

On Optical Diagnostics for Oxide Particles and Temperature Measurement in Metal Containing Flame

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The work is devoted to the discussion of the principle possibility of metal containing flame diagnostics by its thermal radiation. It is shown that the temperature usually obtained by the multi-color method may be incorrect temperature of oxide particles generated within flame. It is due to the exponential spectral dependence of the emissivity of the emitting oxide particles.

It is shown that in the case of real temperature experimentally obtained, the properties of emitting oxide particles differ significantly from bulk material. The substance of these oxide particles contains a large number of defects. This may lead to necessity to take into account the energy of defect formation when calculation of heat evolution at metal combustion

INTRODUCTION

The knowledge of the combustion temperature is very important for understanding the processes occurring within flame. In particular, this temperature determines the rate of soot formation in the flames of organic fuel and the rate of oxide formation in the metal containing flames. The latter one is interesting in order to reduce two-phase loss in the rocket engines. The necessity to control oxide formation during the synthesis of particles within flame requires the knowledge of combustion temperature as well. There exist many different methods of the determination of the combustion temperature. These methods could be separated into two groups: 1) the gas temperature determination, and 2) the condensed particle (CP) temperature determination.

Usually it is assumed that there is no the difference between the temperatures obtained by these methods, when the sizes of CP are small ($\leq 0.1\mu\text{m}$), i.e. that the gas temperature and the condensed phase one are the same. However, according to the new result, it recently appeared, the difference between CP and gas temperatures could be essential [1]. At least for the metal containing flames, where the oxide particles are formed, CP temperature can be above and below the gas temperature, depending on the stage of the oxide particle growth. In this case the gas temperature measurement methods (which often are more exact and simpler) are not applicable for CP temperature determination.

CP temperature determination methods are based on the comparison of flame continuous emission spectrum with the Planck function. This comparison requires the assumption about flame emissivity to restore CP temperature. Usually the assumptions about this emissivity have no physical reason, although they seem to be obvious. For instance, the two-color [2] or more advanced the multi-color method [3] assume the grayness of the light source. However, even if this assumption might be correct with a few limitations for soot containing flame, it is wrong (as we will see) for flame radiation emitted by the oxide particles. Indeed, the oxide particle is wide gap insulator as a rule. Due to this the spectral properties of the emitting particle strongly depend in the visible upon the wavelength. This may lead to the wrong result

on CP temperature restoration. The objective of present work lies in analysis of possibility of CP temperature determination by the radiation spectrum in general case when spectral dependence of flame emissivity is not known *a priori*.

FLAME THERMAL RADIATION

Physical Fundamentals

As a rule, the radiation from optical thin flame is studied. In this case the registered luminosity I_λ is the sum of radiation fluxes emitted by single particles within flame. According to the Kirchhoff law we can write for flame containing spherical nanoparticles:

$$I_\lambda = A\lambda^{-5} f_V \int_{T_{\min}}^{T_{\max}} g(T)q(\lambda, T) \left[\exp\left(\frac{hc}{k_B \lambda T}\right) - 1 \right]^{-1} dT, \quad (1a)$$

here A is the constant containing solid angle of the collection optics and the constant $2\pi hc^2$, f_V is the particle volume fraction, $g(T)$ is the function describing the temperature distribution of emitting particles, $T_{\min}$ and $T_{\max}$ are minimal and maximal particle temperatures. The ratio of nanoparticle emissivity to its radius [4]

$$q(\lambda, T) = \frac{24\pi}{\lambda} \frac{\varepsilon''}{(\varepsilon' + 2)^2 + (\varepsilon'')^2}, \quad (2)$$

here $\varepsilon(\lambda, T) = \varepsilon'(\lambda, T) + i\varepsilon''(\lambda, T)$ is the complex dielectric function of particle substance.

In visible region the unity in brackets in Eq. (1a) can be neglected and flame luminosity can be written as

$$I_\lambda = A\lambda^{-5} f_V \int_{T_{\min}}^{T_{\max}} g(T)q(\lambda, T) \exp\left(-\frac{hc}{k_B \lambda T}\right) dT. \quad (1b)$$

In the simplest case of the gray source of light when particle emission coefficient $q(\lambda, T) = \text{const}$ and for the isothermal system when $g(T) = \delta(T - T_p)$, which is often considered, we obtain

$$I_\lambda = \text{const} \lambda^{-5} \exp\left(-\frac{hc}{k_B \lambda T_p}\right) \quad (3)$$

and particle temperature T_p can be restored by the slope of $\ln(I_\lambda \lambda^5)$ upon inverse wavelength. The processing of experimental data according to this way lies in the basis of multi-color method. However, it is not believable that all particles have the same temperature within reacting system. The constancy of value $q(\lambda)$ is also physical unreasonable in general. Due to this Eq. (3) allows obtain only the "average" temperature. In the case of narrow particle

temperature distribution $g(T)$ and if the value $q(\lambda)$ slightly depends on the wavelength this "average" temperature has a physical meaning. But, even if $g(T)=\delta(T-T_p)$ and, for instance,

$$q(\lambda, T) = \exp \left[\frac{hc}{k_B \lambda} \left(\frac{1}{T_p} - \frac{1}{T_*} \right) \right] \quad (4)$$

the use of Eq. (3) gives the temperature T_* instead the correct temperature T_p . The latter illustrates the principle impossibility to obtain the particle temperature using direct spectral measurements. This conclusion contradicts the paper [3] where it claims that it is possible to restore temperature from the flame spectrum. But the assumption about flame emissivity excludes its exponential behavior that is why we believe the result [3] has no the physical generality.

Oxide Particle Emission

Note that exponential behavior of $q(\lambda)$ just might correspond to light absorption mechanism in oxides, where absorption in the visible occurs due to the transition between tails in the forbidden band and in a wide range the emission coefficient spectral dependence is close to the dependence given by the Urbach rule [5]

$$q \sim \exp \left(\frac{E}{E_U} \right). \quad (5)$$

Here E_U is Urbach tail parameter, which value depends on the defect concentration in substance and for quite pure insulators does not exceed the value about 10 meV. From comparison Eq. (4) and Eq. (5) we obtain that the exponential dependence of the emission coefficient temperature leads to errors in determination of temperature in flame by multi-wave method when, after measurements, instead of an actual particle temperature one gets

$$T_* = T_p \cdot \frac{1}{1 - (k_B T_p / E_0)}. \quad (6)$$

In accordance with Eq. (6) one can obtain a real temperature only in case $E_U \gg k_B T_p$. And, at least, E_U is larger than $k_B T_p$ if the experimentally obtained temperature is not negative. The latter means that in the case of a positive value of a temperature obtained in experiment the value of Urbach tail parameter can not be smaller than 200 meV. And in the case of reasonable value of the temperature, which is close to gas temperature, for instance, and does not exceed the boiling point at least, the value of Urbach tail parameter should be about a few eV. This is possible only if substance of emitting particle contains a large number of defects, which means that properties of these particles differ significantly from bulk material. The reason of this difference is related to high rate of particle formation and is analyzed in [6,7]. It should be noted that if a density of defects is too high that Urbach tail parameter is changed significantly compared with bulk material, the energy needed for formation of these defects may be comparable with energy evolution during oxide condensation. In this case, the heat

evolution during metal combustion should be reduced on the energy value stored in defects at the calculation.

In order to illustrate the principle inapplicability of multi-color method of particle temperature determination let us note the result of study of luminosity of $\text{SiCl}_4/\text{H}_2/\text{O}_2/\text{N}_2$ flame irradiated by CO_2 laser [8], where gas temperature is about 2000 K. In this paper the obtained color temperature of silica particle is reported to be about 4000 K. It is obvious, taking into account silica dissolution temperature 3150 K, this temperature is unreal. As it is mentioned above the reason of this unreal value of temperature is related to exponential behavior of particle emission coefficient. So, the Urbach tail parameter for this particle is about 400 meV [9].

At the same time in paper [10] the temperature of alumina particle in aluminium dust cloud flame at the gas temperature 3100 K is obtained to be about 3150 K that seems to be more or less reasonable. This testifies that the Urbach tail parameter for alumina particles in experiment [10] is much greater than the value 0.4 eV obtained for silica particles. Such a large value of Urbach tail parameter for alumina particle is caused by the condensation mechanism of particle formation in flame [6] and is possible only at very high defect concentration in particle substance.

CONCLUSIONS

For the temperature restoration of a particle within flame from the flame thermal radiation spectrum it is necessary to know the spectral dependence of the flame emissivity. This dependence is determined by the particle substance electronic properties. Since these properties depend on the rate of particle formation process within flame, they can not be calculated *a priori*. That is why the temperature of an oxide particle within flame can not be correctly restored in principle from the flame thermal radiation spectrum. At the same time due to large value of energy stored in defects of particle substance the heat evolution during metal combustion may be smaller than it is usually considered.

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