REACTION BEHAVIOR OF SINGLE SLURRY DROPLET OF ZINC CONCENTRATE IN HIGH TEMPERATURE GAS FLOW[1]

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Abstract

One of the measure route to produced metallic zinc from natural zinc recources is hydrometallurgical path. In this route roasting process of zinc concentrate in which zinc sulfide is converted to zinc oxide is included. Recent change in supply of zinc resources causes operation troubles in this process. To deal with such troubles, it is necessary to clarify the reaction behavior of zinc concentrate slurry. This study investigated the behavior of single droplet of zinc concentrate slurry in high temperature gas flow through experiments and numerical simulations. A slurry droplet of zinc concentrate is suspended by a thin thermocouple and inserted into high temperature gas flow which had uniform velocity. The changes in appearance and temperature of the droplet were recorded. The observation results clarified that the roasting process of the slurry droplet consisted of preheating period, drying period and heating/reaction period. Heat and mass balance equations were applied to each period to analyze temperature variations of the slurry droplets under no oxygen condition. The results showed that the drying period was farther divided into constant drying rate period and decreasing drying rate period. Numerical analyses of heat balance equation on a slurry droplet that took into account heat exchange with gas flow, moisture evaporation and reaction heat were carried out to estimate the temperature variation of the slurry droplet under oxidizing condition. Apparent reaction rate constant used in the analyses was obtained from the difference of temperature variation in no oxygen and oxidizing conditions. The mathematical simulation successfully reproduced the temperature variation obtained in the experiments under various conditions.

Key words: Zinc concentrate; Roasting; Single slurry droplet.

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1 INTRODUCTION

One of the measure route to produced metallic zinc from natural zinc resources is hydrometallurgical path. In this route roasting process of zinc concentrate is included, and fluidized bed roaster is widely used for this process. The fluidized bed roasters have shallow bed of zinc concentrate in which zinc sulfide is converted to zinc oxide. A part of the roasted concentrate that have smaller diameter flows out with gas flow as carry over, and the other part spills out from fluidized bed as over flow.

Recent change in supply of zinc resources causes operation troubles in this process, for example increase in carry over particles and deterioration of fluidization due to irregular enlargement of particles. To deal with such troubles, it is necessary to understand the reaction behavior of zinc concentrate in the roasting fluidized bed. There are various method to feed the zinc concentrate to the roaster, such as slurry, agglomerate, and so on. This study investigated the behavior of single droplet of zinc concentrate slurry in high temperature gas flow through experiments and numerical simulations.

2 EXPERIMENTS

To clarify the effect of various reaction parameters on roasting behavior of zinc concentrate in the fluidized bed roaster, reaction behavior of single slurry droplet in high temperature gas flow is observed. Figure 1 shows a schematic diagram of the experimental apparatus. Air and nitrogen gas are fed respectively from the compressor and gas cylinder and their flow rates are appropriately controlled. The mixture of these two gases are heated up to the preset temperature. The interior of gas heater has a shape which makes outlet gas velocity uniform at the exit of the gas heater. A slurry droplet of zinc concentrate is suspended by a thermocouple having diameter of 200 μm and inserted into the upward high temperature gas flow. The temperature of slurry droplet is recorded by the data acquisition device and the appearance of the droplet is videotaped during roasting. The conditions for the measurements are set as follows; a) volume of the slurry droplet is from 1×10^{-8} to 3×10^{-8} m^3, b) oxygen concentration in the gas flow from 0 to 21 vol-%, c) gas flow temperature from 380 to 800°C, gas flow velocity at 0.5 m/s.

3 HEAT BALANCE OF SLURRY DROPLET

To derive a heat balance equation which describes temperature variation of slurry droplet of zinc concentrate, uniform temperature in a slurry droplet is assumed. The heat balance equation takes into account the heat exchange between the droplet and gas flow, latent heat of water evaporation, and oxidation of zinc sulfide.

$$m_{\mathrm{SL}} C_{P,\mathrm{SL}} \frac{dT_{\mathrm{SL}}}{dt} = hA_{\mathrm{SL}}(T_{\mathrm{g}} - T_{\mathrm{SL}}) - L_{\mathrm{w}} \frac{dm_{\mathrm{w}}}{dt} + \alpha \Delta H_{\mathrm{ZnO}} \frac{dm_{\mathrm{ZnS}}}{dt} - T_{\mathrm{SL}} \frac{d(m_{\mathrm{SL}} C_{P\mathrm{SL}})}{dt} \tag{1}$$

The heat transfer coefficient h in the first term of left side is estimated by the Ranz-Marshall equation.[1]

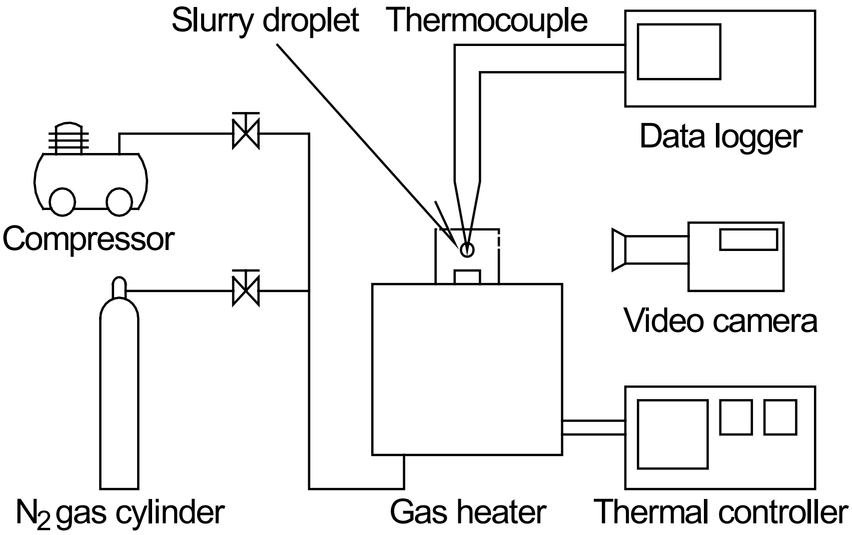

Figure 1 Schematic diagram of experimental apparatus.

$$\frac{h\, d_{\mathrm{SL}}}{\lambda_{\mathrm{mix}}} = 2.0 + 0.6\left(\frac{C_{P,\mathrm{mix}}\, \mu_{\mathrm{mix}}}{\lambda_{\mathrm{mix}}}\right)^{1/3}\left(\frac{d_{\mathrm{SL}}\, u_{\mathrm{g}}\, \rho_{\mathrm{mix}}}{\mu_{\mathrm{mix}}}\right)^{1/2} \tag{2}$$

4 RESULTS AND DISCUSSION

4.1 Experimental Results

Figure 2 compares temperature variations of slurry droplet having volume of $2\text{x}10^{-8}$ m^3 in 800 $^{\text{o}}$C gas flows of which oxygen concentrations are 0 and 15 vol-%. In both case, the droplets are heated up to about 70$^{\text{o}}$C in 4 s after being inserted into the high temperature gas flow, and the temperatures are kept almost constant for about 13 s. Then the droplet temperatures rise again. Under no oxygen condition, the droplet temperature monotonically rises up to a final temperature. Contrarily under the oxidizing condition, the droplet temperature once exceeds the final temperature and shows peak value, then cools down to the final temperature. The heating rate in this step is higher than non-oxidation condition. These differences are considered due to the reaction heat of oxidation of the zinc sulfide. The final temperatures in these cases are the same and are slightly lower than the gas flow temperature. The period in which the droplet temperature is higher than the final droplet temperature in the oxidizing condition is called “overshoot period” hereinafter.

From the videotaped appearance of slurry droplet and the above temperature variations, it is considered that the roasting of a slurry droplet of zinc concentrate consists of three sequential periods as shown in Figure 3. First one is preheating period in which the droplet is heated up to water evaporation temperature. Second is drying period in which the water in the slurry droplet evaporates and droplet tempreature is almost constant. Third is heating/reaction period in which the droplet temperature rises again and the zinc sulfide in the concentrate is oxidized to zinc oxide.

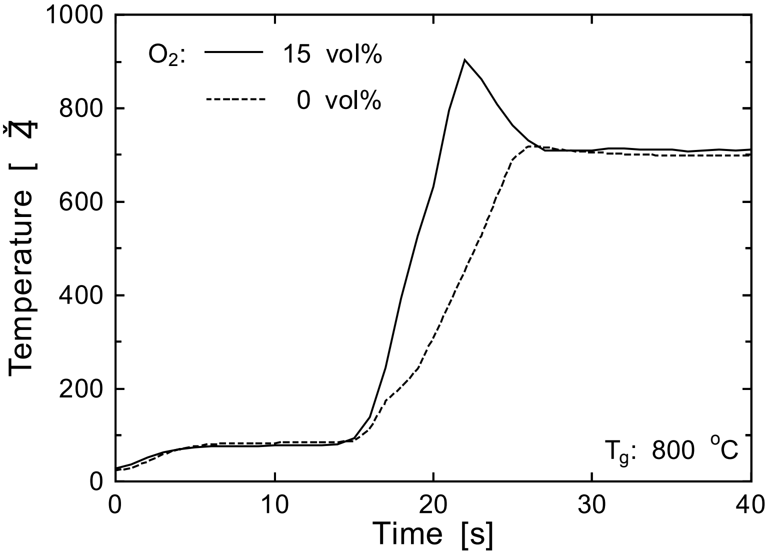

Figure 2 Typical temperature variations of ZnS-H_2O slurry droplets in high temperature gas flow.

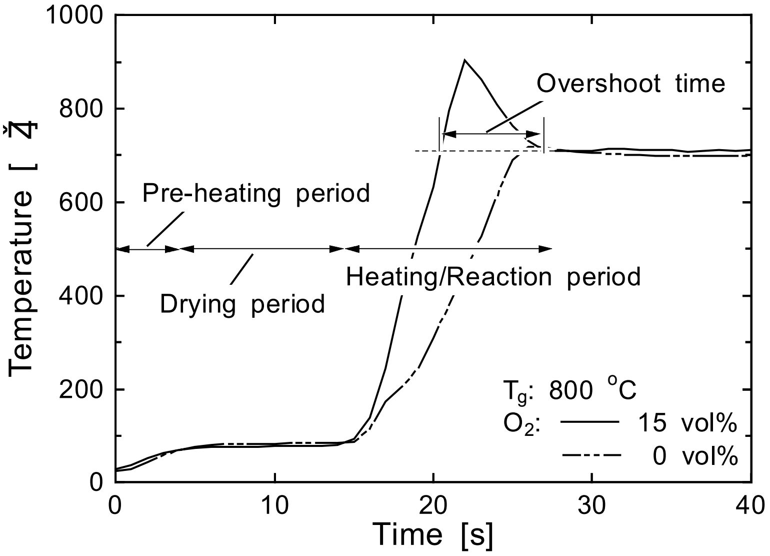

Figure 3 Roasting process of ZnS-H_2O slurry droplets.

Figure 4 compares the droplet temperature variations in 570 °C gas flows of which oxygen concentrations are 0, 5, 10 and 15 vol-%. The temperature variations show similar trend shown in Figure 3. Among these variations, the heating rate in the preheating period, the temperature and the constant temperature duration in the drying period, and the final temperature are common. The heating rate in the heating/reaction period and duration of overshoot period depends on the oxygen concentration. The heating rate and the peak temperature increase with oxygen concentration while the overshoot period shortens.

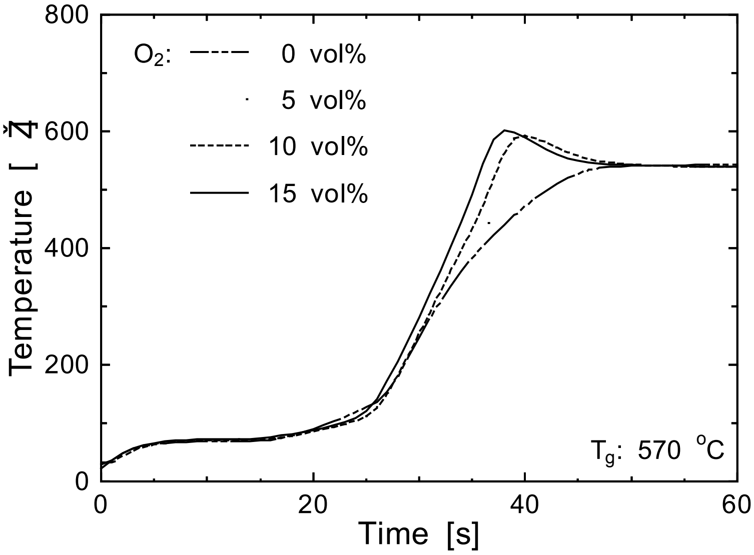

Figure 4 Effect of oxygen concentration on temperature variation of slurry droplet.

Figure 5 shows the effect of gas flow temperature on the variation of slurry droplet temperature. The variations obtained in the 800, 570 and 380 °C gas flow and the oxygen concentrations of 0 and 15 vol-%. Although the temperature variation follows the trend shown in Fig. 3, details in each period depend on the gas temperature. The heating rate in the preheating period and the temperature in the drying period increase with the gas flow temperature. In the heating/reaction period, the heating rate and overshoot temperature increases with gas flow temperature while the duration of overshoot period gets shorter. No overshoot appears in the condition under gas temperature of 380°C because the temperature is too low to oxidation of zinc sulfide occur.

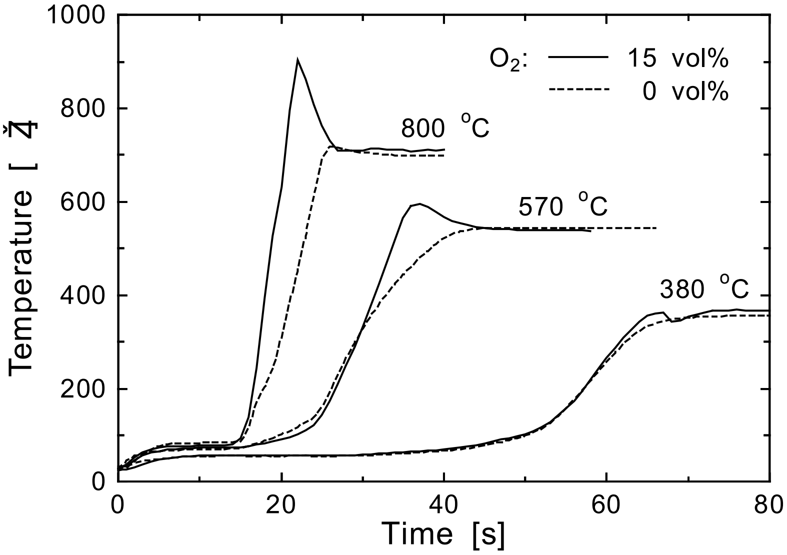

Figure 5 Effect of gas flow temperature on variation of slurry droplet temperature.

Figure 6 shows the effect of slurry droplet volume on the temperature variation. Three variations for droplet volumes of 1, 2 and 3 x 10^{-8} m^3 in gas flow of 570 °C and 15 vol-% of oxygen concentration are shown in the figure. The peak and final temperatures are almost same among these droplet volume. The heating rates in the preheating and heating/reaction periods and the temperature in the drying period increase, and durations of drying period and overshoot become shorter with decrease in droplet volume.

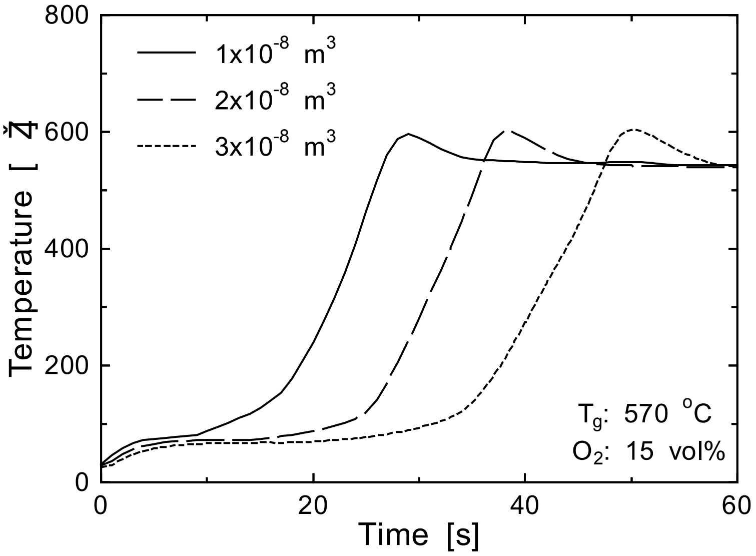

Figure 6 Effect of slurry droplet volume on temperature variation.

From these results, the trend of temperature variation is independent of reaction conditions. Thus the roasting of slurry droplet of zinc concentrate is considered to proceed through preheating, drying and heating/reaction periods.

4.2 Analysis of Temperature Variation under Non-Oxidizing Condition

In the condition under which there is no oxygen in the gas flow and no oxidation of ZnS occurs, the temperature variation of a single droplet of zinc concentrate slurry is able to be analytically estimated by using the heat transfer equations transformed from Eq. (1) for each reaction period. In the preheating period, the heat balance equation is given as follows with the assumption of no water evaporation and reaction.

$$m_{\mathrm{SL}} C_{p,\mathrm{SL}} \frac{dT_{\mathrm{SL}}}{dt} = hS_{\mathrm{SL}} (T_{\mathrm{g}} - T_{\mathrm{SL}}) - T_{\mathrm{SL}} \frac{d(m_{\mathrm{SL}} C_{p,\mathrm{SL}})}{dt} \tag{3}$$

The preheating period finishes when the droplet temperature reaches water evaporation temperature. In the drying period the droplet temperature is constant and the heat transferred from gas flow to slurry droplet is consumed as the latent heat of water evaporation. Thus the drying rate in this period is given as follows.

$$\frac{dm_{\mathrm{w}}}{dt} = \frac{hS_{\mathrm{SL}} (T_{\mathrm{g}} - T_{\mathrm{SL}})}{T_{\mathrm{SL}} C_{\mathrm{p,w}} - L_{\mathrm{w}}} \tag{4}$$

The drying period is assumed to continue while the water in the slurry droplet exist. For the heating/reaction period under non-oxidizing condition, no evaporation and reaction of ZnS occurs. Thus the temperature variation in this period is also described by Eq. (3). The temperature variations during whole roasting process are obtained by connecting the transient temperature profiles of three reaction periods.

Initial temperature of each period is given by the final temperature of preceding period.

The comparisons between measured and estimated temperature variations for gas flow temperatures of 380 and 800°C are shown in Figure 7. The estimated temperature variations well describes measured trend. They, however, show some discrepancy in heating rate in preheating period, initial behavior in heating/reaction period, and final temperature.

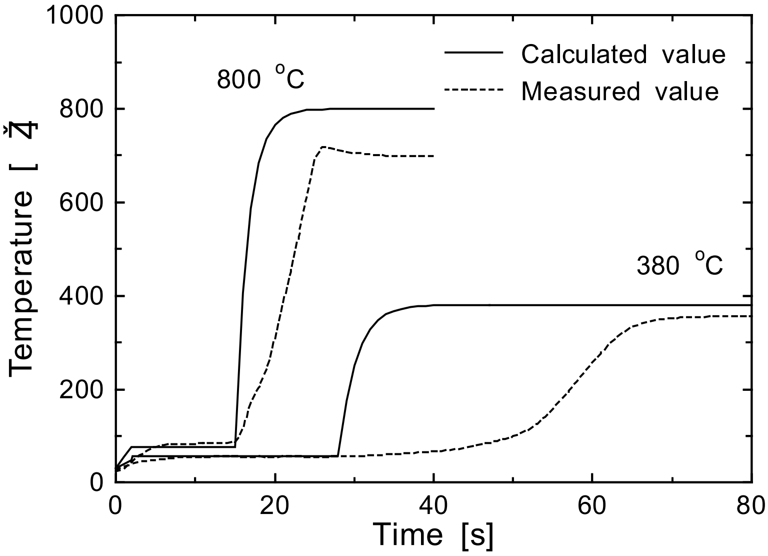

Figure 7 Calculated and measured temperature variations of slurry droplet in high temperature gas flow.

The estimated heating rates in the preheating period is slightly higher than the calculated ones. It is considered that the temperature difference is formed even in a small droplet, and this decreases heat transfer rate from gas flow to the droplet. Additionally the water evaporation from the droplet surface is possibly to occur. The calculated heating rates in the heating/reaction period are also higher than the measured one.

In the analysis the drying period finishes when the water evaporation completes, and then the temperature starts to rise. The rates of water evaporation and heating are determined by Eqs. (4) and (3), respectively. In the measured temperature variation, the period of slow heating exists between drying and heating/reaction periods. Many drying processes consists of two steps. One is constant rate drying period in which the temperature of drying material and drying rate are almost constant, and the other is decreasing rate drying period in which the temperature of the material rises and drying rate decreases with proceed of drying. It is considered that the period with slow temperature rise corresponds to the decreasing rate drying period. The moisture content at which drying scheme changes from constant to decreasing rate is called the critical moisture content. The moisture content when the droplet temperature starts to rise is calculated from the duration that the droplet temperature is kept constant and Eq. (4), and summarized in Table 1. The moisture content is almost independent of reaction condition. The average value is about 2.2 kg-H_2O/kg-ZnS and is used as the critical mositure content for the materials used in this study.

The calculated final temperatures are slightly higher than measured ones. The discrepancy increases with the gas flow temperature. Thus it is due to the heat loss through the thermocouple and thermal radiation.

Table 1 Effect of gas flow temperature on drying behavior of slurry droplets.

Gas temperature [^{o}C]	Drying time [s]	Drying rate [kg/s]	Moisture content [kg-H_2O/kg-ZnS]
380	19	-6.19×10^{-7}	2.19
570	10	-1.44×10^{-6}	2.25
800	6	-2.71×10^{-6}	2.24

4.3 Analysis of Temperature Variation under Oxidizing Condition

For the analysis of temperature variation of zinc concentrate slurry droplet, it is necessary to estimate the moisture evaporation rate in decreasing rate drying period and releasing rate of reaction heat of ZnS oxidation. Additionally the consective roasting steps overlap each other. Thus the Eq. (1) is numerically integrated using the Runge-Kutta-Gill method to analyze the temperature variation of slurry droplet. The water evaporation rate in the constant rate period is given by Eq. (4). The rate in the decreasing rate period depends on the moisture content in general. In this analysis it is assumed that the drying rate is a half of one in constant rate period and the heat transferred from the gas flow to the droplet is equally used for droplet heating and water evaporation.

The oxidation reaction of ZnS takes place at the surface and inside of the slurry droplet. The reaction heat is given to the droplet and surrounding gas. It is postulated that the ratio of the heat supplied to the droplet is given by the following equation.

$$\alpha = \frac{m_{\mathrm{ZnO}} C_{P,\mathrm{ZnO}}}{m_{\mathrm{ZnO}} C_{p,\mathrm{ZnO}} + m_{\mathrm{N_2}} C_{p,\mathrm{N_2}} + m_{\mathrm{SO_2}} C_{p,\mathrm{SO_2}}} \tag{5}$$

The reaction rate is assumed proportional to both oxygen concentration in the gas flow (C_{O2}) and ZnS content in the slurry droplet (C_{ZnS}).

$$\frac{dm_{\mathrm{ZnS}}}{dt} = -A_{\mathrm{SL}} k C_{\mathrm{O_2}} C_{\mathrm{ZnS}} \tag{6}$$

where the reaction rate constant k is expressed as the Arrhenius type equation.

Figure 8 shows a comparison of measured and estimated temperature variation under temperature of 800 ^{o}C, oxygen concentration of 21 % and droplet volume of $2\mathrm{x}10^{-8}$ m^3. The estimated temperature variation well describes measured variation while some discrepancies exist in heating rate in preheating period, temperature level in heating/reaction period and final temperature. The reason for these discrepancies are considered same in the non-oxidizing condition. The temperature variations in the other conditions are also estimated well.

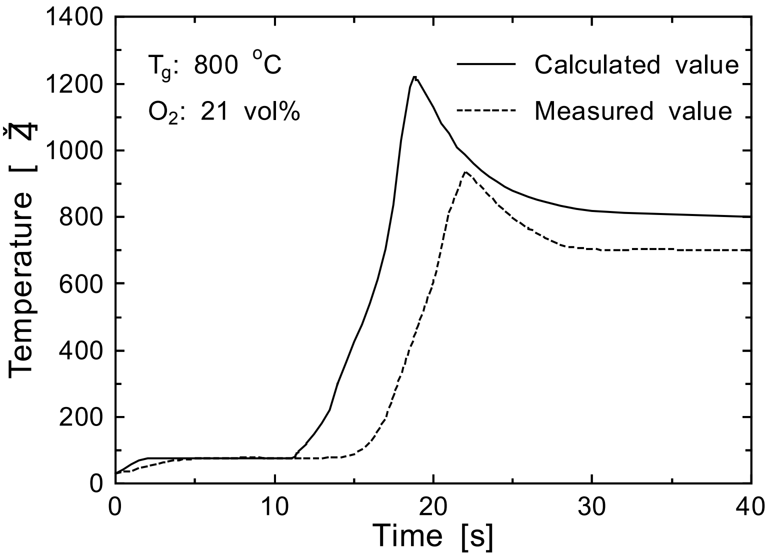

Figure 8 Comparison of measured and calculated temperature variations in oxidizing condition.

5 CONCLUSIONS

Reaction behavior of single slurry droplet of zinc concentrate in high temperature gas flow was investigated. From the experimental results obtained under various reaction condition, it was showed that the roasting process consisted of preheating, drying and heating/reaction periods. The mathematical discussion revealed that the drying process was further divided into constant rate and decreasing rate drying periods even in the small droplet conditions. According to these results, a mathematical model of temperature variation of zinc concentrate slurry droplet was formulated by including fairly simplified expressions of decreasing rate drying and oxidation of ZnS. This model successfully reproduced temperature variation during roasting process of zinc concentrate.

NOMENCLATURE

A: surface area [m^2]
C: concentrate [mol m^{-3}]
C_P: heat capacity [J mol^{-1} K^{-1}]
d: diameter [m]
h: heat transfer coefficient [W m^{-2} K^{-1}]
ΔH: reaction heat [J mol^{-1}]
k: reaction rate constant
L: latent heat of vaporization [J mol^{-1}]
m: amount of substance [mol]
T: temperature [K]
t: time [s]
u: velocity [m s^{-1}]

Greek symbols

α: factor [-]
λ: thermal conductivity [W m^{-1} K^{-1}]
μ: viscosity [Pa s]
ρ: density [kg m^{-3}]

Subscript

g: gas flow
mix: mixture
N_2: nitrogen
O_2: oxygen
SL: slurry
SO_2: sulfur dioxide
w: water
ZnS: zinc sulfide
ZnO: zinc oxide

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