Reaction Mechanisms in Slow Cook-off Tests of GAP/AP Propellants

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Abstract

In order to evaluate the IMness, sub-scale slow cook-off (SCO) tests were conducted for GAP/AP propellant and also for HTPB/AP propellants. Steel tubes of 25mm inner-diameter were used for the confinements. The propellant mass of each test was 100g. In those tests the heating rate was set as 3.3°C/hr (6°F/hr) as specified in MIL-STD-2105. The reaction of the GAP/AP propellant occurred at 190-196°C, while that of HTPB/AP propellants occurred 211-233°C. The results were compared with the results of Deferential Scanning Calorimetry (DSC) and Accelerating Rate Calorimetry (ARC). The sample masses of the DSC and ARC measurements were around 0.5mg and 1g respectively. The SCO reaction temperature of the GAP/AP propellant was about the same as the DSC decomposition temperature, while that was somewhat higher than the ARC reaction temperature. The temperatures were also compared with those of energetic ingredients. Since the decomposition temperature of AP is much higher than that of GAP/AP SCO temperature, it is obvious that AP is not the major ingredient for initiating the SCO reaction of GAP/AP. Thus, the SCO reaction of GAP/AP propellant is initiated by the decomposition of GAP. According to the results of sub-scale SCO, it is considered that the reaction of GAP/AP propellants in SCO is much moderate than that of HTPB/AP propellants.

1 Introduction

Recent years insensitive munitions technology has been receiving great attention because of necessity to minimize the risk of loosing the munitions and other resources during the storage, transportation and operation. In the field of rocket motors, it is reported that the responses of rocket motors loaded with ammonium perchlorate (AP) and hydroxy-terminated polybutadiene (HTPB) binder will not pass the slow cook-off (SCO) tests[1) 2)]. Therefore, moderating the responses in SCO tests is one of the keys to achieving IMness for rocket motors.

NOF Corporation has been conducting fundamental research of Glycidyl Azide Polymer (GAP) and development of propellants that contain GAP as the binder for more than 20 years. Then it is verified that the technology of GAP propellants is mature enough for practical application[3)]. However, the behavior of GAP/AP propellants in SCO tests is not well understood.

The objectives of this study are to provide fundamental understandings of response in SCO tests of GAP/AP propellants.

2 Experimental

2.1 Formulations

The propellant formulations evaluated in this study are listed in the table 1. Two kinds of HTPB/AP propellants were also evaluated for comparison with GAP/AP propellant. Figure 1 shows the theoretical performances of the samples. NASA SP-273 chemical equilibrium code was used for the calculations. The maximum specific impulse (I_{sp}) of GAP/AP propellant obtained from the calculation is slightly lower than that of HTPB/AP propellants. However, the maximum I_{sp} of HTPB/AP propellant can't be practically obtained because of the processing constraint. Thus, practical I_{sp} of GAP/AP propellants is equivalent to that of HTPB/AP propellants.

Table 1. Formulations of the Samples

Sample	GAP*	HTPB*	AP	Fe_2O_3	CS**
G-1	20	-	80	1	2
H-1	-	13	87	-	1
H-2	-	13	87	1	1

* Includes curatives and plasticizers

** Combustion Stabilizer

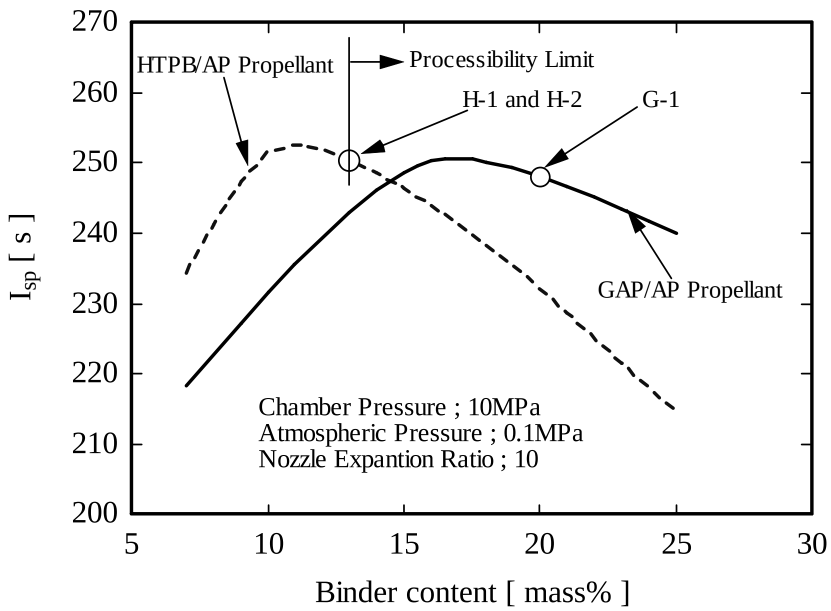

Figure 1. Theoretical Performance of the Samples

2.2 DSC

Differential Scanning Calorimetry (DSC) measurements for the samples listed in table 1 under various heating rates were conducted. The sample mass of each measurement was approximately 0.5mg. The heating rates were from 0.05 to 10°C/min. Then the decomposition temperatures under the condition of 3.3°C/hr (6°F/hr), which is the heating rate in SCO tests, were calculated. Also, the same measurements and calculations were conducted for neat GAP and AP.

2.3 ARC

Accelerated Rate Calorimeter (ARC) is a kind of adiabatic calorimeters which can detect exothermic reaction with heating rate of 0.02°C/min or over. Sample is heated with the heating rate of 0.02°C/min in step-wise manner. Once the exothermic event with heating rate more than 0.02°C/min is detected, the heating is stopped so the self-heating of the sample can be measured. The ARC test vessel is shown in Figure 2 and Photo 1. A 9 cm^3 sample bomb is placed in an insulated vessel of which the temperature is controlled.

Measurements for samples listed in table 1 were conducted. The sample mass of each measurement was approximately 0.5g. The temperatures under that the self-heating rate became 3.3°C/hr (6°F/hr) were calculated. Also, the same measurements and calculations were conducted for neat GAP and AP.

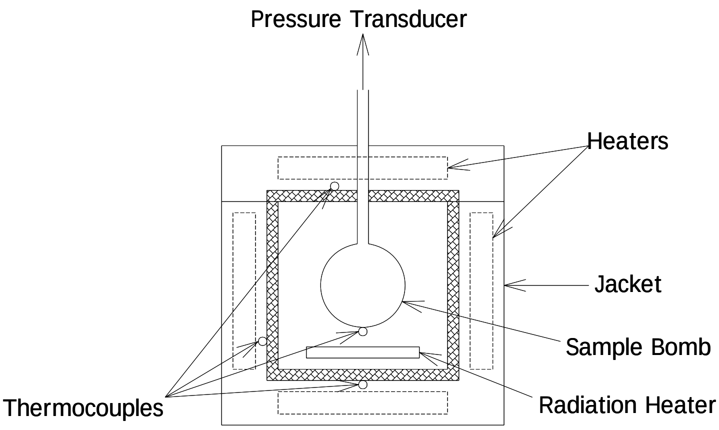

Figure 2. A Schematic of ARC Test Vessel

Photo 1-1. ARC Test Vessel

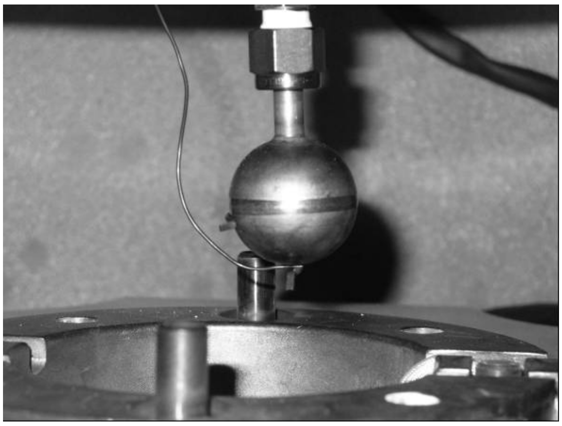

Photo 1-2. ARC Sample Bomb

2.4 Sub-scale SCO Tests

Sub-scale SCO tests for G-1, H-1 and H-2 were conducted. In those tests the heating rate was set as 3.3°C/hr (6°F/hr) as specified in MIL-STD-2105. The test vessel is shown in the figure 3 and photo 1. Propellant mass of each test was 100g. A steel tube with inner diameter of 25mm was used as the vessel. Both ends were sealed with aluminum shear plates that open when the internal pressure reaches 15 MPa, which is common maximum expected operational pressure (MEOP) of rocket motors. The vessel was heated with a tape heater wrapped around the vessel. Temperature was measured at three locations, center of the propellant (T1), interface between the propellant and the tube (T2) and outside the tube (T3). The electric current through the tape heater was controlled so that the heating rate at T3 was 3.3°C/hr (6°F/hr). The experimental setup of the sub-scale SCO tests was shown in figure 4. All the measurements were done in the control room. The temperature was recorded with the data recorder and the response was recorded with the DVD.

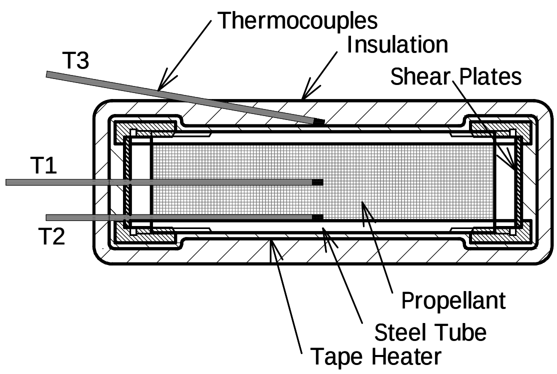

Figure 3. Schematic of Sub-scale SCO Test Vessel

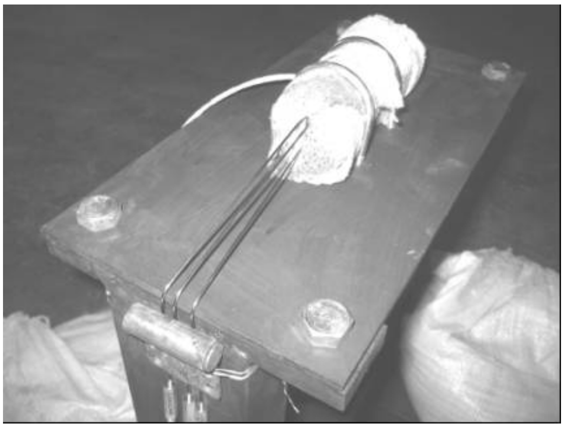

Photo 2. Sub-scale SCO Test Vessel

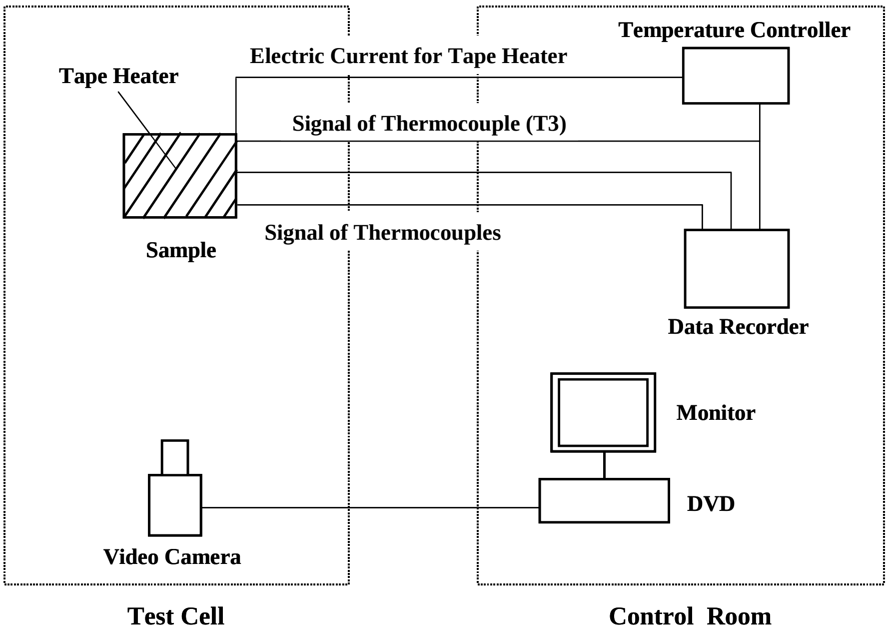

Figure 4. Experimental Setup of sub-scale SCO test

3 Results and Discussions

3.1 DSC

DSC results of G-1 in various heating rates were plotted in figure 5. The horizontal axis is the first substantial exothermic peak temperature (T_m) in reciprocal number, and the vertical axis is the heating rate (ϕ). From the results, the decomposition temperature in 3.3°C/hr (6°F/hr) was calculated. The same operations were conducted also for H-1, H-2, GAP and AP. The results were plotted in the figures 6 and 7. The T_m in 3.3°C/hr (6°F/hr) was listed in table 2. The T_m of G-1 was the similar to that of GAP itself. This indicates that the decomposition of G-1 in the heating rate of SCO was caused by the decomposition of GAP. Also it should be noted that the T_m of GAP/AP propellant or GAP itself was somewhat lower than that of HTPB/AP propellant or AP. The T_m of H-2 was close to that of G-1 rather than H-1. It is considered that the decomposition temperature was reduced by ferric oxide[4].

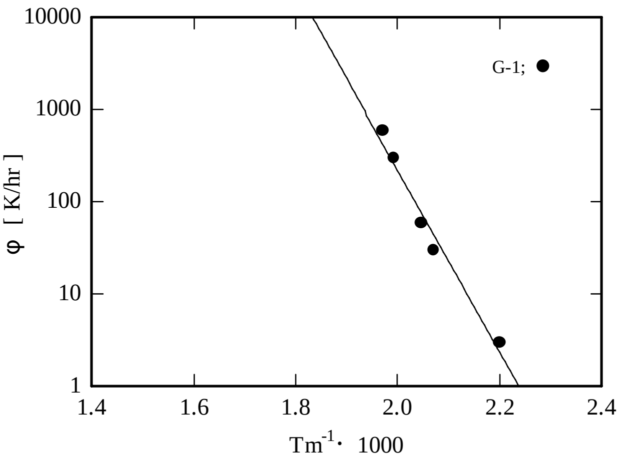

Figure 5. DSC Results of G-1

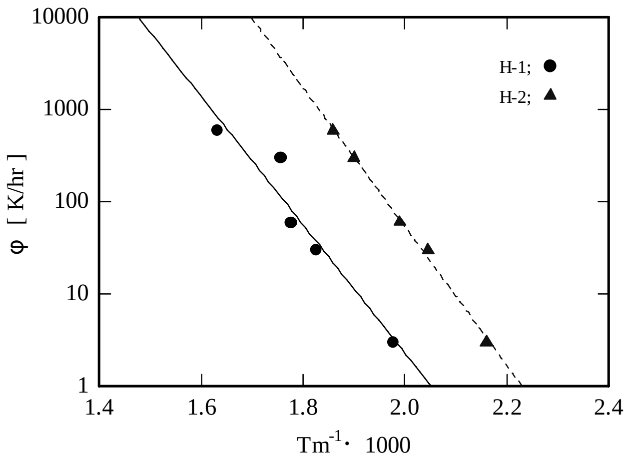

Figure 6. DSC Results of H-1 and H-2

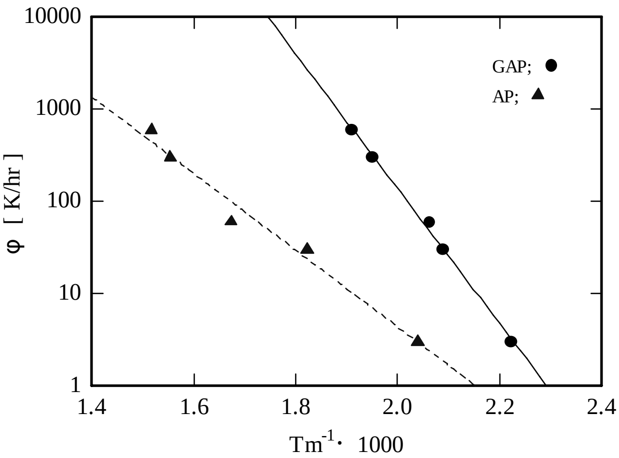

Figure 7. DSC Results of GAP and AP

Table 2. Summary of the DSC Results

Sample	First Exothermic Peak Temp., T_m (°C)
G-1	184.8
H-1	232.8
H-2	189.8
GAP	177.1
AP	220.1

3.2 ARC

Figure 8, 9 and 10 show the results of ARC measurements of G-1, H-1 and H-2 respectively. The horizontal axis is the temperature, and the vertical axis is the self-heating rate of the samples. In the case of GAP/AP propellant, the self-heating was detected in approximately 130°C. Then the self-heating rate drastically increased after 175°C. It shows that the runaway reaction occurred under the condition of 175°C or higher temperature. The self-heating was detected in similar temperature for HTPB/AP propellants. However, the profiles of the self-heating rate were different. The runaway reactions occurred in 300°C or higher temperature both in H-1 and H-2 measurements.

The temperatures under that the self-heating rate became 3.3°C/hr (6°F/hr) are listed in the table 3 as $T_{3.3}$. The $T_{3.3}$ of G-1 was equivalent to that of GAP itself. It indicates that the initial reaction of GAP propellant is promoted by the decomposition of GAP.

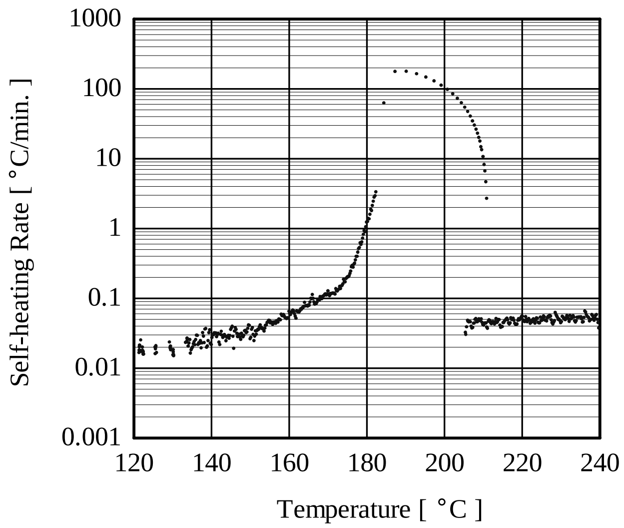

Figure 8. ARC Result of G-1

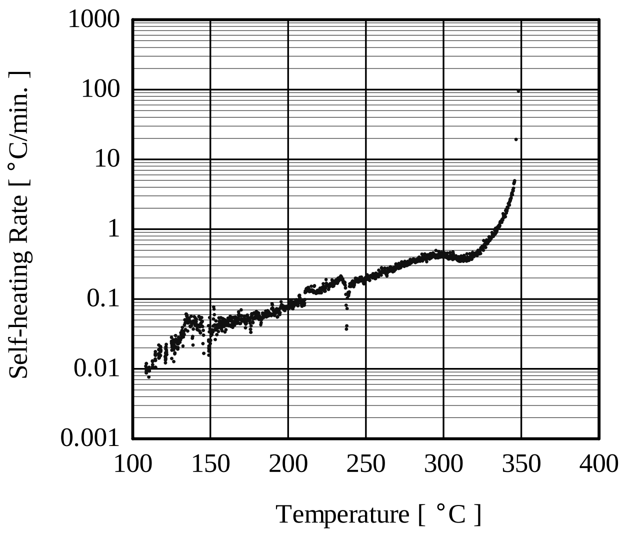

Figure 9. ARC Result of H-1

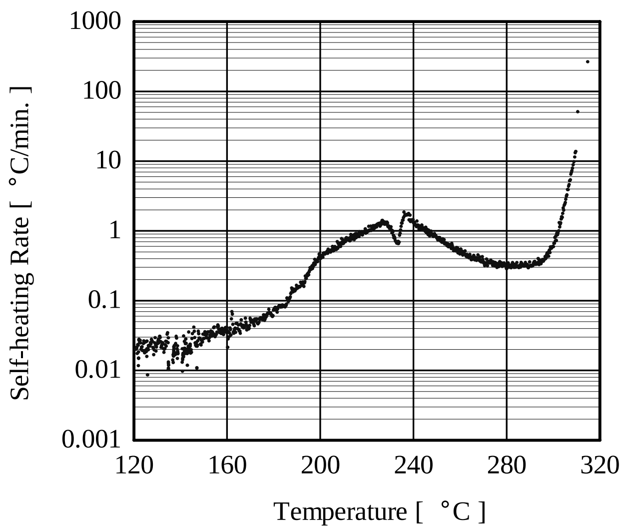

Figure 10. ARC Result of H-2

Table 3. Summary of the ARC Results

Sample	$T_{3.3}$ (°C)
G-1	160
H-1	185
H-2	175
GAP	161
AP	225

3.3 Sub-scale SCO Tests

Figure 11 shows the temperature trace of sub-scale SCO test for G-1. Two experiments were conducted for the same propellant formulation. The reactions occurred when the temperature in the middle of the propellant were 190 and 196°C.

The test vessel after the reaction is shown in photo 3. Only the shear plates opened, while the steel tube wasn't destroyed. It is considered that the responses will be ranked as IV if the classification is made following the criteria of MIL-STD-2105.

Figures 12 and 13 show the temperature traces of sub-scale SCO test for H-1 and H-2 respectively. The reaction temperature of H-1 was higher than that of G-1. Also the test vessels after the reaction are shown in photo 4 and 5. Not only the shear plates but also the steel tubes were destroyed. This indicates that the response of G-1 was more moderate than that of H-1 and H-2. Even though the reaction temperature of H-2 was close to that of G-1, the violence of the responses was different. It is considered that the responses of H-1 and H-2 will be ranked as III if the classification is made following the criteria of MIL-STD-2105.

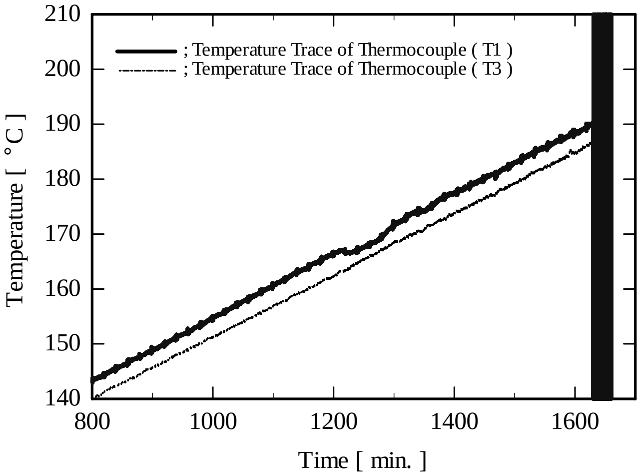

Figure 11. Temperature Trace of Test G-1

Photo 3. Test Vessel of G-1 after the Test

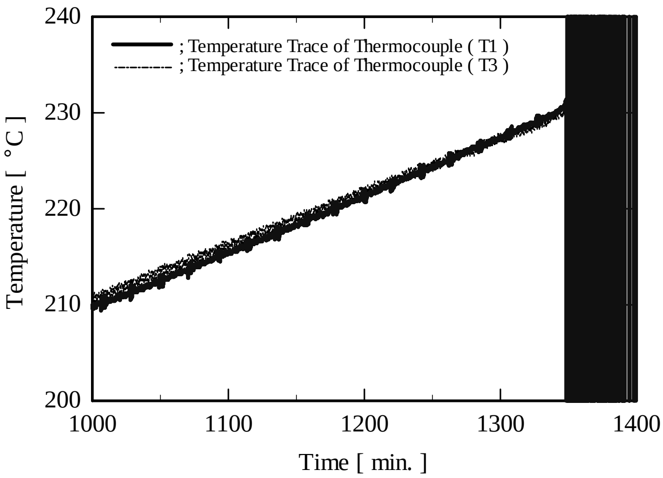

Figure 12. Temperature Trace of Test H-1 Test

Photo 4. Test Vessel of H-1 after the Test

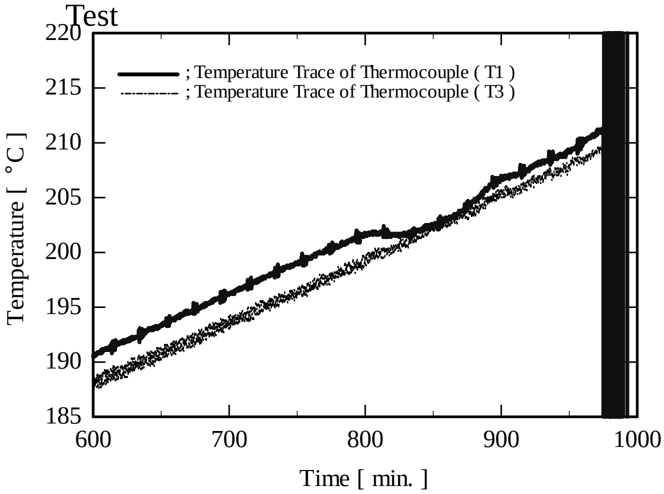

Figure 13. Temperature Trace of Test H-2

Photo 5. Test Vessel of H-2 after the Test

The results of the sub-scale SCO tests were summarized in table 3. The reaction temperature of G-1 in SCO was equivalent to the result of DSC, while it was somewhat different from the result of ARC. Therefore, it can be said that the reaction of G-1 in sub-scale SCO is caused by the decomposition of GAP. However, further analysis may be needed to explain the temperature difference between the SCO and ARC.

Table 3. Summary of the Sub-scale SCO Tests Results

Sample	Sub-scale SCO			DSC	ARC
	T1 (°C)	T2 (°C)	T3 (°C)	T_m (°C)	$T_{3.3}$ (°C)
G-1	190.1	190.1	186.6	184.8	160
	196.2	197.0	195.5		
H-1	231.4	230.7	229.6	232.8	185
	233.1	232.9	227.6		
H-2	211.2	212.2	209.0	189.8	175
	212.5	213.4	214.1		
GAP	-		-	177.1	161
AP	-		-	220.1	225

4 Conclusion

(1) Both DSC results and ARC results indicate that the reaction of GAP/AP propellants is initiated bye the decomposition of GAP. Also, it is considered that the reaction of GAP/AP propellant in sub-scale SCO is caused by the decomposition of GAP.

(2) The reaction temperature of GAP/AP propellant in sub-scale SCO was equivalent to the DSC results, but they were somewhat higher than the ARC results in the same heating rate.

(3) The reaction of GAP/AP propellants in SCO is more moderate than that of HTPB/AP propellants

if the sample size is 100g.

5 References

1) Comfort, T. F., Dillman, L. G., Hartman, K. O., Mangum, M. G., and Steckman, R. M., “Insensitive HTPE Propellants,” Proceedings of 1996 ADPA Insensitive Munitions Technology Symposium, March 1996.
2) Graham, K. J., Spear, G. N., Williams, E. M., Demay, S., and Smith, A., “Improved Slow Cookoff Response of HTPB Propellants,” Proceedings of 1998 ADPA Insensitive Munitions Technology Symposium, Nov. 1998.
3) Kato, K., Kobayashi, K., Seike, Y., Sakai, K., and Matsuzawa, Y., “Mechanical Properties of GAP Reduced Smoke Propellants,” AIAA Paper 96-3253, July 1996.
4) Price, E. W., and Sambamurthi, J. K., “Mechanism of Burning Rate Enhancement by Ferric Oxide,” Proceedings of 21st JANNAF Combustion Meeting, Oct. 1984.