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Brief Communications

Effect of surface tension on the temperature of burning metal droplets

Edward L. Dreizin

New Jersey Institute of Technology, Newark, NJ, United States

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ABSTRACT

An effect of Laplace pressure resulting in elevated boiling temperatures for fine burning metal droplets is discussed. The effect is evaluated for both Al and Mg. An increase in the boiling temperature suggests that the temperature of fine Al particles can become equal to or even higher than the temperature of the vapor phase Al flame. The high particle surface temperature may be associated with accelerated surface reaction rates. For Al, such surface reactions may generate vapor-phase aluminum suboxides, resulting in a reduced heat effect and extended burn times for fine particles and nanoparticles. For Mg, the particle temperature remains below the vapor phase flame temperature despite an elevated boiling point. For fine particles, surface reaction producing solid MgO growing directly on the particle surface is possible.

1. Introduction

Vapor phase combustion of fuel droplets is ubiquitous in various practical systems. The droplet temperature is commonly accepted to be at the boiling point of the respective fuel [1,2]. This assumption is used equally for hydrocarbon and metal fuel droplets. It is also commonly recognized that as the droplet size decreases, the vapor phase flame becomes more and more difficult to maintain because of accelerated rates of heat and mass transfer from the droplet surface. Respectively, at some point, combustion reactions begin primarily occurring at the surface of the burning droplet [3–5]. Predicting the droplet size and conditions for which the transition from the vapor phase to surface controlled reaction will occur is very important for designing respective combustion systems. Recently, this issue was closely looked at for aluminum particle combustion [6–8]. This was prompted by the availability of and combustion test results for fine, submicron and nano-sized Al powders. The identification of the range of particle sizes, which can burn in the vapor phase, focused on detailed analysis of heat and mass transfer for burning particles. Specifically, heat transfer in the transition regime was considered [8,9] and further work coupling both heat and mass transfer analyses for that regime was proposed. Clearly, an accurate assessment of the surface temperature of the burning particle is critical for such analysis. A possible correction for this temperature, that is commonly assumed to be the metal's boiling point, is the subject of this letter.

In the studies of Al combustion cited above, as well as elsewhere, the effect of the droplet surface tension on the pressure inside it and, respectively, on the fuel's boiling point, was neglected. The effect was considered briefly in an early Russian paper [10], however, specific corrections for the burning particle temperatures were not discussed. For large droplets and for fuels with weak surface tension, such as common hydrocarbons, this effect may be negligible. It needs to be accounted for when fine droplets with high surface tension are dealt with. In particular, combustion of fine fuel particles with small sizes becomes increasingly important for metal fuels, for which the surface tension is quite significant. This letter describes the expected effect considering specific examples of combustion of aluminum and magnesium droplets.

2. Boiling point as a function of pressure

The effect of pressure on the boiling point is readily obtained from Clausius–Clapeyron equation, written with an assumption that the vapor behaves as an ideal gas:

$$\frac{dp}{p} = \frac{\Delta H_{vap}}{RT^2} dT \tag{1}$$

where p is pressure, ΔH_{vap} is the heat of formation of the metal vapor, R is the universal gas constant, and T is temperature. Based on data from NIST chemistry web book [11], the effect of temperature on ΔH_{vap} is given as:

$$\Delta H_{vap} = \Delta_f H_{gas}^o + A\frac{T}{1000} + \frac{B}{2}\left(\frac{T}{1000}\right)^2 + \frac{C}{3}\left(\frac{T}{1000}\right)^3$$
$$+ \frac{D}{4}\left(\frac{T}{1000}\right)^4 - \frac{1000E}{RT} + F - H \tag{2}$$
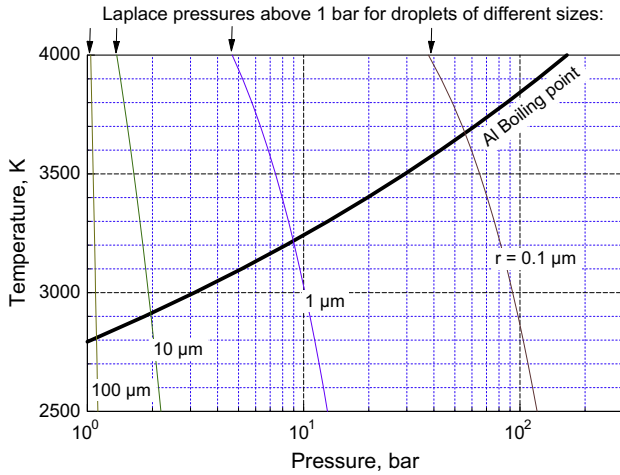
Fig. 1. Elevated boiling point of aluminum as a function of pressure (bold line) and Laplace pressures in aluminum droplets of different radii at varied temperatures (thin lines). A dashed line shows the boiling point for aluminum oxide.
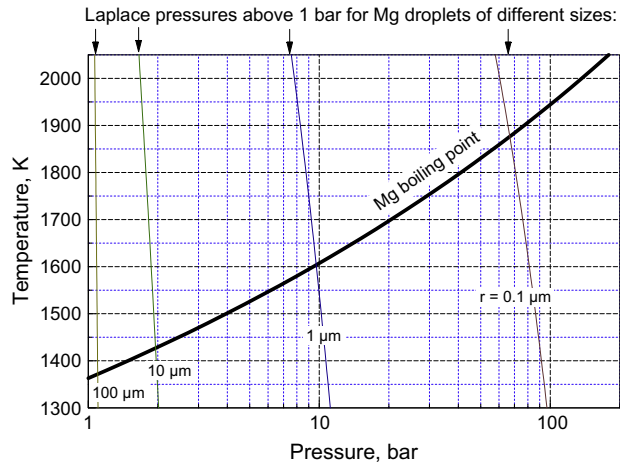

Fig. 2. Elevated boiling point of magnesium as a function of pressure (bold line) and Laplace pressures in magnesium droplets of different radii at varied temperatures (thin lines).

where $\Delta_f H^o_{gas}$ is the standard heat of formation of the metal vapor and A, B, C, D, E, F, and H are constants. Plugging Eq. (2) in (1) and integrating the result from 1 bar and boiling temperature at 1 bar, T^o_{boil}, to the pressure p and respective boiling temperature T, we obtain

$$\ln(p) = -\left(\frac{\Delta_f H^o_{gas} + F - H}{R}\right)\left(\frac{1}{T} - \frac{1}{T^o_{boil}}\right) + \frac{A}{1000R}\ln\left(\frac{T}{T^o_{boil}}\right)$$
$$+ \frac{B}{2R \cdot 10^6}(T - T^o_{boil}) + \frac{C}{6R \cdot 10^9}[T^2 - (T^o_{boil})^2]$$
$$+ \frac{D}{12R \cdot 10^{12}}[T^3 - (T^o_{boil})^3] + \frac{1000E}{3R}\left[\frac{1}{T^3} - \frac{1}{(T^o_{boil})^3}\right] \quad (3)$$

Eq. (3) gives the correlation between the pressure and boiling temperature. Specific correlations for Al and Mg calculated using the constants A, B, C, D, E, F, and H as well as respective values of $\Delta_f H^o_{gas}$ for each metal [11] are shown as bold lines in Figs. 1 and 2, respectively. All constants used in Eq. (3) are given in Table 1.

Note that Kelvin effect resulting in an increase of the vapor pressure above the surface of a small droplet is quite small for

Table 1
Constants used in Eq. (3) taken from Ref. [11].

Constant	Al	Mg
A	20.37692	20.77306
B	0.660817	0.035592
C	−0.313631	−0.031917
D	0.045106	0.009109
E	0.078173	0.000461
F	323.8575	140.9071
H	329.6992	147.1002
T_{boil}, K	2793	1363
$\Delta_f H^o_{gas}$, kJ/mol	329.7	147.1
R, J/(mol K)	8.31	

relatively high-density metals for elevated temperatures characteristic of metal combustion; for 100-nm radius droplets the effect is causing only ~1% correction for the pressure. Because of the relatively insignificant correction, this effect is neglected here.

3. Laplace pressure as a function of temperature

For a spherical droplet, Laplace pressure, p_L is inversely proportional to its radius, r:

$$p_L = 2\frac{\sigma}{r} \quad (4)$$

where σ is the surface tension. It is commonly accepted that a linear trend describes the effect of temperature on surface tension for metal melts. For aluminum in an oxidizing environment, the following equation was proposed [12]:

$$\sigma_{Al}\left[\frac{mN}{m}\right] = 875 - 0.18(T - 933) \quad (5)$$

where temperature is in K. Similarly, for magnesium, the effect of temperature on the surface tension was described as [12]:

$$\sigma_{Mg}\left[\frac{mN}{m}\right] = 577 - 0.26(T - 923) \quad (6)$$

With the above information, the Laplace pressure can be easily estimated for metal droplets of different sizes for both Al and Mg. Thin lines in Figs. 1 and 2 represent such pressures added to an assumed surrounding pressure of 1 bar for particles of different sizes for Al and Mg, respectively.

The intersections of the bold and thin lines indicate the boiling temperatures expected for the respectively sized particles burning in an oxidizing environment at 1 bar.

4. Implications for metal combustion

The effect of Laplace pressure on temperature of the burning Al particles is quite strong. The temperature that a particle can reach increases substantially for finer particles, possibly exceeding the boiling point of Al_2O_3, which is commonly considered to be a practical upper limit for the flame temperature for Al [13]. The precise determination of the boiling temperature of Al_2O_3 is difficult. A considerable disagreement exists between different sources reporting it to be in the range from 3253 K [14,15] to 3800 K [16]. It may be more rational to consider whether fine Al particles can burn in the vapor phase by comparing the predicted boiling temperatures with the reported measured temperatures for the vapor-phase aluminum flames. These temperatures are consistently reported to be in the range of 3000–3300 [17–20] and are likely affected by formation of metastable gaseous products, such as AlO, Al_2O, and AlO_2 and by radiation heat losses. From Fig. 1, it is apparent that particles with radii close to 1 µm and finer can