Research paper

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Mechanism of high burning rate of HAN-based solution

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Abstract

In order to elucidate the mechanism of extremely high burning rates of some Hydroxylammonium Nitrate (HAN) based solutions, the combustion characteristics of HAN aqueous solutions were studied. It was found that the role of the two-phase region is very important and the intense boiling of water by superheat is responsible for the high burning rate. The evaluated bubble nucleation rate coincides with burning rate at very high region. Further, the combustion mechanism of propellant solution is discussed. Hydrodynamic instability was taken into account and the pressure dependency of the instability was estimated. The estimation of hydrodynamic instability supports the observed phenomena. It was found that the instability is strongly affected by Markstein number.

Keywords : combustion mechanism, hydroxylammonium nitrate, linear burning rate, nucleation rate, hydrodynamic instability

1. Introduction

Hydroxylammonium nitrate based solutions have been considered as candidates for monopropellant and liquid oxidizer because of their promises in the area of storability, environmental/health, performance, density and thermal management[1]. However, some HAN-based solutions exhibit extremely high burning rates, and these characteristics have retarded the use of the solutions in those applications.

Combustion characteristics and mechanisms of HAN-based solutions have been studied by several researchers over a period of many years. S. R. Vosen[2), 3)] associated the decomposition rates of HAN-water mixtures with the density ratio, $\rho_{product}/\rho_{reactant}$. In the case of low-density ratios, decomposition rates depend primarily upon the density ratio. In higher ratios, these rates are independent of the density ratio. In addition, the overall burning rate decreases with an increase in pressure up to 26 MPa, which is caused by hydrodynamic instabilities ; above 26 MPa, the burning rate is independent of pressure. Y. P. Chang and K. K. Kuo[4)] assessed the combustion characteristics and mechanisms of the HAN-glycine-water solution for pressures ranging from 1.5 to 14.5 MPa. The slope break point in the curve of the burning rate occurs as the result of a change in the burning mechanism. In another paper, Y. P. Chang et al.[5)] studied the combustion characteristics of HAN-AN-water-methanol solutions between 0.74 and 7.3 MPa. Combustion behaviors were influenced by the content of water and methanol, and there was a change in the combustion mechanism at the pressure of the break point also in HAN-ammonium nitrate (AN)-methanol-water solutions.

Regardless of these studies, the combustion mechanism still has not been clarified completely, especially the mechanism of the extremely high burning rate of HAN-based solutions. In our previous study[6)], the combustion characteristics of the propellant solutions whose composition were HAN-AN-water-methanol were studied ; however the combustion mechanism was not understood fully. Therefore, focusing on the mechanism of the extremely high burning rate, the combustion characteristics of the HAN aqueous solutions eliminating other ingredients were investigated. From dependencies of pressure and HAN concentration, it was found that the role of two-phase region is very important for the linear burning rate. In this paper, the nucleation rate is evaluated and discussed

High burning rate mechanism of HAN aqueous solutions can be applied to the propellant solutions ; however it is not sufficient for its comprehensive combustion model. In our previous study of HAN-based propellants, it was found that hydrodynamic instability might be the trigger for the jump to the extremely high burning rate region. Margolis[7] showed the stability criteria of the combustion wave obey the Landau-Levich instability ; however these criteria do not meet our data because the pressure ranges are different form each other. In this paper, the effect of flame stretch on the hydrodynamic instability is estimated with Markstein number which expresses the relation between the burning rate of laminar flame and stretched flame. Based upon the relationship between the pressure dependency of hydrodynamic instability and our data, the critical Markstein number where the burning rate jumps to the very high region is defined and its details are discussed.

2. Combustion mechanism of aqueous solution

2.1 Liner burning rate and combustion mode

Seven aqueous solutions whose HAN concentrations were 95, 85, 82.5, 80, 77.5, 64, and 50 mass% were prepared in order to assess the effects of HAN concentration. 95 mass% is the maximum concentration which can be prepared at room temperature. In previous study of the aqueous solution[8], the combustion characteristics in a glass tube were obtained. In the previous study, it was found that the linear burning rates were classified by combustion modes. The correlation between the pressure dependency of the burning rates and the combustion modes of aqueous solutions is shown in Figure 1. In the case of Zone1 (Figure 1), the combustion wave showed a layered structure (liquid layer, two-phase layer and gas layer). In the case of Zone2 (Figure 1), many fine bubbles are generated in the front of the combustion wave, which propagates rapidly. In the case of Zone3 (Figure 1), the two modes of combustion wave propagation appear alternately.

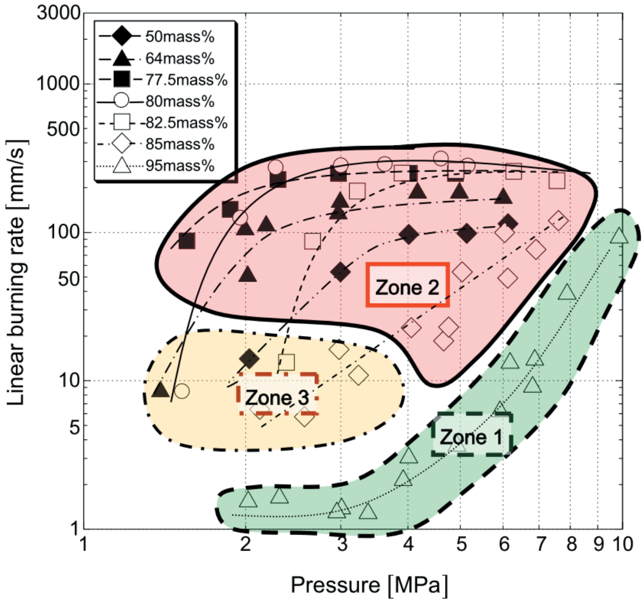

Figure 1 Correlation of linear burning rates and combustion modes.

2.2 Combustion wave structure

As the conclusion of previous study of aqueous solutions[8], the combustion mode is basically two types (Figure 2), which is based upon the observation and the temperature mesurement.

In the case of low water content (Figure 2(a)), the temperature rises gradually from its initial value to boiling temperature (Tbp). At the boiling temperature, the fine bubble of water vapor starts to be generated. The boiling temperature (Tbp) is kept in the two-phase region, and the temperature increases after the water vaporizes completely. Chemical reaction occurs mainly in the gas phase which is brown color, and temperature increases to the flame temperature (Tf). In the case of high water content (Figure 2(b)), the temperature rises from the initial value and is kept at boiling temperature, as in the case of low water content. However, the temperature does not increase more than the boiling temperature, and the

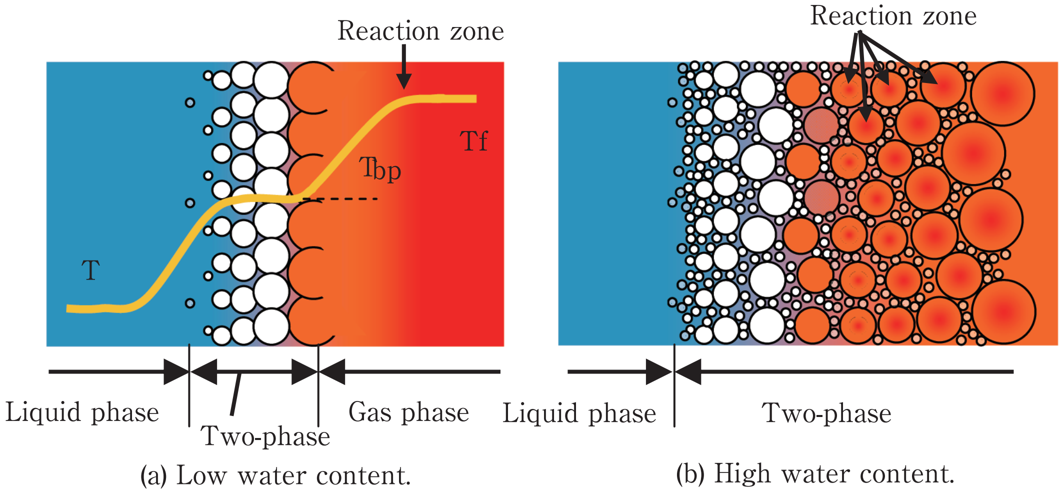

Figure 2 Combustion wave structure.

two-phase region becomes longer than that of the proposed wave structure in low water content, due to larger amount of water. The bubbles are transparent in the vicinity of the liquid phase and turn gradually brown in the two-phase region. Consequently, chemical reaction should occur in the bubbles, and the temperature in the brown bubble may be higher than the measured value.

2.2 Rate of vapor nucleation

Superheat increases by the chemical reaction progress in the bubbles, and generates the vapor nuclei in the vicinity of the bubble. In general, the nucleation rate[9] increases exponentially with superheat and pressure. For example, significant nucleation rates between 10^9 and 10^{13} m^3/s correspond to a very narrow range of gas temperatures from 224 to 225.2°C for benzene (boiling temperature ; 80.1°C). In this case, when the superheat exceeds a certain critical value for each aqueous solution, the nucleation rate increases abruptly in the two-phase region. Therefore, it is assumed that this rapid nucleation makes the apparent burning rate extremely high, and nucleation rate is estimated below.

The estimated nucleation rate, dn/dt, is expressed in Equation (1). Here, λ is a collision frequency, N is a constant approximately equal to the number of molecules per unit volume, k is the Boltzmann constant, T_g is vapor temperature in the bubble, and $\Delta G\ (r^*)$ is formation energy of bubble radius r^*, $\Delta G\ (r^*) = 4\pi r^* \sigma/3$

$$\frac{dn}{dt} = \lambda N e^{-\Delta G\ (r^*)/kT_g} \tag{1}$$

$$r^* = \frac{2RT_{SAT}^2\sigma}{i_{fg} M p_f \Delta T} \tag{2}$$

r^* is the radius of the spherical vapor nucleus, which is calculated with the following formula. R ; universal gas constant, T_{SAT} ; saturation temperature, σ, surface tension of the aqueous solution, i_{fg} ; latent heat of vaporization, M ; molecular weight, p_f ; pressure in liquid phase, ΔT ; superheat, $T_g - T_{SAT}$. The nucleation rates of pure water are calculated as functions of pressure and gas temperature (T_g) in bubbles with these formulas. Minimum radius of the vapor nucleus (r^*) is set at 2 nm according to Matsumoto[10]. Further, multiplying dn/dt by the nucleus volume gives dv/dt, the increase rate of nucleus volume per unit volume by nucleation, as shown in Equation (3).

$$\frac{dv}{dt} = \pi r^{*2} \frac{dn}{dt} \tag{3}$$

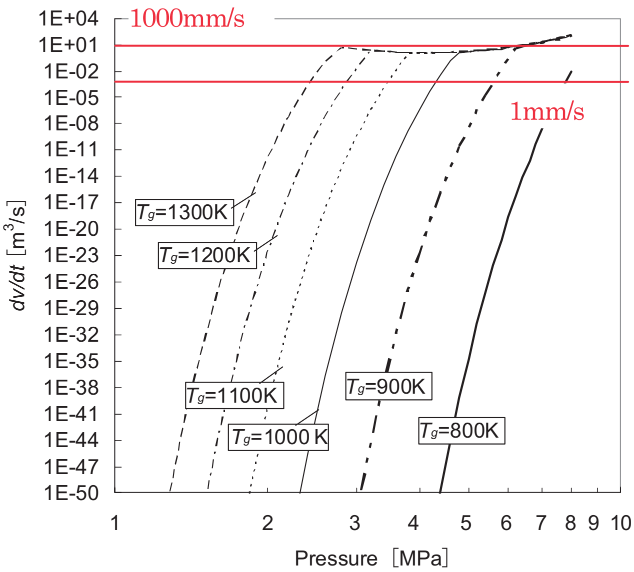

Figure 3 Increase rate of bubble volume.

As Figure 3 illustrates, the dependency of dv/dt on pressure is same as the linear burning rates of the aqueous solution. dv/dt is directly related with linear burning rate by dividing by unit area, and for example, 10^{-2} m^3/s of area corresponds 10 mm/s of linear burning rate. Therefore, the assumption that the nucleation process governs the linear burning rate may be supported by this result. In the case of low water content, the gas temperature of bubble in the two-phase region may be low, as the two-phase region is short. The superheating may be less, and the nucleation and apparent burning rates low. In the high water content, two-phase region is long ; however the gas temperature in the bubbles may be low. Due to the diminished superheating, the nucleation and burning rates become low.

3. Combustion mechanism of propellant solution

3.1 Linear burning rate

In previous study of the propellant solution[6], the linear burning rates of propellant solutions were measured and are shown in Figure 4. The compositions of propellant solutions which include HAN, AN, water and methanol are listed in Table 1. As shown in the Figure 4, the Control and SHP069 have apparently two regimes. At a certain critical pressure, the burning rate jumps from a moderate rate to an extremely high rate. The high burning rate mechanism of aqueous solutions can be applied to the propellant solutions at high pressure ; however the jump of burning rate to very high region cannot be explained with the combustion mechanism of aqueous solutions. Hydrodynamic instability is incorporated successfully to explain these phenomena.

3.2 Hydrodynamic instability

In the combustion of HAN-based solution, hydrodynamic instability should be caused by large difference in density of between unburnt liquid and burnt gas ; however combustion wave was stable at low pressure in the observation. Therefore, some factor suppresses the instability of combustion wave. Because the each Lewis numbers are more than 1.0, the effect of

Table 1 Compositions of propellant solutions. Unit is mass ratio.

	HAN	AN	H_2O	CH_3OH
Control	95	5	8	0
SHP069	95	5	8	8
SHP163	95	5	8	21

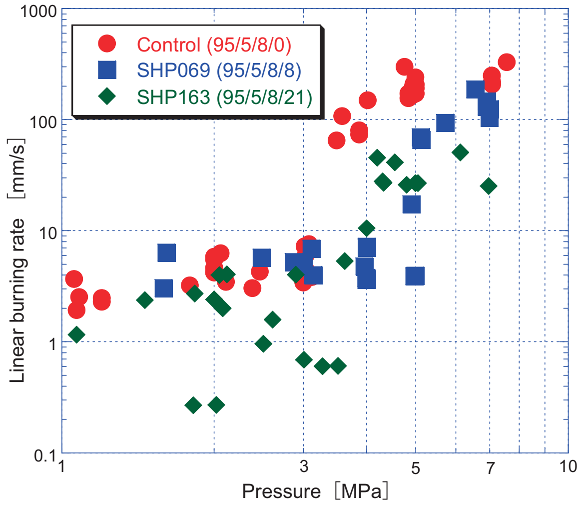

Figure 4 Burning rate of the propellant solutions.

flame stretch was taken account of. However, Lewis number has no dependency on pressure. Markstein number is used to correlate the effect of the stretch to Karlovitz number as in Equation (4).

$$\frac{S_{u(l)} - S_{u(s)}}{S_{u(l)}} = Ma \cdot Ka \quad (4)$$

$$Ma = \frac{1}{1-\rho}\ln\frac{1}{\rho} + \frac{\beta(Le-1)}{2}\frac{\rho}{1-\rho}\int_0^{\frac{1-\rho}{\rho}}\frac{\ln(1+x)}{x}dx \quad (5)$$

Kitagawa et al.[11] obtained the characteristics of the flame instability as a function of the pressure and the Markstein number. They reported that the hydrodynamic instability was suppressed when the Markstein number was relatively large. In this paper, the Markstein number is calculated with Equation (5), which was indicated as an asymptotic solution by Clavin et al.[12] In Equation (5), β is Zel'dovich number. The hydrodynamic instability of our propellant solutions is estimated with the Markstein number and the pressure dependency of Markstein number of each solution is shown in Figure 5.

The Markstein number decreases with the increase of pressure and increases with the decrease of methanol content. Thus, these results support the observed phenomena that the combustion wave is unstable at higher pressure than the critical pressure and the methanol addition shifts the critical pressure to higher pressure. Markstein numbers at the critical pressure are nearly same value, which is defined as critical Markstein number, $Ma\,(cr)$. Although the critical pressure of SHP 163 is not clear, the combustion wave structure changed at the critical Markstein number. Therefore, the hydrodynamic instability is affected by flame stretch and determines the critical pressure where the linear burning rate of propellant solutions jumps to high rate region. As the pressure increases, Ma decrease and combustion wave is more unstable, and the motion of gas phase flow is more energetic. At the $Ma\,(cr)$, hot gases start to invade the liquid zone and the induced local superheat becomes the trigger of the very high apparent burning rate.

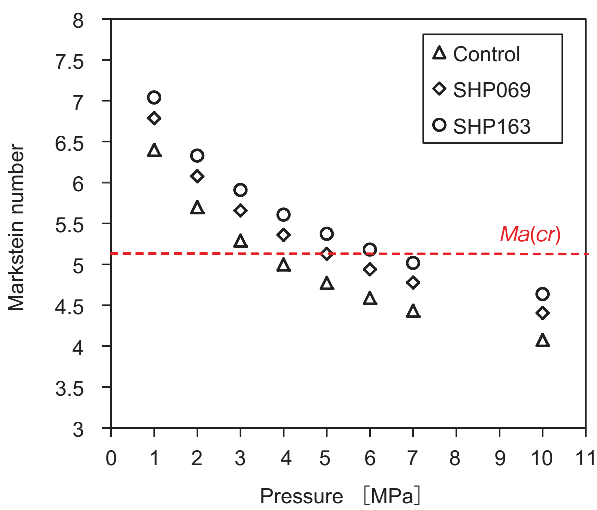

Figure 5 Dependency of Markstein number on pressure.

4. Conclusion

Two types of combustion wave structures were proposed. The structure of 95 mass% HAN aqueous solution is layered, and the reaction zone is in the gas phase. This structure is established in the case of low water content. In the case of 80 mass%, the reaction zone may be in the two-phase region, and the rapid nucleation by the superheat causes a high burning rate. The gas temperature in bubbles of the two-phase region and the water content of a particular solution may determine the combustion wave structure and the linear burning rate. In the case of propellant solution, the high burning rate mechanism of aqueous solutions can be applied to the propellant solutions at high pressures. Hydrodynamic instability is incorporated successfully to explain the jump of burning rate to very high region. The estimation of stabilize effect of flame stretch supports the observed phenomena that the hydrodynamic instability occurs at higher than the critical pressure and the methanol addition shifts the critical pressure to higher. The factor determining the burning rate is the bubble nucleation rate in the case of aqueous solutions and is the hydrodynamic instability in the case of propellant solution.

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HAN系溶液の非常に高い燃焼速度を示すメカニズム

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硝酸ヒドロキシルアンモニウム（HAN）系溶液の非常に高い燃焼速度を示すメカニズムを明らかにするため，これまでにHAN水溶液の燃焼特性を取得し，二相領域における水の気化過程が重要であることがわかっている．その知見に基づき，単純な水の気泡核生成速度について評価した結果，気泡核生成速度の圧力依存性が燃焼速度の圧力依存性と同じ傾向を示し，過熱による水の急激な沸騰が非常に高い燃焼速度の要因であることが判明した．これらの結果を基に推進剤の燃焼機構についても議論する．気液界面の不安定性が燃焼速度の急上昇に影響を及ぼすことが，これまでの実験で確認されているため，流体力学的不安定性の圧力依存性および組成の影響について，予混合燃焼における火炎伸張による安定性評価によく用いられるMarkstein数を用いて評価を行った．その結果，流体力学的不安定性の圧力依存性が，実験で観察された現象と一致した．

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