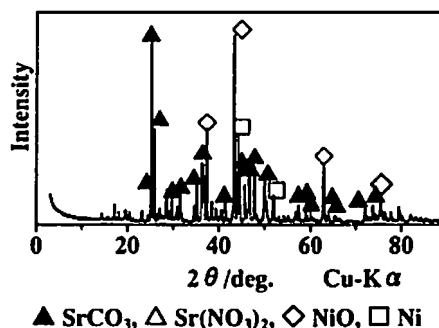
in the value level in both complex systems: NiCDH 1300℃, NiAG 1400℃. On the other hand, the burning rate of the NiCDH system was about two times as fast as that of the NiAG system.

Fig. 7 shows the pressure dependence of the burning rate in both systems, in which the results of the Mg complex of CDH (MgCDH, hereafter)[7] and the Cu complex of AG (CuAG, hereafter)[18] was also shown for comparison. The MgCDH has three CDH molecules coordinated to Mg, while the CuAG has two AG molecules coordinated to Cu. Table 3 listed the constants of the burning rate calculated based on the Vieille's equation $(V = aP^n)$ in all systems. When comparing the metal complexes with the same ligand coodinated, a slope of the obtained
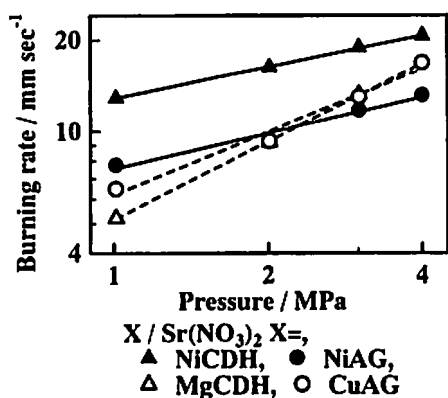
Fig. 7 Burning rate characteristics of the stoichiometric mixtures

X / Sr(NO₃)₂ X=,
▲ NiCDH, ● NiAG,
△ MgCDH, O CuAG

Table 3 Constants of the burning rate

X/Sr(NO₃)₂ X=;	a	N
NiCDH	1.285	0.344
NiAG	0.771	0.377
MgCDH	0.520	0.896
CuAG	0.618	0.722

lines for two kinds of the Ni complex was smaller than the ones for each complex in which the ligand, CDH or AG, was coordinated to the another metal. As also seen in Table 3, the pressure exponent "n" for the Ni complexes was smaller than those for the others, while the constant "a" was larger. This means that, in the case of the Ni complex, the reaction in the gas phase was more inactive compared with another metal complexes, while the reaction in the condensation phase was more active[19]. In addition, the burning rate in a tube in the NiCDH system was about two times as fast as that in the MgCDH system at 1.01 MPa. The burning rate in a tube is decided by some factors, such as the combustion reaction rate, the heat conductivity in the direction of the combustion, and so on. The difference between the Ni complex system and the others was the final metal oxide; NiO might be acting as a catalysis for the combustion reaction, in particular, of the reaction in the condensation phase. Though the metal Ni, which has high heat conductivity, was also produced during the decomposition of the Ni complex, it was thought that there was no influence on the burning rate. Note the data for the CuAG system in Fig. 7; not CuO but only Cu of high heat conductivity was produced[17].
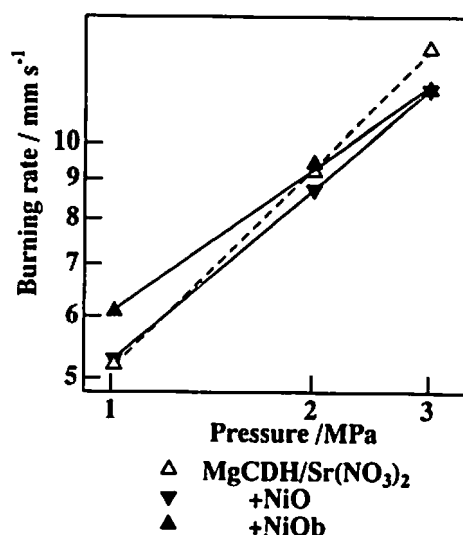

△ MgCDH/Sr(NO₃)₂
▼ +NiO
▲ +NiOb

Fig. 8 The addition effect of various NiO on the burning rate

Table 4 Constants of the burning rate

MgCDH/Sr(NO₃)₂/X, X=;	a	n
NiO	0.524	0.732
NiOb	0.618	0.620

For the difference in the burning rate of two kinds of Ni complexes, the following hypothesis could be proposed as a possibility. There was a difference in the produced NiO in the two kinds of Ni complexes. Fig. 8 shows the pressure dependence of the burning rate in the MgCDH/Sr(NO₃)₂ system with added NiO of Wako pure chemical reagent grade or one produced from Ni(OH)₂·6H₂O (NiOb, hereafter) in a ten percent rise of the weight ratio to the stoichiometric mixture. Table 4 lists the constants of the burning rate calculated based on Vieille's equation (V = aP^n). There was a slight difference in the slope of the line by the addition of NiO as seen in Fig. 8, while the decrease in the slope and the increase in the constant "a" was clearly confirmed by the addition of NiOb. It is suggested that the addition effect, the catalytic effect, varies according to the formation condition of NiO[20]. A non-stoichiometric NiO (Ni²⁺₁₋ₓNi³⁺₂ₓO) produced during some conditions has excess oxygen on the surface of the metal oxide. The infinitesimal addition and reduction of this might be involved as a catalyst in the oxidation-reduction reaction. For this, further

Table 5 The amount of the evolved gases

	NiCDH/Sr(NO₃)₂	NiAG/Sr(NO₃)₂
N_2	7. 24	5. 80
NH_3	1.02×10^3	3.11×10^4
N_2H_4	0. 0	0. 0
NO	2.93×10^{-2}	1.85×10^2
NO_2	4.26×10^{-3}	1.30×10^{-3}
N_2O	0. 0	0. 0
HCN	6.66×10^{-4}	4.63×10^{-4}
CO_2	1. 77	1. 36
CO	0. 13	1.85×10^2
N number	14. 48	11. 62
%	86. 4	96. 8
C number	1. 9	1. 38
%	63. 42	69. 0

investigation is needed.

3. Gas evolution behavior

Table 5 lists the analysis results of the evolved gases during the combustion. N_2 and CO_2 gases account for about 99 percent of all evolved gases. For NiAG, HCN, whose evolution was predicted by the C = N bond in the structure, evolved in the ratio of 10^{-4} mol per 1 mol of the complex. The evolved amount of this gas was about equal to that produced by NiCDH which was no -C = N bond in the structure. The evolution of CO gas in the NiAG system was a slight amount compared with that in the NiCDH system. The carbonyl bond in the structure might be responsible for the evolution of CO gas. The low mass balance of C molecules was due to the formation of $SrCO_3$ by the reaction of SrO and CO_2.

4. Conclusion

As a new gas generant, the Ni complex nitrates of carbohydrazide and aminoguanidine (hereafter, NiCDH and NiAG, respectively) were synthesized, and the thermal behavior was investigated when mixed with $Sr(NO_3)_2$ of the oxidizing agent.

The thermal stability of NiAG was higher than that of the NiCDH based on the results of differential thermal analysis; the initial temperature of the exothermic reaction was 250℃ in the NiCDH system and 270℃ in the NiAG sustem. The reactiv-

ity with $Sr(NO_3)_2$ of NiAG was also higher than that of the NiCDH under mild heating conditions.

The heat of combustion and the burning temperature in a tube was about same value level at the stoichiometric composition in both complex mixtures. For the burning rate in a tube, the NiCDH system was two times as fast as that not only in the NiAG system but also in the MgCDH system in which the CDH was coordinated to another metal, Mg. The pressure dependence of the burning rate in both Ni complex mixtures was smaller compared with that in another metal complex nitrate mixtures. Non-stoichiometric NiO ($Ni^{2+}_{1-x}Ni^{3+}_{2x}O$) might be produced during the decomposition of the Ni complex, and the infinitesimal addition and reduction of the excess oxygen in a non-stoichiometric NiO might be involved as a catalyst in the oxidation-reduction reaction.

N_2 and CO_2 gases account for about 99 percent of all evolved gases in both complex mixtures. In the NiAG system, the evolution amount of HCN gas was 10^{-4} mol per 1 mol of the complex, and was about equal to that in the NiCDH system which was no -C = N bond in the structure. The evolution of CO was also a slight amount.

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種々の金属錯体硝酸塩の熱的挙動（第４報）
—ニッケル錯体硝酸塩—

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新規ガス発生剤として，カルボノヒドラジド，アミノグアニジンのNi錯体硝酸塩(以後，各々NiCDH，NiAGと略)の熱的挙動が硝酸ストロンチウム混合系にて検討された。

2種類のNi錯体の熱安定性は，熱分析結果の比較から，NiAGの方が安定である。酸化剤混合系での反応熱(燃焼熱)，燃焼温度は，両錯体系で大きな差異は認められなかった。しかし，NiCDH系で得られた燃焼速度は，NiAG系だけでなく，同じくカルボノヒドラジドをMgに配位させたMgCDH錯体よりも，2倍近くの値を示した。Ni錯体の分解で生じる非化学量論組成のNiO($Ni^{2+}_{1-x}Ni^{3+}_{2x}O$)が燃焼反応時の酸化還元反応に触媒として作用する可能性が示唆された。

燃焼反応時の発生ガスは，いずれの錯体系においても，99%が窒素と二酸化炭素であった。NiAG系ではシアン化水素ガスの発生は極微量(10^{-4} mol/mol-complex)で，さらに一酸化炭素ガスの発生も少ない結果が得られた(10^{-2} mol/mol-complex)。

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