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Control of LNG Pyrolysis and Application to Regenerative Cooling Rocket Engine

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1. Introduction

Rocket propellant has various requirements, such as higher specific impulse (Isp), large density, non-toxic, storablity, operational reliability and easy handling. In addition, large heat capacity of the fuel is also desirable. A regenerative cooling system is often adopted to cool a combustion chamber because of high combustion temperature (about 3000K), and high heat transfer rates from combustion gas. In the regenerative cooling system, the combustion chamber is a kind of a heat exchanger and fuel of a rocket engine is used as a coolant. The fuel heated in regenerative cooling passage is injected into the combustion chamber and burned. Heat loss from combustion gas to chamber wall is absorbed into the heat capacity of fuel and utilize them to propulsive work again. (regeneration).

Unfortunately, no propellant can satisfy all of those requirements. The requirements of higher Isp and larger thrust trade off each other. For example, Liquid hydrogen (LH_2) has high Isp and "clean" propellant. In addition, hydrogen has large heat capacity, and thus, is favorable coolant for regenerative cooling. However, the molecular weight of hydrogen is the lowest among the all of chemical compounds, thus, it is difficult to obtain larger thrust by using LH_2. For those reasons, LH_2 is suitable for an upper staged rocket engine, rather than an booster staged one. Another disadvantage of LH_2 is diffculity to handle because it is cryogenic fluid (20K at tank) and easy to leak from the tank.

The hydrocarbon fuels have been also widely used for rocket propulsion because they have advantages of non-toxic, lower cost, higher density and easier handling. RP-1 is the typical kerosene fuel for rocket propulsion, which was used for F-1 engien of Saturn 5. Kerosine can produce larger thrust than LH_2, although it has a drawback of lower Isp. Therefore, kerosene fuel is suitable for a booster staged rocket engine. If kerosene fuel would be employed to the regenerative cooling system, the combustion chamber has fuel flow passage within its wall. The regenerative cooling combustion chamber plays role of heat exchanger. The temperature of fuel increases to begin the thermal decomposition and cause soot formation in the regenerative cooling fuel passage. The soot in the fuel passage can clog the fuel flow and deteriorate the heat transfer from a chamber wall to fuel. Thus, the rocket engine designers must pay attention to coking of hydrocarbon fuel.

Liqufied Natural Gas (LNG) is one of the hydrocarbon fuel and its main component is CH_4. The volumetric fraction of CH_4 typically ranges from 85% to 95%. The rest of them are etane

and propane. The average molecular weight of LNG is about 16 g/mol, which is larger than hydrogen but much less than kerosene. Thus, the Isp of LNG propellant is greater than Kerosene. LNG can be stored in a tank at 110K and easier to handle than LH_2, though LNG is cryogenic fluid. However, the application of LNG propellant has not been realized so far. For the booster stage rocket, kerosene can produce greater thrust than LNG. For the upper stage, the Isp of LH_2 is superior to LNG.

Recently, LNG is reconsidered as the propellant for an interplanetary transfer vehicle or an booster rocket engine due to its low cost and easy handling (Brown, C.D. 2004 and Crocker, A. M. 1998). In such engine, the regenerative cooling system and a turbopump are necessary to improve its propulsive performance. As well as kerosene fuel, LNG pyrolysys can be also occurred in high temperature condition, which means that coking problem arise in the regenerative cooling with LNG. Few databases are available about LNG pyrolysis, because LNG propellant has not been utilized in the rocket engine until now. Therefore, such databases must be prepared for a successful development of this engine. For the turbopump, it feeds the propellant to combustion chamber with high pressure and is operated by various cycles, for example, gas generator cycle, staged combustion cycle and expander cycle. In the expander cycled rocket engine, turbopump is driven by the high temperature propellant gas. The propellant cooled the combustion chamber and receive the heat. The higher temperature and the lower molecular weight propellant is, the larger turbine power can be obtained. Therefore, the expander cycle have usually employ the LH_2, however, LNG also has the feasibility for the expander cycled turbopump(Brown, C.D. 2004 and Crocker, A. M. 1998). the efficient heat exchange in cooling passage is one of the most important factors to establish the expander cycled rocket engines. It is necessary to control the LNG pyrolysis in the high temperature environment.

For successful development of LNG rocket engine with regenerative cooling, the fundamental characteristics of LNG pyrolysis must be cleared. The present study focused on 1) the temeperature to begin CH_4 pyrolysis, 2) the catalytic effect of combustion chamber materials, 3) the effects of addition of propane to CH_4. At same time, numerical analyses are conducted to simulate CH_4 and CH_4-propane mixture. Secondary, the authors proposed coking inhibition methods and experimentally evaluate it.
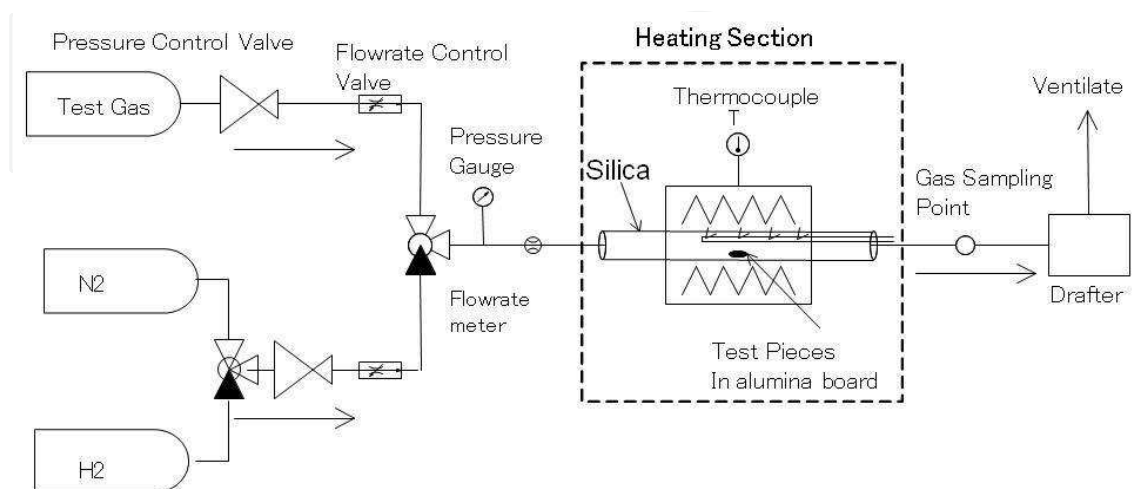

Fig. 1. Schematic of Test Apparatus.

Temperature	^{o}C	500, 700, 800 for Constant Temperature Heating	
		From 500 to 850 for Ascendant Heating	
Pressure	(MPa A)	0.20	
Flowrate	(ml/min)	20.0	
Test Duration		60 min for Constant temperature heating	
		40 min from 500 to 850 ^{o}C	
Test piece materials		Inconel 718, Inconel 600, A286	
Constituents of test piece materials		Inconel 718	Ni: 53.5%, Cr : 19%, Fe: 18%
		Inconel 600	Ni: 78%, Cr : 15%, Fe: 7%
		A286	Ni: 25%, Cr : 15%, Fe: 54.9%

Table 1. Test Conditions of CH_4 Heating Test.

2. Fundamental study on coking characteristics of LNG rocket engine chamber

2.1 Experimental study of CH_4 pyrolysis and catalytic effects of chamber material

To make clear the fundamental characteristics of methane pyrolysis, the authors conducted the experimental investigation. In the present section, we introduced the experimental results by Higashino, K. et. al. (Higashino, K. et. al. 2009A) The test apparatus shown in the Figure 1 is employed. The CH_4 gas (99.99% of purity) is supplied from the test gas bottle to silica glass tube, where is heated by the electronic furnace. The nitrogen gas can be also fed to gas flow passage to purge the CH_4 gas. The flowrates of those gases are controlled by using flowrate control valves and pressure control valves. To investigate its catalytic effects on pyrolysis reaction, 10 pieces of combustion chamber materials (10mm length x 5mm width x 0.5mm thickness) are placed into the alumina board, which are located in this tube. The materials of those test pieces are Inconel 718, Inconel 600 and A286. The formers of two are Nickel based alloy and have mechanical strength under high temperature condition. They were utilized for combustion chamber material, however, Nickel has the catalytic effects to accelerate the thermal decomposition of CH_4. On the other hand, A286 is Iron based alloy, but contains Ni of 25%. The details of test conditions and properties of those materials are summarized in Table.1. Prior to the test, the oxide film on the surface of the test pieces was hydrogenated at 500 ^{0}C because it can hamper accurate evaluation of the catalytic effects. The gas sampling point is located in the downstream of the heating section, where the test gas is sampled to investigate its chemical composition. The test gas was ventilated after diluting with the air at draft.

Two types of heating methods are employed, constant temperature heating and ascendant heating. In ascendant heating, temperature of the electronic furnace increases with time linearly. The existence of pyrolysis can be found by analyzing the sampled gas by using gas chromatograph with thermal conductivity detector. During the heating tests, gas sampling is conducted in every 5 minutes. The volume of the sampled gas is about 0.5 ml per one time. The progression of CH_4 pyrolysis is evaluated by the CH_4 conversion rate (%) as expressed in equation (1)

$$Conversion \ \ Rate \ \ = \left[1 - \frac{\left(A_{CH4} / \lambda_{CH4} \right)}{\left(A_{CH4} / \lambda_{CH4} \right) + \left(A_{H2} / \lambda_{H2} \right)} \right] \times 100 \tag{1}$$

where A and λ indicate the area shown in the gas chromatograph results and thermal conductivity, respectively. The subscripts of CH_4 and H_2 indicate CH_4 and hydrogen, respectively. For the gas chromatograph with thermal conductivity detector, volumetric fractions of chemical species can be A divided by λ.
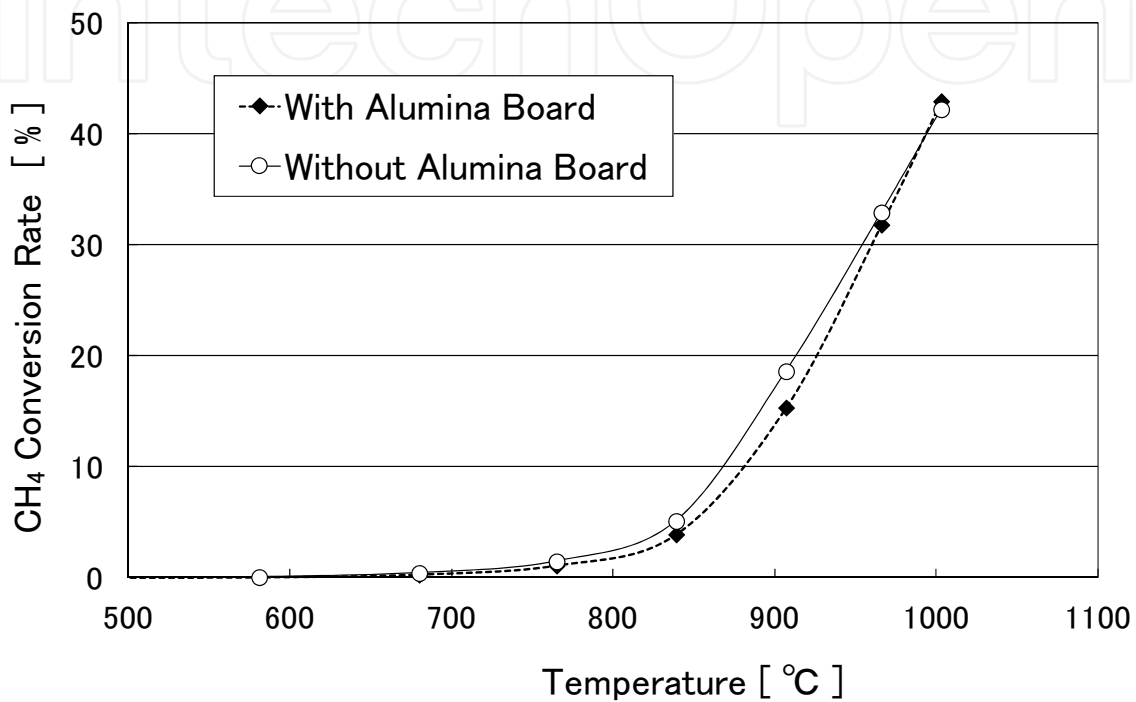
Fig. 2. Effects of Alumina Board on Methane and Propane Pyrolysis.
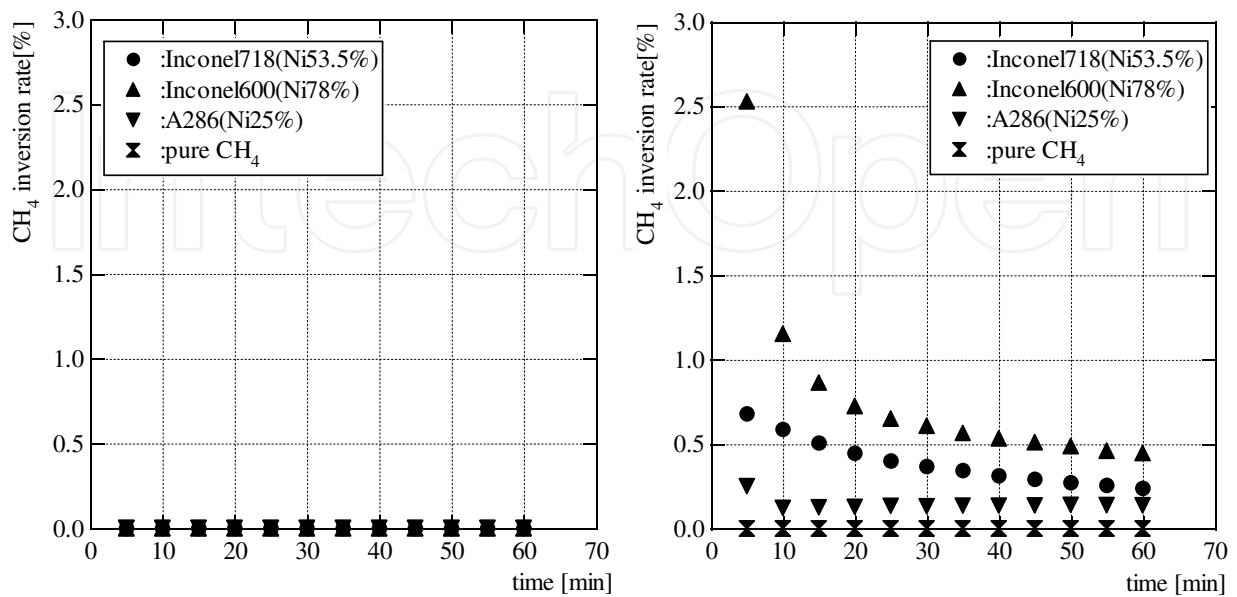
(a) Constant temperature heating at 500 °C   (b) Constant temperature heating at 700 °C
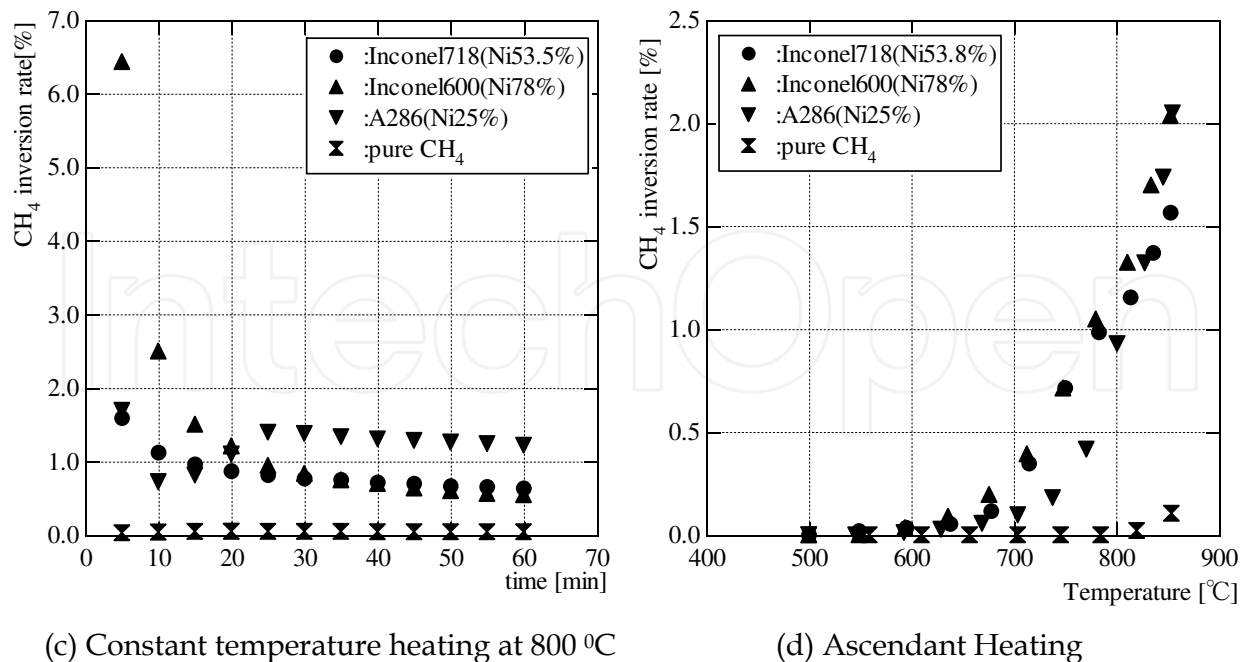
(c) Constant temperature heating at 800 °C   (d) Ascendant Heating

Fig. 3. CH$_4$ Conversion Rate for pure CH$_4$ Gas heating tests.

Before the present tests, it must be evaluated whether the alumina board has any catalytic effects. If this alumina board has the catalytic effects on CH$_4$ or C$_3$H$_8$ decomposition, it is very difficult to evaluate the accurate catalytic effect quantitatively. Figure 2 shows that time histories of methane conversion rates with pseudo LNG of 1 vol% C$_3$H$_8$ for ascendant heating tests. The pseudo LNG mean the gas mixture of CH$_4$ and C$_3$H$_8$. In the heating tube, there is no INCONEL 600 piece, but the test conditions with and without alumina board are conducted. CH$_4$ conversions on those two conditions are compared each other. Those two CH$_4$ conversion rate have no differences and it is clear that the present alumina board has no catalytic effect on the CH$_4$ and C$_3$H$_8$ pyrolysis.

Figure 3 shows the results of pure CH$_4$ gas heating test. Fig.3 (a), (b) and (c) are the results of constant temperature heating test at 500 °C, 700 °C and 800 °C, respectively. As shown Fig.3(a), CH$_4$ conversion rate are always equal to 0 at 500 °C as shown in Fig.3(a). This means CH$_4$ pyrolysis did not occurred at this temperature. However, CH$_4$ pyrolysis is admitted at 700 °C if any test pieces are placed in CH$_4$ gas and CH$_4$ conversion rate are greater in order of Inconel 600, Inconel 718 and A286 condition. The progression of CH$_4$ pyrolysis is proportional to the amounts of Ni in alloys, because Ni contents are 78%, 53.5% and 25% for Inconel 600, Inconel 718 and A286, respectively. This result indicates that Ni has the catalytic effect to promote this reaction. CH$_4$ conversion rate decrease with time for all of test pieces conditions. It is considered that the carbon deposits have adhered on the surface of test pieces and inhibit the catalytic effects. At 800 °C, the time histories of CH$_4$ conversion rate are very different from those at 700 °C, especially for A286 condition. For A286 condition, CH$_4$ conversion rate is decreased until 10 minutes, however, it turned to increase after that. A286 contains more Iron than Inconel 718 and Inconel 600. The carbon deposit on the A286 surface combined with Iron, if CH$_4$ pyrolysis proceeded. The carbon and Iron are combined to produce Iron carbide, which also has the catalytic effects. It is considered that it causes the tendency of A286 condition in Fig.2(c). The results of the ascendant temperature

heating test are shown in Fig.3(d). CH_4 pyrolysis begins at about 800 ^{0}C for no-test piece condition, while it does at 650 ^{0}C if any test pieces are placed in CH_4.

(a) Before Ascendant Heating   (b)After Ascendant Heating
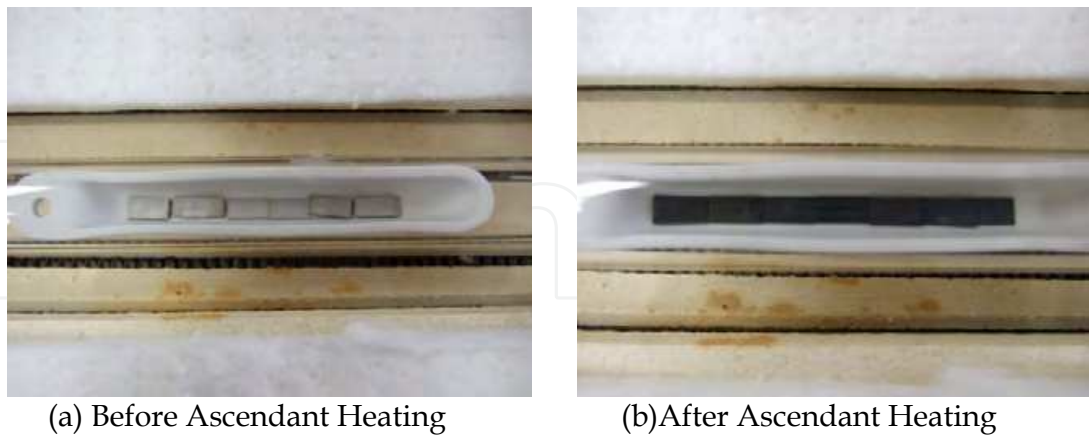
Fig. 4. Photographs of the Inconel 718 Test Pieces Before and After Ascendant Heating test

(a) Before Ascendant Heating Test

(b) After Ascendant Heating Test
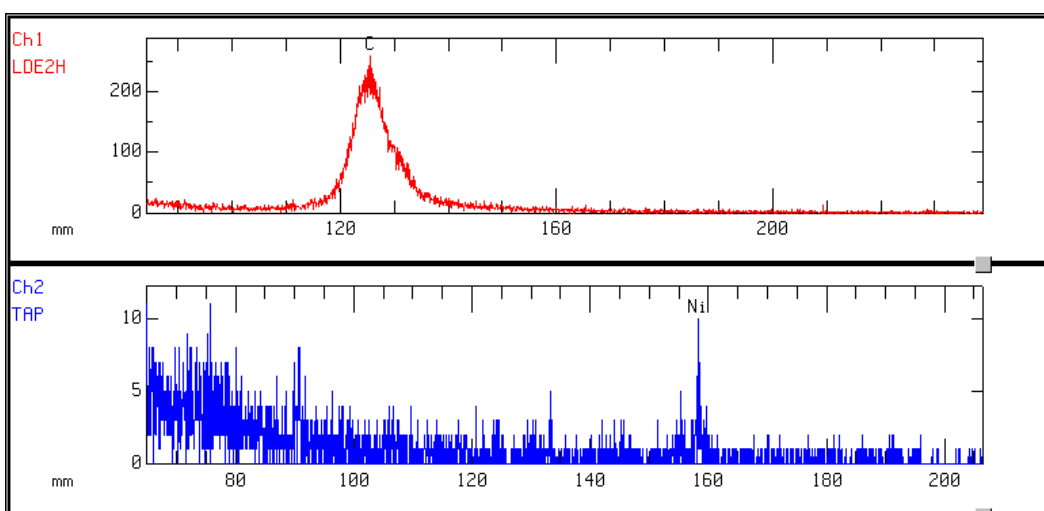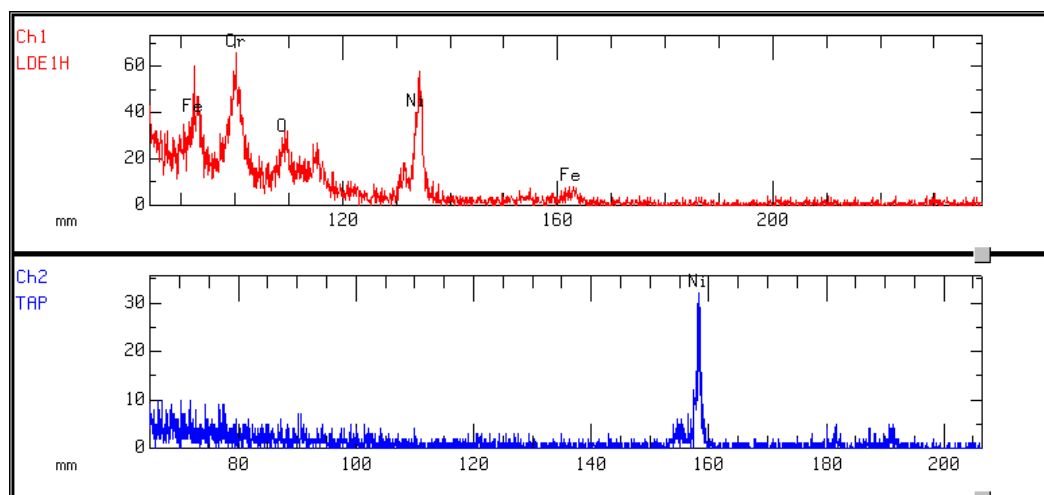
Fig. 5. Results of MPMA Analysis for test pieces in Ascendant Heating test.

Test Condition		Thickness of Carbon deposit films (μm)		
		Inconel 600	Inconel 718	A286
Constant temperature heating Test	700 ⁰C	2.0	—	—
	800 ⁰C	3.5	4.0	6.0
Ascendant Heating Test	up to 850 ⁰C	3.0	—	—

Table 2. Thicknesses of Carbon Deposit Films on the Surface of Test Pieces.

Figure 4 shows the photographs of Inconel 718 test pieces employed for the ascendant heating test. It is clearly observed that carbon deposit on the surface of the test pieces. EPMA analysis is conducted to investigate the chemical constituents of those depositions. Figure 5 shows the results of MPMA analysis for ascendant heating test. These results also indicate that carbon deposits on the surface of the test piece after this test. MPMA can evaluate the thickness of the carbon deposit film on the test piece surfaces, which are indicated in Table 2. In the case of Inconel 600, which has the maximum Ni constituent among these 3 materials, the carbon deposit films are measured in the constant temperature heating test (700 and 800 ⁰C) and the ascendant heating condition. The thickness of the carbon deposit film is 3.0μm at constant temperature heating condition of 800 ⁰C. However, that of A286 is 6.0 μm and the thickest among those 3 materials at same heating condition. Measuring the mass difference of test pieces before and after test, the total mass of carbon deposit is amount to 3.7mg which is equivalent to CH_4 of 4.933mg. The total mass of CH_4 gas fed on can be evaluated as 1.603 g from equation (2).

$$\dot{m}_{CH4} = \frac{PQt}{\left(\hat{R}/M_{CH4}\right)T} \tag{2}$$

where P, Q, $\hat{R}$ and M_{CH4} are pressure(=0.2MPa), volume flowrate(=20ml/min), Universal gas constant and molecular weight of CH_4. T and t are the temperature and test period. The ratio of thermal decomposed CH_4 to total amount of supplied CH_4 is 0.308 %.

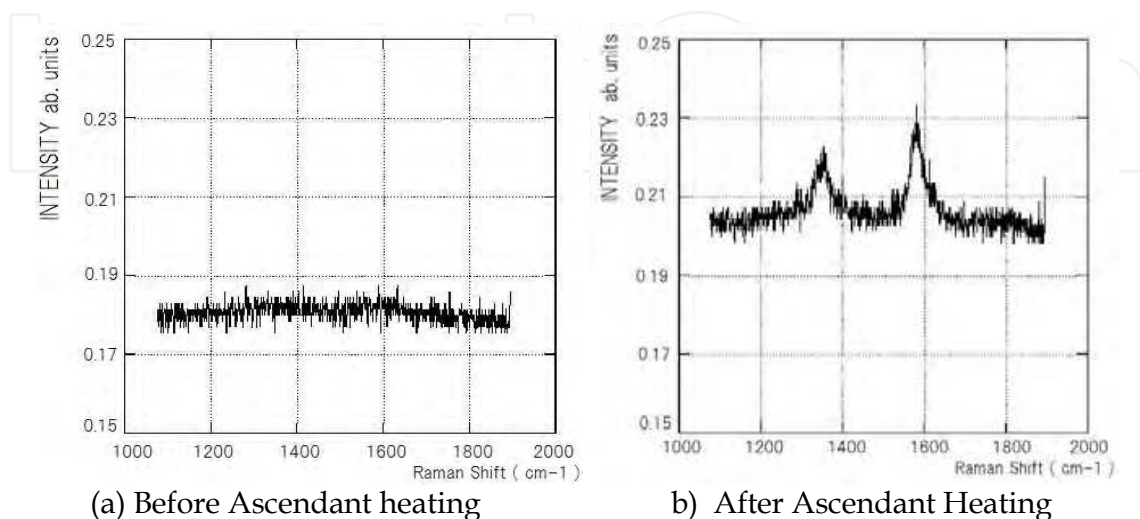(a) Before Ascendant heating   b) After Ascendant Heating

Fig. 6. Results of Raman Analysis of Inconel 718 for Ascendant Heating Test.

The crystal structures of carbon deposits on the test piece surface are investigated by Raman analysis. Figure 6 shows the results of Raman analysis of Inconel 718 test pieces before and after the ascendant heating test. The two peaks are appeared in the test pieces after heating and the right peak is more distinguished than the left one, which means the pyrolytic carbon is deposited [Yoshikawa, S. 1991]. If the left peak would be higher than the right one, amorphous carbon is deposited, in contrast. For other materials in ascendant heating condition, Raman analysis of Inconel 600 shows the same tendencies with Inconel 718, however, that of A286 indicates that the amorphous carbon was deposited. In the constant temperature heating conditions for those 3 materials, pyrolytic carbon is deposited in lower temperature heating and amorphous carbon in higher temperature. The amorphous carbons are appeared in higher than 700 ^{0}C for Inconel 718 and A286 and 800 ^{0}C for Inconel 600. The pyrolytic carbon is easier to peel off from the metallic surface than the amorphous carbon, thus, pyrolytic carbon must be careful for the design of a regenerative cooling engine. It is considered that the crystal of the pyrolytic carbon has a strong combination with a metal.
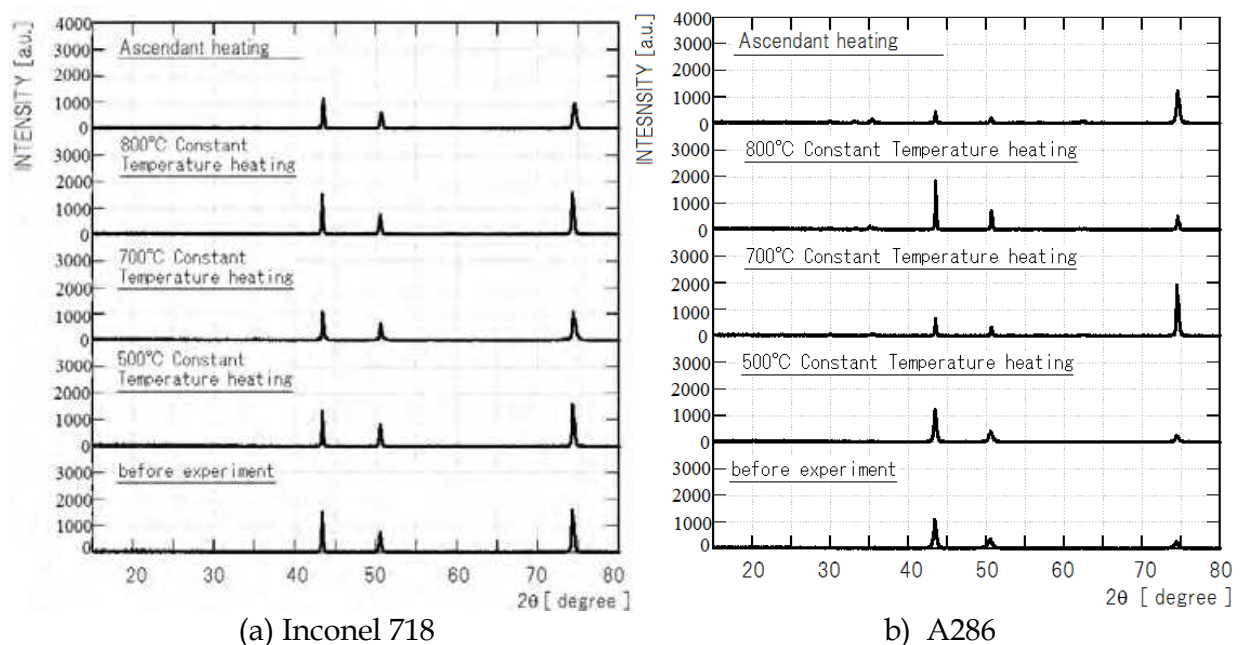

(a) Inconel 718   b) A286

Fig. 7. Results of XRD Analysis of Inconel 718 and A286.

The XRD analysis is also empolyed for these test pieces. XRD analyses can make clear the internal crystal structure of these metallic materials and prevail that the peaks for Inconel 718 do not change after heating test as shown in Figure 7. Those for Inconel 600 also do not change, however for A286, the peaks of XRD analysis are changed after the ascendant heating. This means that the Iron carbide is produced on the surface of A286 test pieces.

2.2 CH$_4$ – C$_3$H$_8$ mixture pyrolysis and catalytic effects

The main constituent of LNG is CH$_4$ and the others are C$_2$H$_6$, C$_3$H$_8$ and larger hydrocarbon molecule. Non-hydrocarbon constituents are N$_2$ or H$_2$S. The higher purity of CH$_4$ is, the more favourable propellant is. LNG from Alaska or Canada have higher purity of CH$_4$, however, those from South East Asia have 10 to 15 vol. % of C$_2$H$_6$ and C$_3$H$_8$, which may be used for a rocket propellant because of cost. C$_3$H$_8$ is known to be decomposed easier than

CH_4 and radical species like H atom, CH_3 and C_2H_5 are produced. The radical species can attack to CH_4 and promote its pyrolysis. The effects of those radical species are significant even if mole fraction of C_3H_8 is a few percent.

The chemical compositions of LNG are varied from the production area. Thus, in the present section, LNG is modelled by CH_4 and C_3H_8 mixture, which is call as pseudo-LNG in the present study. The details of test conditions are listed in Table 3. The test pieces materials are selected as Inconel 600, Haetelloy –X, SMC, OFMC and OMC. Hastelloy-X is one of the Ni-based alloy, as well as Inconel 600. SMC, OFMC and OMC are Copper based Alloys and included in the test pieces materials. Copper has high heat conductivity, thus, is also used for combustion chamber material. Test apparatus is same one shown in Fig.1. The results in this section are referred from Higashino, K. (Higashino, K. et. al 2009B)

To investigate the effects of C_3H_8 addition of CH_4, the ascendant heating test is conducted for pseudo-LNG, whose volumetric fraction of C_3H_8 is 1.0 %. In these tests, the catalytic effects are also experimentally evaluated. C_3H_8 molecules begin to decompose as well as CH_4, if test gas would be heated. The test gas is sampled and the volumetric fractions of the remained C_3H_8 are measured by the gas chromatograph. Figure 8 shows the C_3H_8 residual ratios, which means the ratio of the remained and the initial volumetric fractions of C_3H_8. If there is no test piece, C_3H_8 begin to decrease at 527 ^{0}C (800 K), which is about 300 ^{0}C lower than pure CH_4 pyrolysis without test piece.

Temperature (°C)	Isothermal	627, 727, 827
	Ascendant	From Room temperature to 1273
Pressure (MPaA)		From 0.14 to 0.20
Flowrate (ml/min)		20
Material of Test Pieces		SMC, OMC, Inconel 600, Hastelloy-X
Test Piece configuration		10mm L X 10mm W X 1 or 2 mm T
Test Duration	Isothermal	4800 sec
	Ascendant	15000 sec (max)
Volumetric Fraction of C_3H_8		1 , 3, 5 percent
Constituents of test piece materials	SMC	Cu: 99.13% Zr :0.8% Cr :0.7%
	OFMC	Cu: 99.99%
	OMC	Cu: 99.12% Zr :0.1% Cr :0.7%
	Inconel 600	Ni: 78% Cr : 15% Fe: 7%
	Hastelloy-X	Ni: 47% Cr : 22 % Fe: 19%

Table 3. List of Test Condition of Pseudo-LNG Heating Test.

If the test pieces of Inconel 600 or Hastelly-X are employed, C_3H_8 residual ratios begin to decrease at 377 ^{0}C. Thus, these materials have the catalytic effects to promote the C_3H_8 pyrolysis. On the other hand, tendency of C_3H_8 residual ratio with SMC test pieces are

almost same as that without test pieces. SMC does not have the catalytic effects. If the temperature is more than 727 ^{0}C, C_3H_8 residual ratios are less than 100 ppm, and too low to be detected by gas chromatograph.

The thicknesses of the carbon film on the test piece surface are measured by using the electron microscope and its results are shown in Figure 9. The heating condition of Fig.9 is the constant temperature heating of 727 ^{0}C. The thicknesses of the carbon film on SMC and OMC are less than 10 μm. On the other hands, the thicknesses of the carbon film on Inconel 600 and Hastelloy-X enlarge if the volumetric fraction of C_3H_8 is greater than 3.0 percent. Especially for Inconel 600, the thicknesses of the carbon film grows up to 442.3 mm at 5.0 volumetric percent of C_3H_8, while it is 2.4μm and 38.5μm at 1.0 and 3.0 vol.% of C_3H_8, respectively.
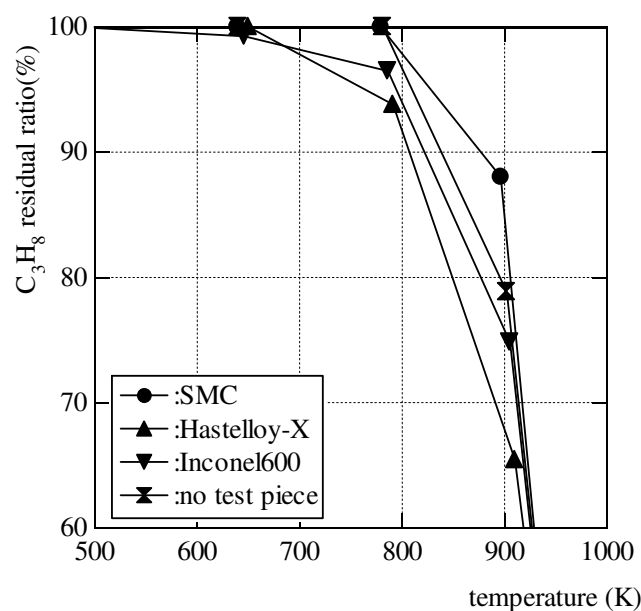
Fig. 8. C_3H_8 residual ratio of Pseudo LNG with C_3H_8 1.0 vol.% at the ascendant heating.
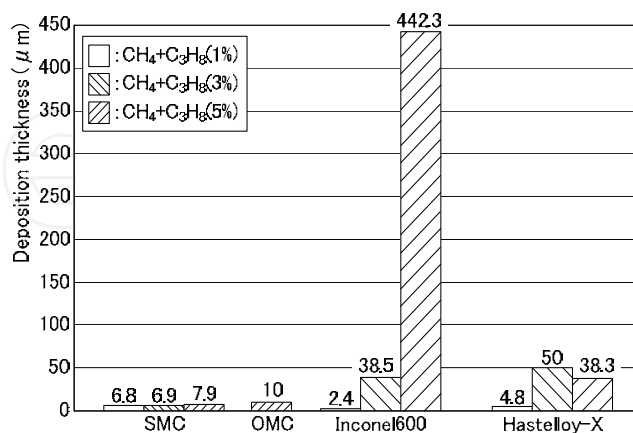
Fig. 9. Thickness of Carbon Films on Test Pieces for Constant temperature heating of 727 ^{0}C.

For Inconel 600 with C_3H_8 5.0 vol.%, the amounts of carbon deposited on the test pieces are measured by the electronic balance and evaluated as 78.2 mg. As well as equation (2) for pure CH_4, the total mass of pseudo LNG can be calculated as 2.324g by equation (3).

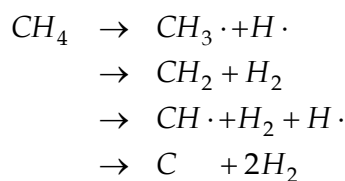$$\dot{m}_{\sup ply} = \frac{PQt}{\left(\hat{R}/\left[0.95M_{CH4} + 0.05M_{C3H8}\right]\right)T} \tag{3}$$

where those notations are same as equation(2), but the subscripts means the chemical species. The mass fraction of carbon atoms in pseudo LNG with C_3H_8 5.0 vol.% is given as equation (4).

$$\frac{\dot{m}_{C\ atom}}{\dot{m}_{\sup ply}} = \frac{0.95M_C + 0.05 \times 3 \times M_C}{0.95M_{CH4} + 0.05M_{C3H8}} \tag{4}$$
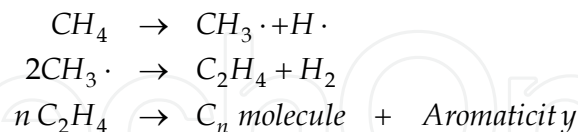
The mass of carbon atom in supplied pseudo LNG is calculated as 1.768 g and, then, the ratio of thermal decomposed gas to total supplied gas are about 4.4 %. In the previous section, the ratio of the decomposed CH_4 gas to total supplied gas are only 0.308 % at the constant temperature heating of 800 ^{0}C. This temperature is higher than the present test; however, higher ratio of pseudo LNG gas is thermally decomposed. The addition of C_3H_8 is very effective to promote the pyrolysis of CH_4 and C_3H_8.

2.3 Analytical model of CH_4 and C_3H_8 pyrolysis

The experimental results described in the previous section are theoretically investigated in the present section. The reaction model of CH_4 pyrolysis are considered as described by Ichikawa [Ichikawa 2001].
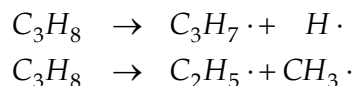
$$
\begin{aligned}
CH_4 \quad &\rightarrow \quad CH_3 \cdot + H \cdot \\
&\rightarrow \quad CH_2 + H_2 \\
&\rightarrow \quad CH \cdot + H_2 + H \cdot \\
&\rightarrow \quad C \quad + 2H_2
\end{aligned}
$$

However, if the catalytic effects are considerable, larger hydrocarbon molecules are produced.

$$
\begin{aligned}
CH_4 \quad &\rightarrow \quad CH_3 \cdot + H \cdot \\
2CH_3 \cdot \quad &\rightarrow \quad C_2H_4 + H_2 \\
n\,C_2H_4 \quad &\rightarrow \quad C_n \ molecule \quad + \quad Aromaticity
\end{aligned}
$$

where n is higher than 3 in C_n molecule.

On the other hand, if C_3H_8 is involved in the CH_4 pyrolysis, the reactions of CH_4 and C_3H_8 pyrolysis proceed as follow. C_3H_8 pyrolysis begins via the following reactions.

$$
\begin{aligned}
C_3H_8 \quad &\rightarrow \quad C_3H_7 \cdot + \quad H \cdot \\
C_3H_8 \quad &\rightarrow \quad C_2H_5 \cdot + CH_3 \cdot
\end{aligned}
$$

Those reactions can occur at the lower temperature than CH_4 pyrolysis. C_2H_5 radicals decompose further and produce H atom and C_2H_4.

$$C_2H_5 \cdot \quad \rightarrow \quad C_2H_4 + \quad H \cdot$$

H atom can attack to CH_4 to decompose it.

$$CH_4 + H \cdot \quad \rightarrow \quad CH_3 \cdot + H_2$$
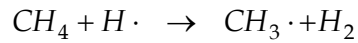
This reaction proceeds much faster than CH_4 solo pyrolysis. Thus, the addition of C_3H_8 to CH_4 can promote the CH_4 pyrolysis. Various reaction models have been proposed to simulate combustion of lighter hydrocarbon molecules like CH_4, C_2H_4, C_2H_6 and C_3H_8. Among them, GRI-Mech Ver.3.0 is one of the most widely employed model (Smith, G. P.). The authors developed the numerical code to simulate those experimental results by using the GRI-Mech. Ver.3.0.
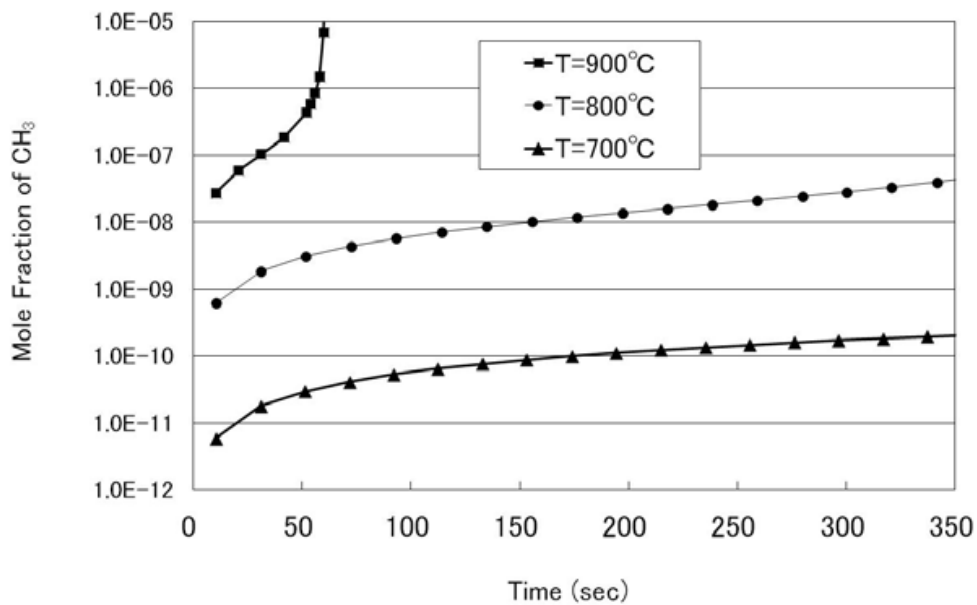
Fig. 10. Time History of CH_3 mole fraction for Constant temperature heating of pure CH_4 gas.
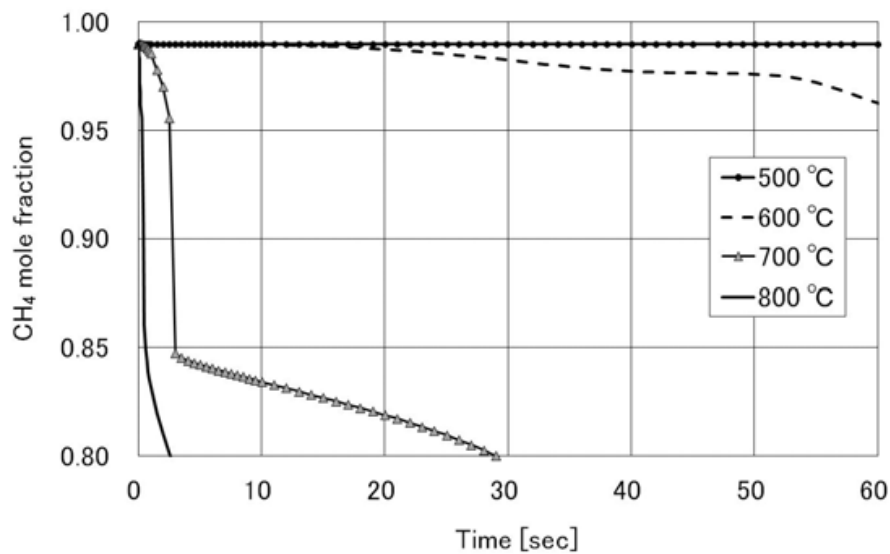
Fig. 11. Time History of CH_4 mole fraction for constant temperature heating of pseudo LNG with C_3H_8 1.0 vol.%.
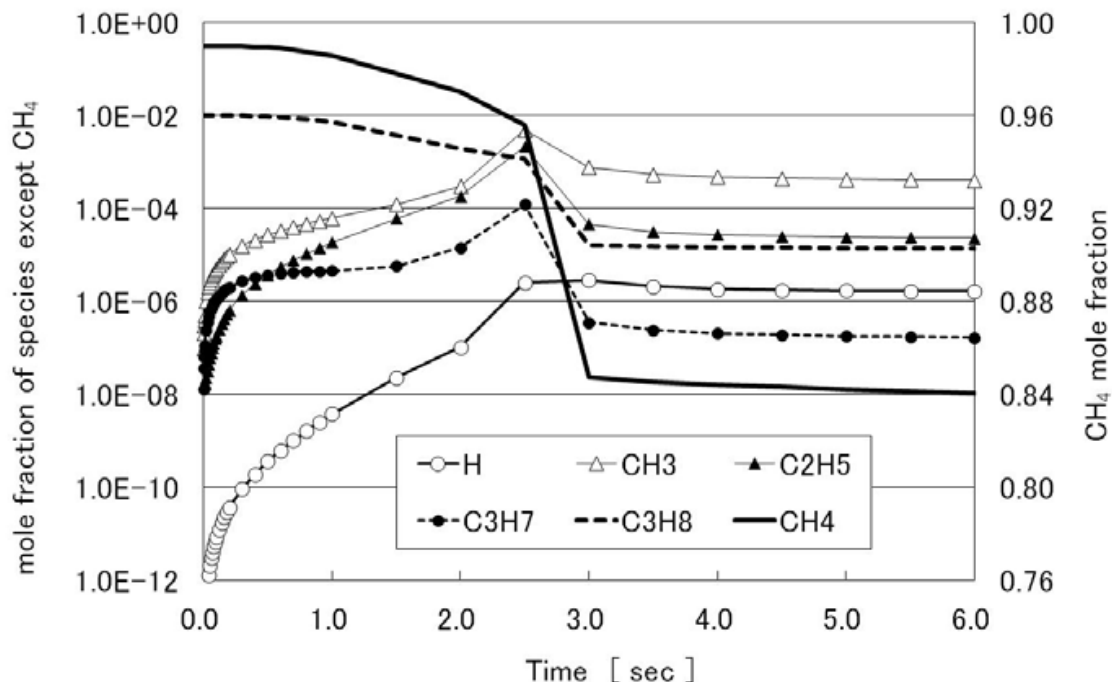
Fig. 12. Time Histories of Principal Chemical Species Mole Fraction for C_3H_8 1.0 vol.% and 700 [0]C.

Figure 10 show the numerical results of the time histories of CH_3 radical for constant temperature heating of CH_4. The mole fraction of CH_3 is rapidly increased at 900 [0]C, while they remain to low values less than 800 [0]C. This figure indicates that the CH_4 pyrolysis begins at temperature between 800 and 900 [0]C, which agrees with the experimental data shown in Figure 3(d). Figure 11 shows the time histories of mole fractions of CH_4 for pseudo LNG with C_3H_8 1.0 vol.% and indicates the simulation of the experimental results in Fig.8. The mole fraction of CH_4 for 700 [0]C is instantaneously decreased, thus this numerical results is also agreed with the experimental data. Figure 12 shows the time histories of mole fraction of the principal chemical species for pseudo LNG with C_3H_8 1.0 vol.% and 700 [0]C. The mole fraction of CH_4 is rapidly decreased at 2.5 sec. At same time, the radical species, such as H atom, CH_3 and C_2H_5 reach to maximum values. As described previously, those radical species are involved in CH_4 pyrolysis. Especially, C_2H_5 and C_3H_7 are the products of C_3H_8 pyrolysis and precursors of CH_3 and H atom. C_2H_5 and C_3H_7 play important role in promoting CH_4 pyrolysis. After 3.0 sec, the mole fractions of those species are constant and reach to equilibrium.

3. Coking inhibition by graphite coating

3.1 Experimental evaluation of graphite coating for coking inhibition

In the previous section, it is indicated that CH_4 or CH_4 and C_3H_8 gas mixture (pseudo LNG) can decomposed under high temperature conditions and carbon deposites. This coking phenomena can be accelerated by the catalytic effects of combustion chamber material. Thus, thermal design of regenerative cooling passage will be difficult because fuel temperature must be kept lower to prevent coking at there. However, if some inert materials would lay on the metallic surface, those catalytic effects might be prevented. Thus, the

authors present to coat the graphite layer on the metallic surface for the purpose of preventing of coking. Graphite is a kind of the carbon materials and chemically inert. Therefore, graphite layer on the metallic surface is considered to confine the catalytic effect. With those test pieces, the heating tests are conducted for CH_4, pseudo LNG and $N_2+C_3H_8$ gas mixture.

The experimental apparatus is same with the previous sections. The conditions of the graphite coating tests are listed as Table 4.

Test Gas (vol％)	CH_4 more than 99.9%
	CH_4 95% + C_3H_8 5%（Pseudo LNG）
	CH_4 99% + C_3H_8 1%（Pseudo LNG）
	N_2 95% + C_3H_8 5%
Test Pieces	Inconel 600 (Ni 73.58%, Cr 16.18%, Fe 9.16%)
	Activated Carbon
	Amorphous Carbon
	Graphite
Heating Condition	Isothermal Heating with 627℃, 700℃, 800℃
	Ascendant Heating from Room Temp. to 1000℃
Heating Time	60 min at Isothermal Heating
	120 min for Ascendant Heating
Flowrate of test gas	20 ml /min
Pressure	0.14 〜 0.20 MPa
Coating Conditions	n-Hexane Coating： test pieces are located in n-hexane vapor for 60 min with 800℃. Then, they are located in N_2 gas for 60min with 800℃.
	Graphite Coating： Graphite powder are mixed with ethanol and Surface of INCONEL 600 are coverd with them. They are located in N_2 gas for 60 min with 800℃

Table 4. Test Conditions for Graphite Coating Tests.

To evaluate the C_3H_8 pyrolysis, C_3H_8 conversion rate is introduced in equation (5) as well as CH_4 conversion rate.

$$Conversion\ \ Rate\ \ = \left[1 - \frac{\left(A_{C3H8}/\lambda_{C3H8}\right)}{\left(A_{C3H8}/\lambda_{C3H8}\right) + \left(A_{H2}/\lambda_{H2}\right)}\right] \times 100 \tag{5}$$

The definition of equation (5) is same as equation (1), except subscript of C_3H_8.

If the carbon deposited in a regenerative cooling passage would have chemical activation, like as amorphous or activated carbon, these might be able to accelerate the thermal decomposition of CH_4 and C_3H_8 because those carbon deposit will play role of catalysis.
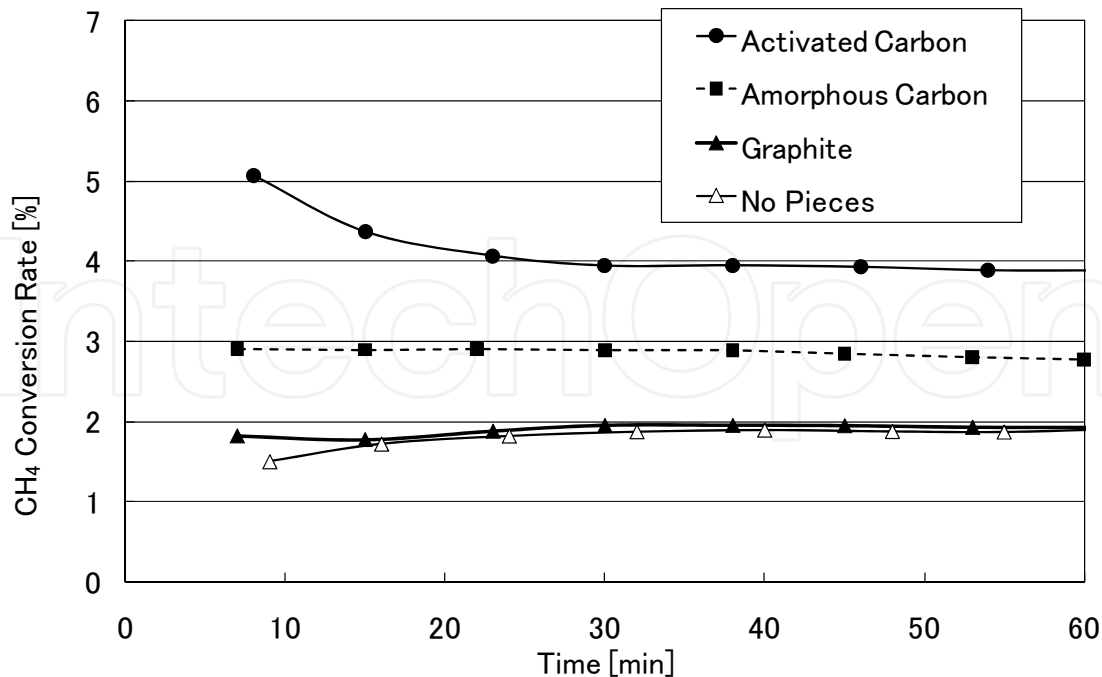
Fig. 13. CH_4 conversion rate of pseudo LNG with C_3H_8 5.0 vol.% for constant temperature heating of 700 ^{0}C.

In the present section, the authors investigate the catalytic effects of carbon compounds such as, graphite, amorphous and activated carbon. Figure 13 indicates time histories of the CH_4 conversion rate in 700 ^{0}C constant temperature heating tests. The test gas is the pseudo LNG gas with C_3H_8 5.0 vol.%.Activated carbon, amorphous carbon and graphite are used for test pieces to investigate their catalytic effects. It is indicated that activated and amorphous carbon have the catalytic effects to thermal decomposition for this gas. On the other hand, graphite does not have them. This reason is considered that graphite would have been chemically inert. The results in Fig.13 indicate that graphite is chemically inert for LNG thermal decomposition. Based on these results, inhibition effects of graphite coating on the surface of INCONEL 600 test pieces are experimentally evaluated. For comparison, conditions of n-hexane coating, no coating and no test pieces conditions (Only alumina board is located.) are also investigated. Figure 14 show the CH_4 conversion rates in ascendant heating test for those four carbon coating conditions. Ten test pieces are used for one heating test. From Fig.14(a), CH_4 begins to decompose at 600 to 700 ^{0}C. As described in the previous section, it begins to decompose at 800 or 900 ^{0}C with no catalytic conditions. Addition of C_3H_8 can reduce the CH_4 decomposition temperature. C_3H_8 can be decomposed at lower temperature than CH_4, and radical species caused by C_3H_8 pyrolysis can attack to CH_4, resulting of reduction of thermal decomposition temperature. In Fig.14(a) and (b), pyrolysis inhibition by graphite coating is apparent. Conversion rates for graphite coating condition increase more moderate than even those for no piece condition. Although, this reason is not clear, it is no doubt that graphite coating is effective to inhibit the catalytic effect of INCONEL 600. Moreover, these inhibitions are more effective for the decomposition of C_3H_8 than that of CH_4. This fact is more meaningful for the practical application of LNG rocket engine because most of LNG gas contains a few percent of C_3H_8. LNG highly purified by CH_4 is very costly.
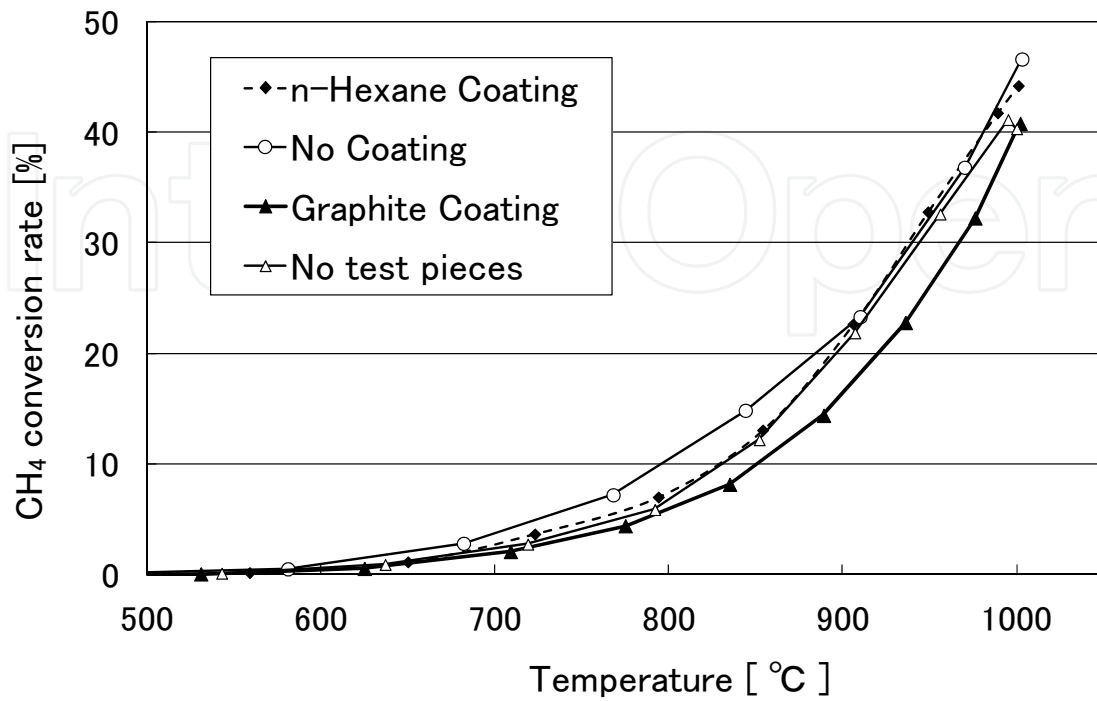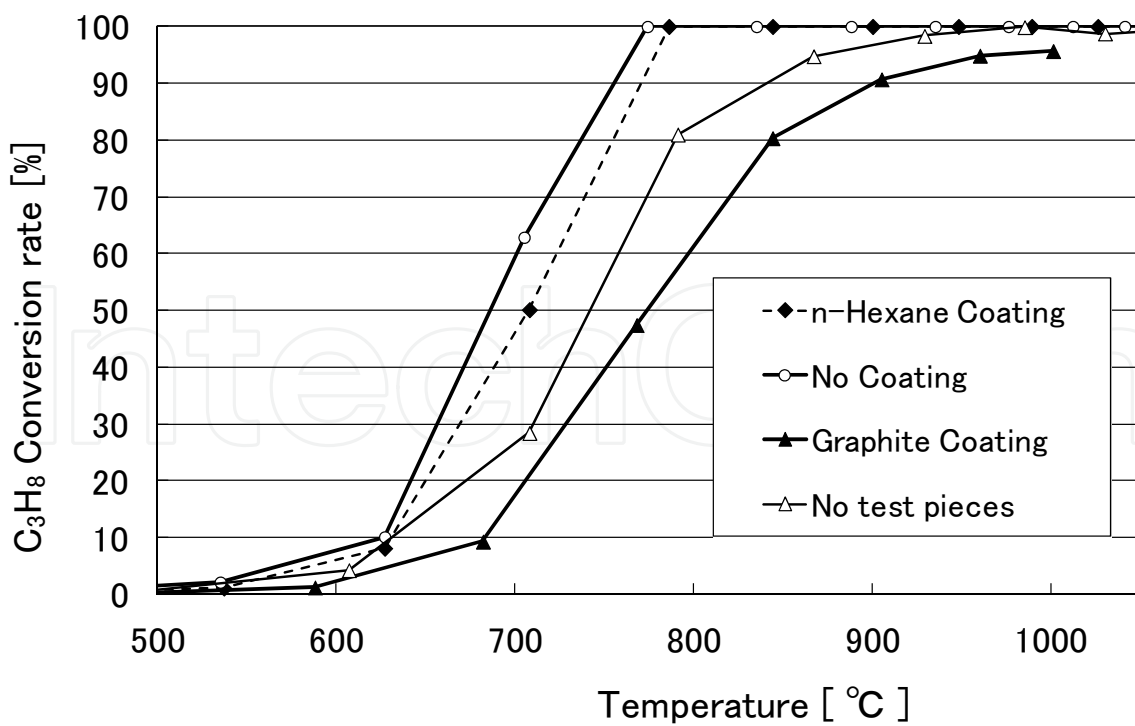
(a)Pseudo LNG with C_3H_8 5.0 vol.%

(b) N_2 95 vol.% + C_3H_8 5.0 vol.%

Fig. 14. The Effects of Carbon Coating for Ascendant Heating.
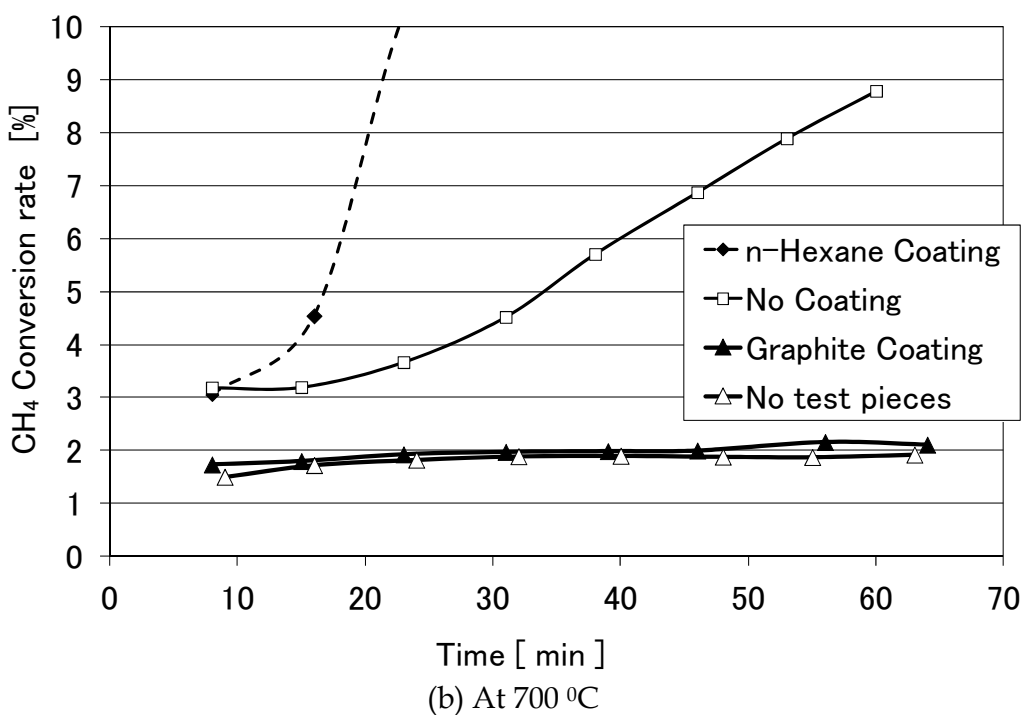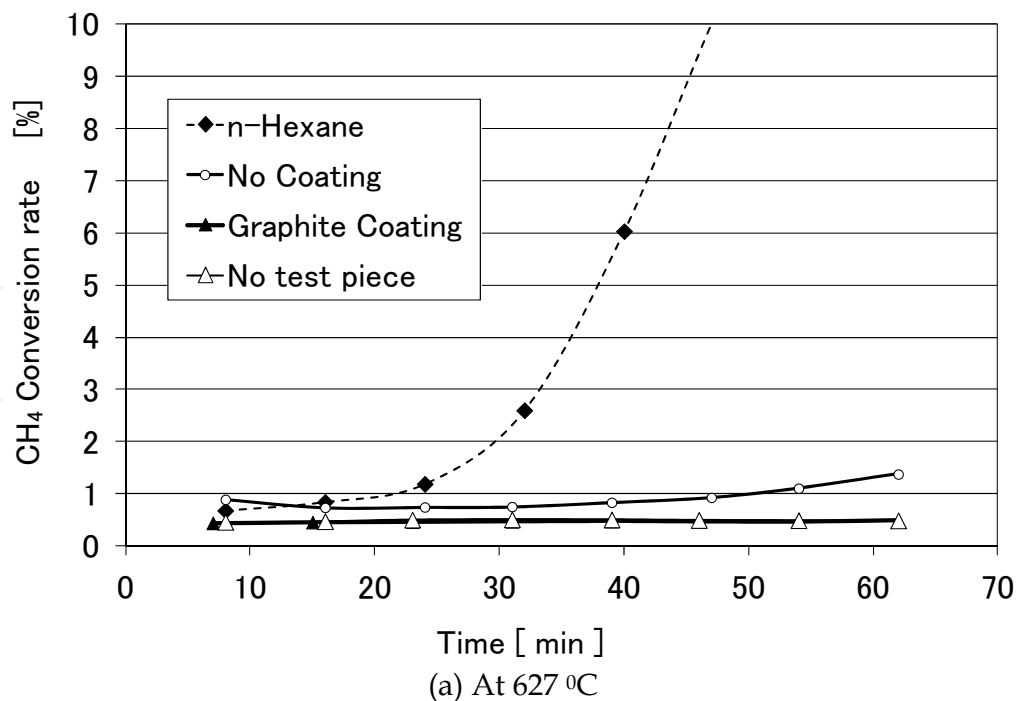
(a) At 627 °C

(b) At 700 °C

Fig. 15. The Effects of Carbon Coating on CH_4 pyrolysis for Constant temperature heating.

On the other hand, n-hexane coating can accelerate CH_4 or C_3H_8 pyrolysis more than no coating test pieces. This means the carbon in n-hexane coating have chemical activation.

For the practical LNG rocket engine, fuel temperature at the exit of regenerative cooling passage may be lower than the pyrolysis initiation temperature. However, it is necessary to grasp this temperature because high temperature turbine driven gas can obtain the turbine

power. In addition, catalyses are generally effective to accelerate pyrolysis around this temperature range. Therefore, constant temperature heating tests at 627, 700 and 800 $^{\circ}$C are conducted for pseudo LNG gas with 5 vol % C_3H_8 and Figure 15(a) to (c) show the time histories of those CH_4 conversion rates. Five test pieces are employed for one heating test. For 627 $^{\circ}$C and 700 $^{\circ}$C heating test, CH_4 conversion rates for graphite coating condition are much lower than those for n-hexane and No coating conditions and are same level with those for no test piece condition. For 800 $^{\circ}$C heating test, no difference appeared in CH_4 conversion rates amaong those 4 conditions and catalytic effect is not observed. At 800 $^{\circ}$C, the decomposition rates of CH_4 or C_3H_8 may mainly depend on temperature rather than catalytic effect. The results in Fig.15(a) to (c) remarkably show the inhibition effect of graphite coating for LNG gas pyrolysis.
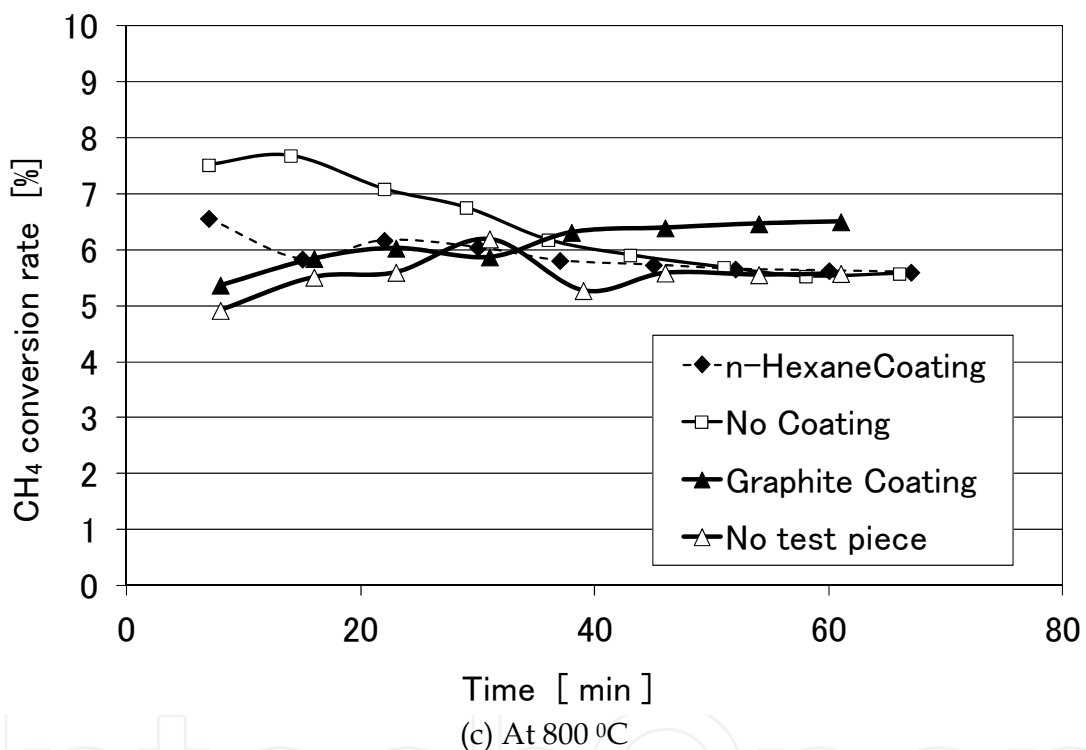

(c) At 800 $^{\circ}$C

Fig. 15. (cont.) The Effects of Carbon Coating on CH_4 pyrolysis for Constant temperature heating.

It is remarkable that CH_4 conversion rates for n-hexane coating and no coating conditions increase more rapidly at 627 and 700 $^{\circ}$C than at 800 $^{\circ}$C. In general, catalysis used in cracking of hydrocarbon become to deactivate with time passing because cokes deposit on its surface and reduce the catalytic effects. This reason is considered that for less than 700 $^{\circ}$C heating, carbon deposited at test pieces is similar compound to amorphous or activated carbon. They are chemically activated and play role of catalysis. Thus, the types of the deposits on the test pieces after constant temperature heating tests are analyzed by Raman spectroscopy. Figure 16(a) and (b) show the reference peaks of graphite and activated carbon, respectively. Raman spectroscopy of graphite has a peak at 1350 cm^{-1} and that of activated carbon has two peaks at 1300 and 1570cm^{-1}. Peak at 1300cm^{-1} is higher than 1570cm^{-1}.
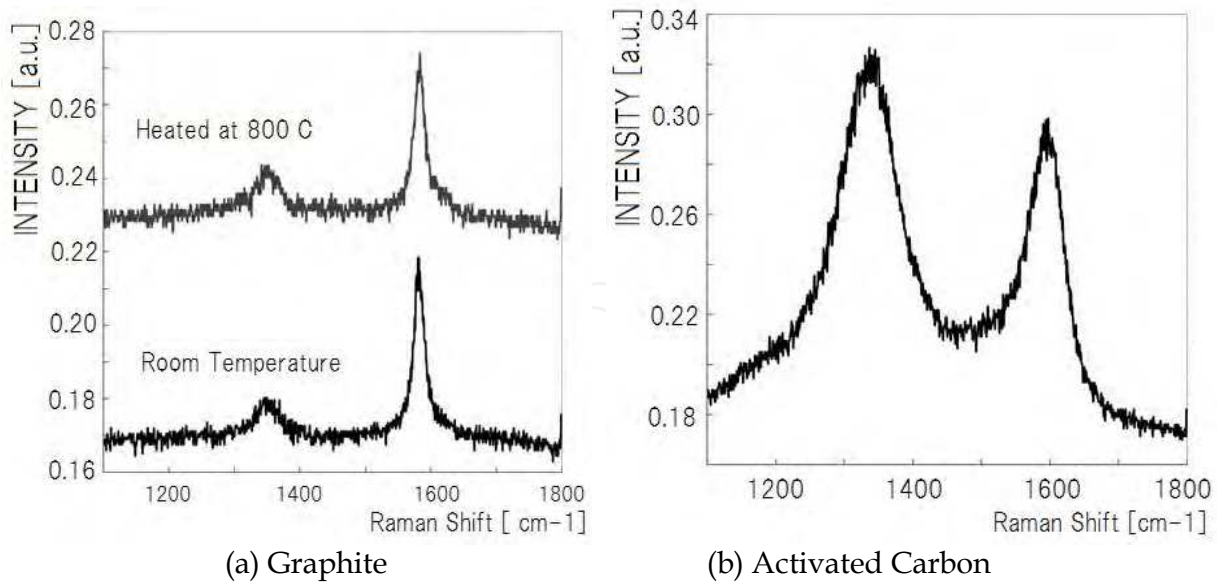
(a) Graphite   (b) Activated Carbon

Fig. 16. Reference Peaks of Carbon Compounds of Raman Spectroscopy.

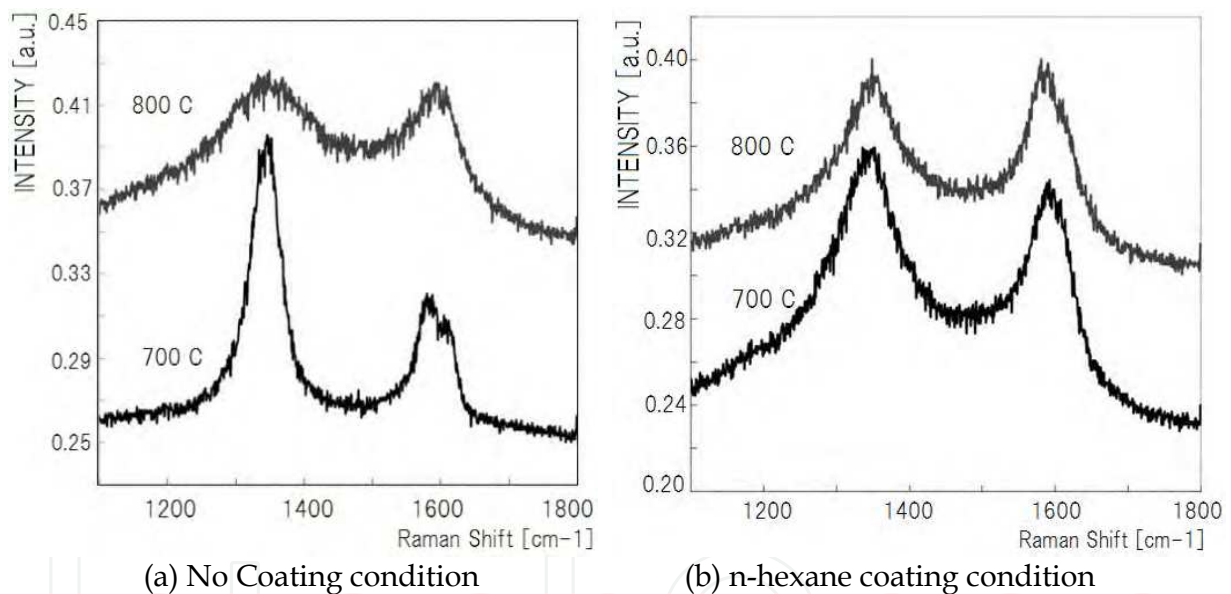(a) No Coating condition   (b) n-hexane coating condition

Fig. 17. Raman spectroscopy peaks of deposits on the test pieces after constant temperature heating test.

Figure 17 shows the Raman spectroscopy peaks of the deposits on the test pieces after constant temperature heating test. Those pieces are used in No coating and n-hexane coating conditions. For both two conditions at constant temperature heating 700 ^{0}C, the peaks at 1350cm^{-1} is higher than 1570cm^{-1}. On the other hand, at constant temperature heating of 800 ^{0}C, peaks at 1350cm^{-1} are close to that at 1570cm^{-1}. The results in Fig.17 indicate the deposit at 700 ^{0}C is similar to activated carbon and has catalytic effects. They are considered to accelerate the pyrolysis of CH_4 or C_3H_8. However, deposits at 800 ^{0}C differ from those at 700 ^{0}C and are less activated. For practical application to rocket engine designing, heating 700 ^{0}C at regenerative cooling passage should be avoided without graphite coating. For heating of LNG at this temperature, coke begins to deposit within fuel passages and promote the thermal decomposition by itself. However, graphite coating is effective to inhibit the coking

deposit for such heating conditions. Figure 15 indicate the graphite coating can inhibit coking to thermal decomposition in those temperature ranges.
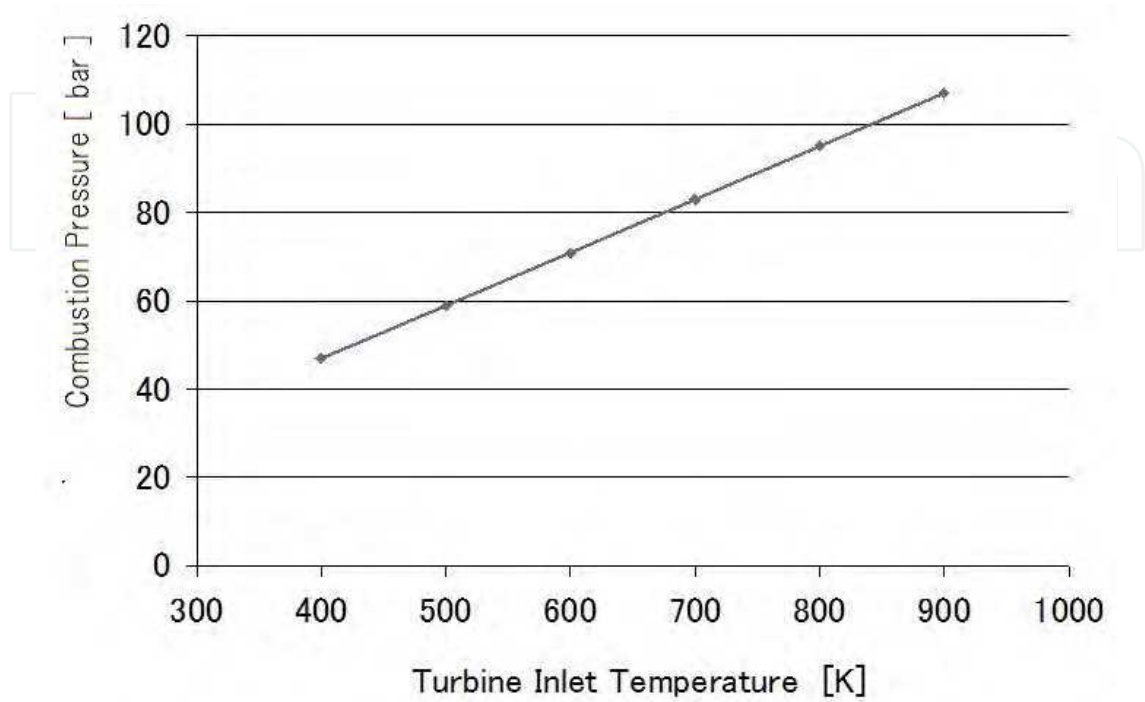

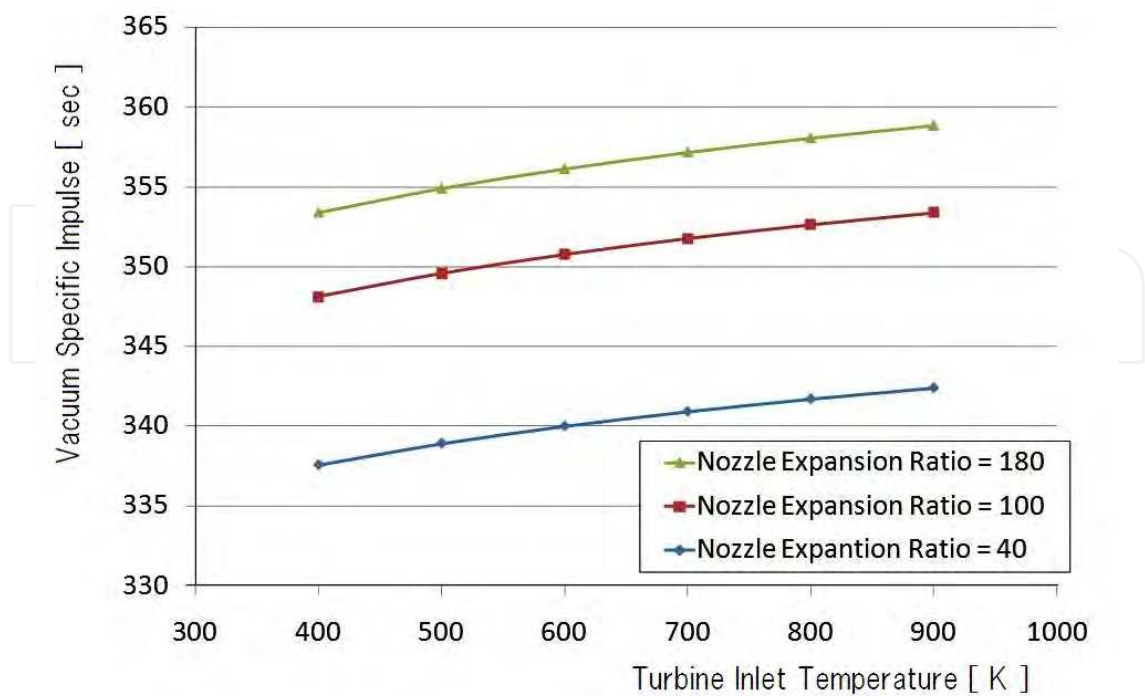Fig. 18. Effect of TIT on chamber pressure for Expander Cycled Rocket Engine.

Fig. 19. Effect of TIT on Vacuum Isp for Expander Cycled Rocket Engine.

3.2 Application of graphite coating to expander cycle rocket engine

The graphite coating has the possibility to improve an expander cycle rocket engine performance because temperature at an exit of regenerative cooling passage can be higher. That leads to increase the turbine power. Simple analysis of turbopump is considered in the present study. The specification of turbopump and rocket engine are considered as Table.2. The specification of turbopump and rocket engine are same as those studied by Schuff (2006). 90 percent of LNG fuel is used to drive the turbopump and the rest of them are bypassed.

The combustion chamber pressure, Pc, can be given by the power balance and pressure loss at fuel passage. although the detailed analysis is still necessary. Figure 18 show the combustion chamber pressure, Pc, versus Turbine Inlet Temperature (TIT). TIT is considered to be equal to the maximum allowable temperature at the exit of regenerative cooling passage.

The effects of TIT on Pc and vacuum Isp are indicated in Figure 18 and 19, respectively. Vacuum Isp is evaluated with chemical frozen flow in a nozzle and calculated by computational code by Gordon and Mcbride [6]. The higher TIT is, the greater vacuum Isp can be obtained, however, improvement of vacuum Isp is not so great. For example, in the case of nozzle expansion of 40, only 4 sec of vacuum Isp increment (from 337.5 sec to 342.4 sec) can be expected when TIT would be varied from 400 K to 900 K. However, combustion pressure can be increased to about twice as shown in Fig.18.

Therefore, practical application of graphite coating may be useful to minimize the combustion chamber size, rather than the improvement of Isp. In such cases, the size of combustion chamber will be depended on heat exchange between fuel and combustor. In our future study, more detailed and practical estimation should be conducted on heat transfer analysis and turbopump specification.

4. Conclusion

In the present chapter, the experimental and numerical studies on fundamental chemical phenomena of CH_4 and LNG pyrolysis are conducted. CH_4 pyrolysis is promoted by the catalytic effects of chamber material and the addition of C_3H_8. CH_4 pyrolysis can begin at temperature of 800 to 900 ^{0}C, however, the catalytic effect of combustion chamber materials can reduce the temperature which CH_4 pyrolysis begins by 200 ^{0}C. In addition, the addition of C_3H_8 can promote the coking on the test pieces, especially it is apparent if the volumetric fraction of C_3H_8 is more than 3.0 %. The numerical simulation can predict the experimental results of CH_4 and C_3H_8 pyrolysis.

Based on those experimental results, the effective coking inhibition method by graphite coating for LNG rocket engine can be developed and confine pyrolysis temperature up to 700 ^{0}C. INCONEL 600 with the graphite coating did not have their catalytic effect on LNG pyrolysis absolutely.

If this method can be applied to expander cycle rocket engine, the improvement of vacuum Isp can be achieved from 338.6 to 342.5 sec when the nozzle expansion ratio is 40. However, it is expected that the size of combustion chamber may be dramatically reduced. In the next phase, more detailed investigations for heat transfer in regenerative cooling passage and

turbopump must be done for practical application of the graphite coating on the expander cycle LNG rocket engine.

5. Nomenclature

A_i Area indicated in the results of Gas Chromatograph for species i

$\dot{m}_{carbon}$ Mass flow rate of carbon contained in supplied test gas [kg/sec]

$\dot{m}_{supply}$ Mass flow rate of supplied test gas [kg/sec]

M_i Molecular weight of species i [kg/kmol]

P Pressure [Pa]

Q Volumetric flow rate of gas [m³/sec]

$\hat{R}$ Universal gas constant (= 8.3143 [J/(mol K)])

t Time [sec]

T Temperature [K]

λ_i Heat transfer rate of species i [J/(m K)]

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Heat Exchangers - Basics Design Applications

Edited by Dr. Jovan Mitrovic

Selecting and bringing together matter provided by specialists, this project offers comprehensive information on particular cases of heat exchangers. The selection was guided by actual and future demands of applied research and industry, mainly focusing on the efficient use and conversion energy in changing environment. Beside the questions of thermodynamic basics, the book addresses several important issues, such as conceptions, design, operations, fouling and cleaning of heat exchangers. It includes also storage of thermal energy and geothermal energy use, directly or by application of heat pumps. The contributions are thematically grouped in sections and the content of each section is introduced by summarising the main objectives of the encompassed chapters. The book is not necessarily intended to be an elementary source of the knowledge in the area it covers, but rather a mentor while pursuing detailed solutions of specific technical problems which face engineers and technicians engaged in research and development in the fields of heat transfer and heat exchangers.

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