Quasi-Stable Temperature of the Steady State of Microwave Heated Hematite

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Abstract

Microwave heated materials often reach a quasi-stable temperature resulting in thermal runaway. To control the quasi-stable temperature in microwave processing, it is important to predict the quasi-stable temperature of the steady state. We demonstrated that the microwave heating behavior of hematite varies significantly with its initial temperature. In microwave heating experiments, the temperature of hematite that had not been preheated did not increase, whereas hematite that had been preheated to 410 °C or higher was heated to a temperature of 1020 °C. The microwave heating behavior can be accurately predicted by considering the steady-state energy balance.

Keywords: [metal oxides, 2.45 GHz, microwave processing, hematite, stability of processing]

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1. INTRODUCTION

Microwave heating has been attracting great interest as a new means of supplying energy to processes. Microwave heating can produce metal sintered compacts that differ from conventional ones due to the generation of non-equilibrium temperatures on the microscale [1-6]. Ishizaki and Nagata [2] constructed a high-power (12 kW) continuous 2.45-GHz microwave furnace and Peng *et al.* [3] constructed a 915-MHz, 225-kW microwave furnace to scale up steel production. The above mentioned studies all used microwave energies, resulting in rapid chemical synthesis. Microwave heating of powder compacts has been studied for several decades with a view to applying such a technique to industrial processes. Cheng *et al.* [7] compared the heating rates of metals, ceramics, and metal-ceramic composites in different microwave fields. They found that the magnetic component cannot be ignored when considering the energy loss in metals subjected to a microwave field. Ma *et al.* [8] systematically investigated the absorption and heating characteristics and the microstructural evolution of porous copper powder metal compacts irradiated with 2.45-GHz microwaves. They observed the heating characteristics of copper particles with various radii. The above studies [7-9] demonstrate that the Mie theory for a single particle can account for the high heating rates generated by the microwave magnetic field in microwave sintering experiments.

In contrast, few studies have used stability theory to predict the steady-state temperature of microwave heating despite the importance of steady-state temperature prediction for industrial processing. To realize efficient microwave processing, the temperature of high temperature in the steady

state (i.e., the thermal runaway) should be predicted (In this paper, this temperature is defined as the quasi-stable temperature). However, two problems need to be overcome to make this possible. The first is the scarcity of data for the absorption properties as a function of temperature. Most measurements of microwave absorption properties have been performed at temperatures near room temperature. The absorption properties of materials like ceramics change drastically at high temperatures [10-11], which greatly affects the steady-state temperature. The absorption properties of a material need to be known to accurately predict steady-state temperatures. The second problem is the difficultly in constructing a high-power microwave applicator. It is in the microwave heating behavior of a poor microwave absorber that a quasi-steady temperature is likely to be observed. However, it is difficult to heat poor absorbers using pure microwaves.

In the present study, we experimentally demonstrate that the microwave heating behavior of high-power microwave applicators can be predicted by considering the steady-state energy balance. We first investigate the temperature dependence of the microwave absorption properties of hematite at frequencies in the range 1-13.5 GHz (hematite is considered to be a poor microwave absorber; we selected hematite to observe the quasi-steady-state temperature). Using a system whose reaction system is separate from the heating system, we found that the heating behavior of hematite varies significantly with its initial temperature.

2. EXPERIMENTAL PROCEDURE

2.1. ABSORPTION PROPERTIES OF HEMATITE

This study used hematite powder consisting of 0.5-μm-diameter α-Fe$_2$O$_3$. The real and imaginary parts of the relative permittivity (ϵ'_r and ϵ''_r) were measured over the temperature range 25-1000 °C by the coaxial transmission line method using a network analyzer (Agilent Technologies, N5230A), coaxial cables, and an APC7 coaxial sample holder over a microwave frequency range of 1-13.5 GHz (see Fig. 1). Using an electric resistance furnace, the temperature was increased at a rate of 10 °C/min during measurements. The transmission and reflection (S parameters) of the irradiated microwaves were measured about every 50 °C during the heating cycle. The network analyzer had an output power of ca. 1 mW. Each measurement was performed over a frequency range of 1-13.5 GHz and took about 2 s. The complex permittivity was calculated from the S parameters using the algorithm of the NIST precision method [12].

The compressions were applied to both sides of the powder and the compacts were fixed to a volume of ϕ3.04 x 7 mm^3 in this measurement. Because hematite particles have a diameter of 0.5 μm and a weight of 0.875 g, this device made compacts with a constant relative density of 1.75 g/cm^3.

In this experiment, the sample was heated using an electric resistance furnace. The heat was generated in an isolated furnace, meaning there was some latency in terms of the heat reaching the center of the coaxial chamber. The temperature was measured by a thermocouple attached to the outer wall of the holder instead of a thermocouple embedded in the sample (the heating rate was 10 °C /min). The measured temperatures were hence indicated

4

temperatures, so calibration was necessary to obtain the true temperatures. To calibrate the outer thermocouple, the apparent and true temperatures were measured simultaneously during a heating cycle using an additional thermocouple embedded in the sample.

2.2. HEATING SYSTEM

Figure 2 shows a schematic diagram of the microwave applicator used. This applicator has a 2.45-GHz magnetron oscillator ($\times$ 8), an isolator, WRJ-2 waveguides, stirrers, and a furnace body. The magnetrons generate 2.45 GHz microwaves at a total output power of 12 kW (1.5 $\times$ 8 kW). The body consists of a hexagonal cylinder and a half sphere ($\times$ 2); these shapes focus microwaves onto the sample. In this system, the reaction system is separate from the heating system. The sample was preheated by an electric furnace to a sufficiently high temperature and microwaves (3 kW) were focused onto the sample, as shown in Fig. 2. In these experiments, carbon and magnetite powders were also employed as samples for comparison with hematite.

3. RESULTS AND DISCUSSION

3.1. ABSORPTION PROPERTIES

Before discussing the quasi-stable temperature of the steady state during microwave heating, we must understand the absorption properties. Figures 3(a)-(e) show plots of the real and imaginary parts of the relative permittivity (ϵ'_r and ϵ''_r) of α-Fe_2O_3 powders (particle size: 0.5 μm; relative density: 1.75 g/cm^3) as a function of temperature for frequencies of 1, 2.45, 5 7.5, 10, and 13.5 GHz, respectively. At all frequencies, ϵ''_r was observed to increase with

increasing temperature at temperatures of 800 °C or lower. Since ceramics are highly conductive in this temperature, the permittivity of the α-Fe_2O_3 powder is $\epsilon"_r \approx (\sigma/\omega) \times i$ (where σ is the static electrical conductivity and i was the current from the electrical gradient). The increase in $\epsilon"_r$ must be due to an increase in the electrical conductivity, considering that there were no chemical reactions in this experiment. Some researchers reported anomalous behaviors of chemical reactions even though the phase diagram indicates that hematite is stable at high oxygen partial pressures. We did consider the possibility of permeability changes due to chemical reactions; however, we removed this possibility by measuring the stability of hematite in air using XRD at high temperatures; no reaction was observed. As a result of this, we thought that Fe_2O_3 exhibits metallic behavior at the present microwave frequencies due to the high free electron density near the Fermi level at temperatures of 800 °C and higher. Consequently, $\epsilon"_r$ decreases with increasing temperature above 800 °C (see Refs. 9, 11, and 13-14 for detailed descriptions of the mechanism in terms of polarization and polaritons).

3.2. METASTABLE TEMPERATURE IN MICROWAVE HEATING

Steady-state theory predicts metastable temperatures in the steady state for microwave heating. Considering the above results, we regard the input and output powers as functions of temperature. The input power of the hematite powder compact per volume is given by

$$w_{in}(T) = \int_V \frac{1}{2}(\omega\epsilon^{''}(T) \mid E \mid^2 + \omega\mu^{''}(T) \mid H \mid^2)dV \qquad (1)$$

, where $w_{in}(T)$ is the input power per volume at the observation point (note another form of eq. (1) includes the energy transition induced by the cur-

rent; in this paper, we employ the above form), $\epsilon''(T)$ is the imaginary part of the dielectric permittivity (N/V^2), $\mu''(T)$ is the magnetic permeability (N/A^2), E (or H) is the electric (or magnetic) intensity (V/m or A/m), and ω is the angular frequency (rad/sec) of electromagnetic field. For hematite, the second term in eq. (1) is negligible so that $w_{in}(T)$ is proportional to $\epsilon''(T)$ (permittivity >> permeability) [15]. Assuming that hematite does not modify the electric field strength, the temperature dependence of $w_{in}(T)$ is entirely contained in $\epsilon''(T)$ (in this paper, the integral was taken to be the total input energy for a sample, $P_{in}(T)$). In contrast, the substrate energy from a hematite powder compact is given by

$$w_{out}(T) = \int_S h(T - T_{air})dS + \frac{d}{dt}\int_V \int \rho C(T)dTdV + \int_S \theta\delta(T^4 - T_{sur}^4)dS$$

(2)

, where h is the heat transfer coefficient (Wm^{-2} K^{-1}), T_{air} is the temperature of air (K), T_{sur} is the surrounding wall temperature (K), $C(T)$ is the heat capacity at constant volume ($Jmol^{-1}K^{-1}$), δ is the Stefan-Boltzmann constant ($= 5.67 \times 10^{-8}Wm^{-2}K^{-4}$), θ is the emissivity (=0.96), t is time (sec^{-1}), and ρ is the molar density(mol m^{-3}). When $w_{in}(T) = w_{out}(T)$, the second term on the right-hand side of eq. (2) is nearly zero. The third term on the right-hand side of eq. (2) affects $w_{out}(T)$ at high temperatures; hematite exhibits a nonlinear relationship between $w_{out}(T)$ and temperature in this temperature range.

Figure 4 shows a schematic plot of P_{out} (black line) and P_{in} for a poor absorber like hematite (red line) and a good absorber like magnetite or carbon (blue line) as a function of temperature. In this figure, the P_{in} curves are for non-magnetic materials. For poor absorbers, $P_{in} = P_{out}$ at temperatures of

7

Ta, Tb, and Tc. As Fig. 4 shows, $P_{in} < P_{out}$ at T', whereas $P_{in} > P_{out}$ at T''. Hematite exhibits a steady temperature between Ta and Tc. In contrast, hematite exhibits chaotic heating behavior at Tb. Hematite is expected to exhibit an unsteady temperature at this temperature. For absorbers, $P_{in} > P_{out}$ at temperatures lower than that indicated by the blue circle in Fig. 4. In this region, the excess energy causes the temperature to vary greatly, as indicated by the blue circle.

Here, we will introduce a comparison of the concept illustrated in Fig. 4 with experiment results. Figures 5(a)-(b) show plots of the temperature over time for hematite and preheated hematite for different particle sizes. Microwave absorbers such as graphite and magnetite powder compacts exhibit steady temperatures without preheating (carbon powders showed maximum microwave absorption at 1000 °C or higher [16]). For the case, $P_{in} > P_{out}$ at any temperature below that indicated by the blue circle in Fig. 4 and the concept accounts for phenomena well. In this experiment poor absorbers exhibited the predicted heating behavior, which was dependent on the temperature range. Preheated hematite exhibits a temperature dependence different to that of hematite that was not preheated. The temperature of hematite that had not been preheated did not increase because it did not gain sufficient energy to be heated by the electric field. In contrast, hematite that had been preheated to a temperature of 410-600 °C or greater was microwave heated to a temperature of 1020-1220 °C. In this case, hematite gained sufficient energy to be heated by the electric field. Tb and Tc can be predicted by steady-state theory. Using eqs. (1) and (2), Tc was estimated to be 1080-1100 °C (where $V = 3.38$ x 10^{-5} m^3, $S = 6.45$ x 10^{-3} m^2, $\theta = 0.96$, h = 75.8 Wm^{-2} K^{-1},

8

T_{air} =25 °C, and T_{sur} = 25 °C) and the relation $\mid E \mid^2 = \sqrt{\frac{\mu}{\epsilon}} W_{mw}$ F/m was employed to convert W_{mw} (Microwave power) to E [17]. The estimated values for Tc agree well with the experimentally measured values. Steady-state theory predicts that ceramics with poor absorption properties can be heated to a high temperature; it is also useful for predicting the steady-state temperature in microwave processing. Considering that we used XRD during the microwave irradiation and no magnetite peaks were observed, the application of the concept is adequate and the concept describes the phenomena well.

However, the estimated value of Tb (680 °C) differs greatly from the measured value (410-600 °C). This is because the estimation was based on a model in which the temperature distribution is assumed to be uniform within the material. Microwaves generate micro-hot spots, which have higher temperatures than other places. These micro-hot spots generate higher temperatures in their vicinity because they are selectively heated. Further studies are needed to address the micro-hot spots quantitatively.

4. SUMMARY

We experimentally demonstrated the temperature behavior in given temperature ranges for microwave heated materials and observed the existence of quasi-stable-state temperature in microwave heating. Applying high-power microwaves, the temperature of hematite that had not been preheated did not increase, whereas hematite that had been preheated to 410-600 °C or higher was heated to a temperature of 1020-1220 °C. This is because the preheated hematite gained sufficient energy to be heated by the electric field due to its good absorption. To predict the heating behavior, we investigated the temperature dependence of the absorption properties of hematite at microwave frequencies in the range of 1-13.5 GHz. The microwave heating behavior can be accurately predicted by considering the steady-state energy balance and we found that the heating behavior and properties of hematite vary significantly with initial temperature.

To control thermal runaway in microwave processing, it is important to predict the quasi-stable-state temperature. From these results, we confirmed that the microwave heating behavior of hematite varies significantly with initial temperature as predicted by the theory and models. This theory is useful for determining the process temperature for microwave processing.

REFERENCES

[1] R. Roy, D. Agrawal, J. Cheng and S. Gedevanshvili: Nature, 399 (1999) 668

[2] K. Ishizaki and K. Nagata: ISIJ International, 47, 6 (2007) 811-816

[3] Z. Peng, J. Y. Hwang, M. Andriese, W. Bell, X. Huang and X. Wang: ISIJ International, 51, 6 (2011) 884-888

[4] W. Sutton: Am. Ceram. Soc. Bull 68, 2, (1989) 376-86

[5] J. H. Booske, R. F. Cooper, S. A. Freeman: Mater. Res. Innovat. 1 (1997) 77-84

[6] N. Yoshikawa, E. Ishizuka, K. Mashiko, S. Taniguchi: Mater. Lett. 61 (2007) 2096-2099

[7] J. Cheng, R. Roy, D. Agrawal: Journal of Materials Science Letters, 20 (2001) 1561-1563

[8] J. Ma, J. F. Diehl, E. J. Johnson, K. R. Martin, N. M. Miskovsky, C. T. Smith, G. J. Weisel, B. L. Weiss and D. T. Zimmermana: Journal of Applied Physics, 101 (2007) 074906

[9] K. Kashimura, S. Suzuki, M. Hayashi, T. Mitani, K. Nagata and N. Shinohara: Journal of Applied Physics., 112, 3 (2012) 034905

[10] M. Hotta, M. Hayashi, A. Nishikata and K. Nagata: ISIJ International, 49, 9 (2009) 1443-1448

[11] Z. Peng, J. Hwang, J. Mouris, R. Hutcheon and X. Huang: ISIJ International., 50, 11 (2010) 1590-1596

[12] J. B. Jarvis: Transmission/Reflection and Short-circuit Line Permittivity Measurements, NIST (1990) [http://www.nist.gov/pml/, Access: 2012-10-18]

[13] R. Roy, P. Peelamedu, L. Hurtt, J. P. Cheng and D. Agrawal: Materials Research Innovations, 6 (2002) 128-140

[14] M. Hotta, M. Hayashi and K. Nagata: ISIJ International, 51, 3 (2011) 491-497

[15] Supporting information: This is a very common assumption used when measuring samples that are thought to be non-magnetic. These measurements do however take into account the possibility of non-zero magnetic permeability, but these results seem to never have been saved for high temperature measurements. In house measurements at room temperature shows an imaginary effective permeability of less than background (<0.1 at 2.45GHz). Similar results at higher temperatures are shown by Peng *et al.* : ISIJ International, Vol. 52 (2012), No. 9, pp. 1535-1538

[16] M. Hayashi, K. Takeda, K. Kashimura T. Watanabe and K. Nagata: Carbothermic reduction of hematite powders by microwave heating, ISIJ International, Vol. 53, 7 (2013) 1125-1130

[17] Supporting information: Supplement Figure indicates heating behavior of cooling in this apparatus. Parameters for P_{out} ($\theta = 0.96$, h = 75.8 Wm^{-2} K^{-1}) were estimated from this behavior. In this estimations, h were estimated from the cooling behavior of low temperature and θ were from that of high temperature because P_{out} are described by eq. (2). In this case, the forward and reflect power meters have a large margin of error because closed systems focuses microwave on (or away from) the power meter. We gave no credence to information that the reflected wave showed less than 10 % of input in their powers and employed traveling wave approximation for this estimation.

FIGURE CAPTIONS

FIG. 1: Setup used to measure the relative permittivity. The sample holder is made of SUS316L stainless steel and is 300 mm long. An R-type thermocouple was attached to the sample holder using Pt wire. The apparent temperature ($Tapp$) varies almost linearly with the true temperature ($Ttrue$) according to $Tapp = Ttrue \times 1.0313 + 43.237$. This equation was used to correct the temperature for all data.

FIG. 2: Schematic diagram of the microwave applicator. The magnetrons generate 2.45 GHz microwaves with a total output power of 12 kW (1.5 x 8 kW). The applicator chamber in the shape of a hexagonal cylinder was closed by two half spheres; this shape promotes focusing of the microwaves onto the sample. In this experiment, 3 kW microwaves were applied to the sample. The samples, which were in a reaction room, were separated from the heating system using quartz tubes (quartz A, I.D.: 46 mm) and the temperature of the chamber was maintained by thermal insulation around the tubes.

FIG. 3: Temperature dependences of the relative complex permittivity (ϵ'_r and ϵ''_r) of α-Fe_2O_3 powder (particle size: 0.5 μm; relative density: 1.75 g/cm^3) at frequencies of (a) 1, (b) 2.45, (c) 5, (d) 7.5, (e) 10, and (f) 13.5 GHz. At all frequencies, ϵ''_r was observed to increase with increasing temperature at temperatures of 800 °C or lower. At high temperature, hematite's absorption properties decrease similarly to metal.

FIG. 4: Schematic illustration of Pout (black line) and Pin for a poor

14

absorber such as hematite (red line) and a good absorber such as magnetite and carbon (blue line). For poor absorbers, $P_{in} = P_{out}$ at Ta, Tb, and Tc. The material temperature rises from Ta to Tb during which time $P_{in} < P_{out}$ ($T\,'$). Between Tb and Tc $P_{in} > P_{out}$ ($T\,''$). For absorbers, $P_{in} > P_{out}$ at temperatures lower than that indicated by the blue circle. In this region, the excess energy causes the temperature to vary greatly, as indicated by the blue circle.

FIG. 5: Temperature against time for hematite and preheated hematite with particle sizes of 300-600 μm (a) and 38-75 μm (b). For the particles 300-600 μm in size, hematite that had not been preheated did not increase in temperature, whereas hematite preheated to 480 °C or higher was heated to 1020 °C. This is because the absorption of the preheated hematite was sufficiently high, meaning that it could be heated by the electric field. The microwave heating behavior of hematite varies significantly with its initial temperature as predicted by the theory. For particles of 38-75 μm in size, Tb took a different value: 410 °C or higher.

Supplemental Figure: Cooling behavior in this apparatus. We measured the properties of the microwave heating system to estimate the substrate energy. In this experiment, the microwaves were turned off after 212 sec. Parameters for P_{out} ($\theta = 0.96$, $\alpha = 75.8$ Wm^{-2} K^{-1}) were estimated from this behavior.
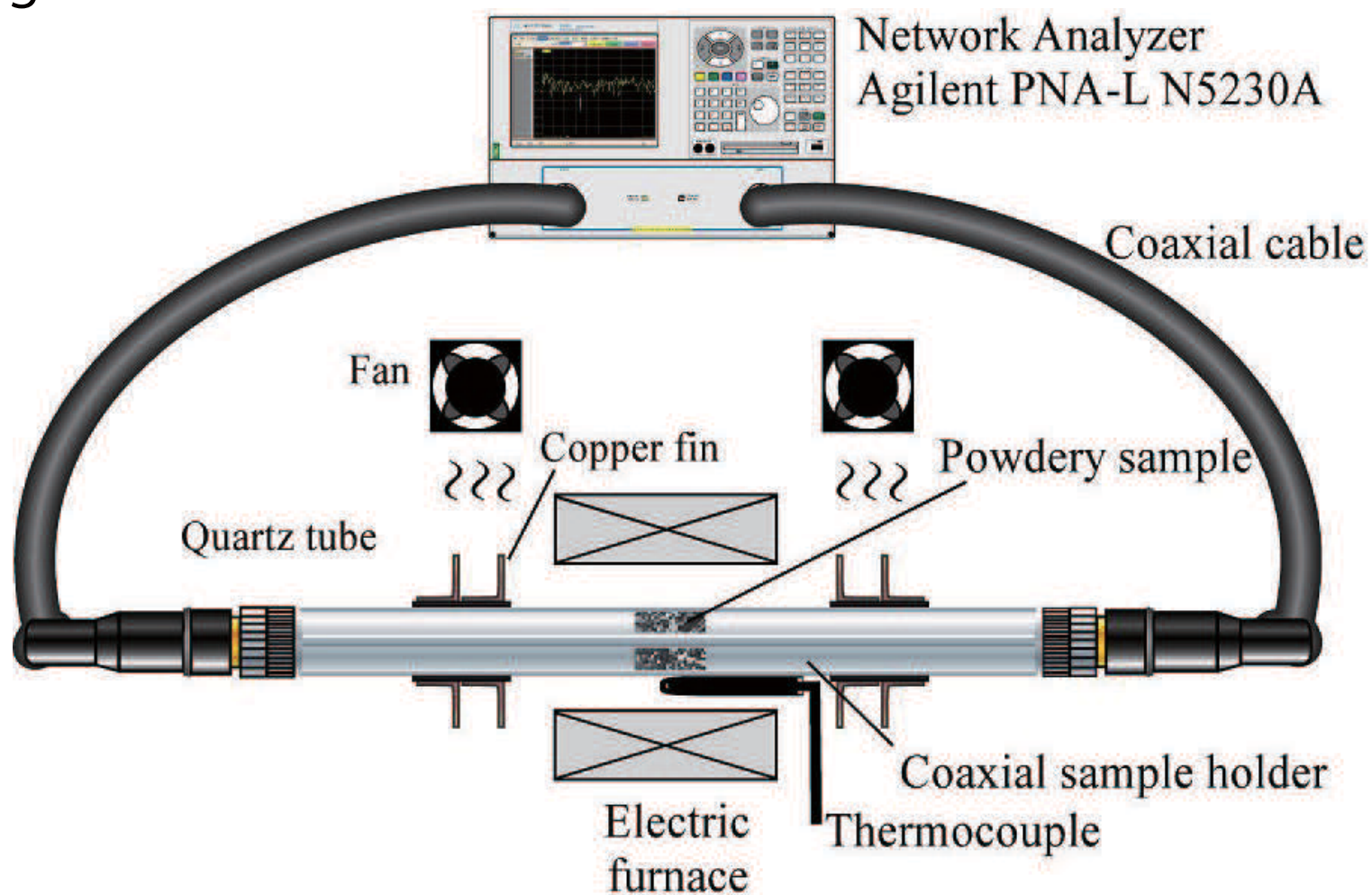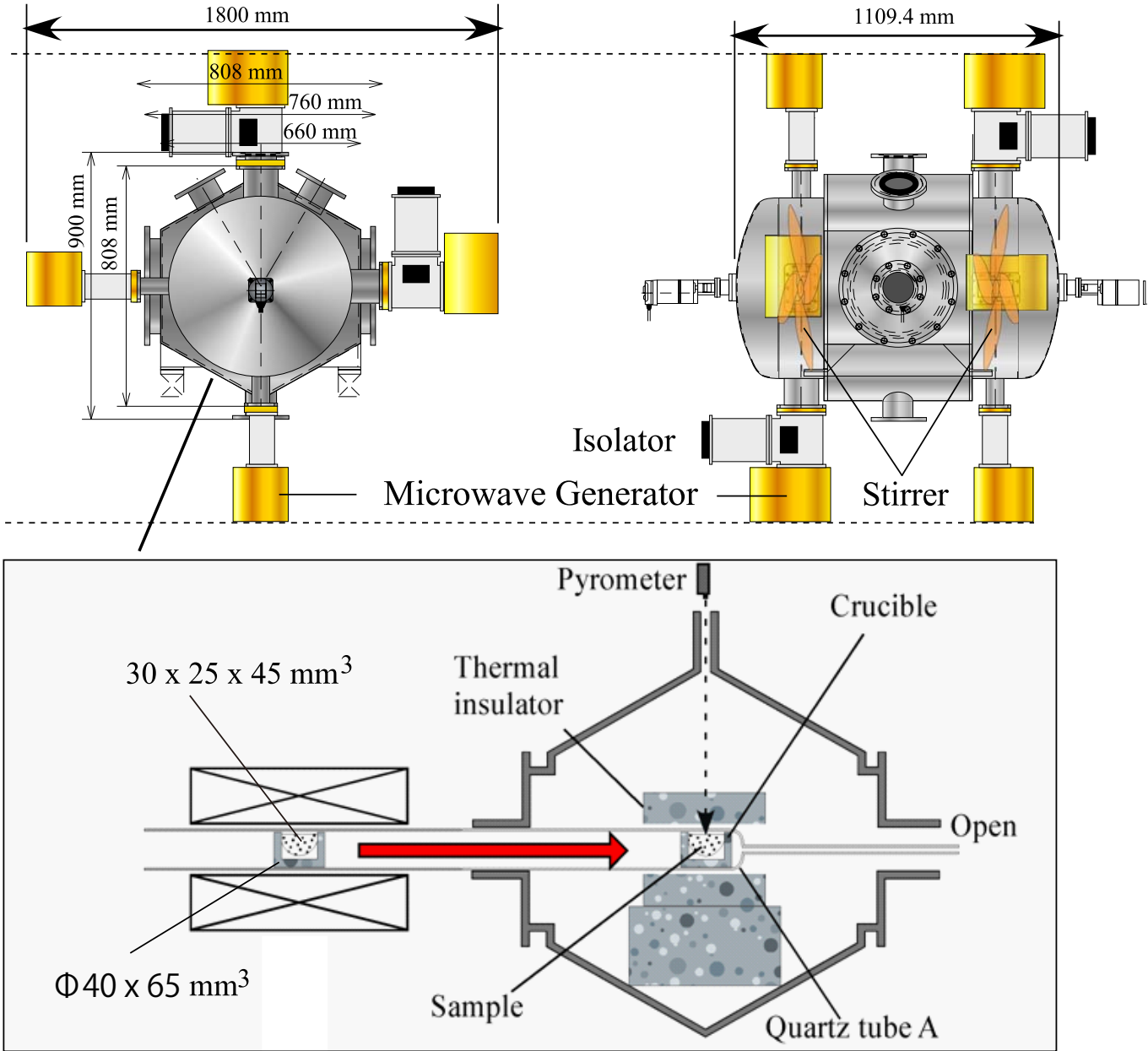
Fig. 1 Kashimura et al.

Fig. 2 Kashimura et al.

Microwave Applicator

1800 mm

808 mm

760 mm

660 mm

900 mm

808 mm

1109.4 mm

Isolator

Microwave Generator

Stirrer

Pyrometer

Crucible

30 x 25 x 45 mm^3

Thermal insulator

Ф40 x 65 mm^3

Open
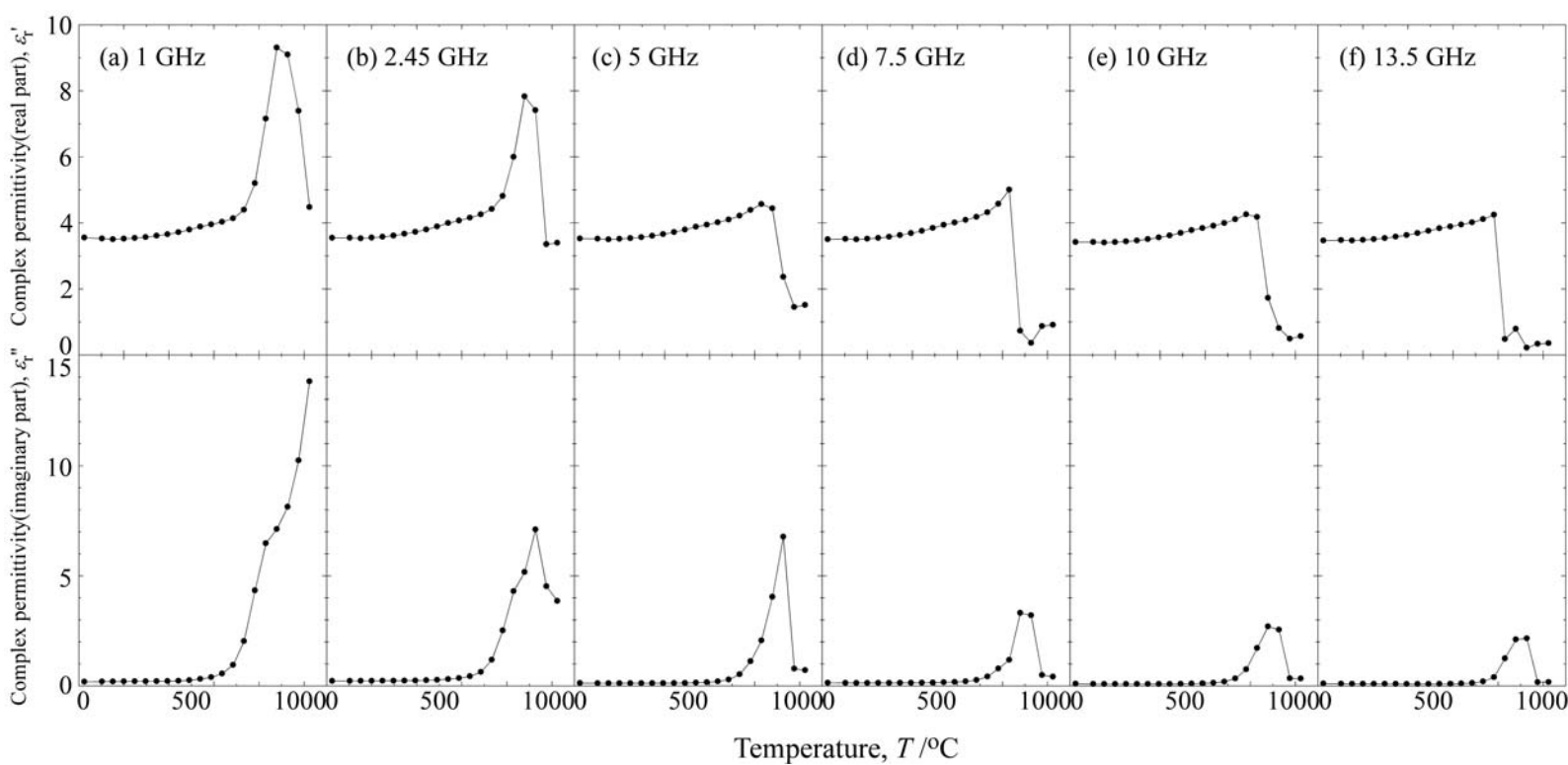
Sample

Quartz tube A

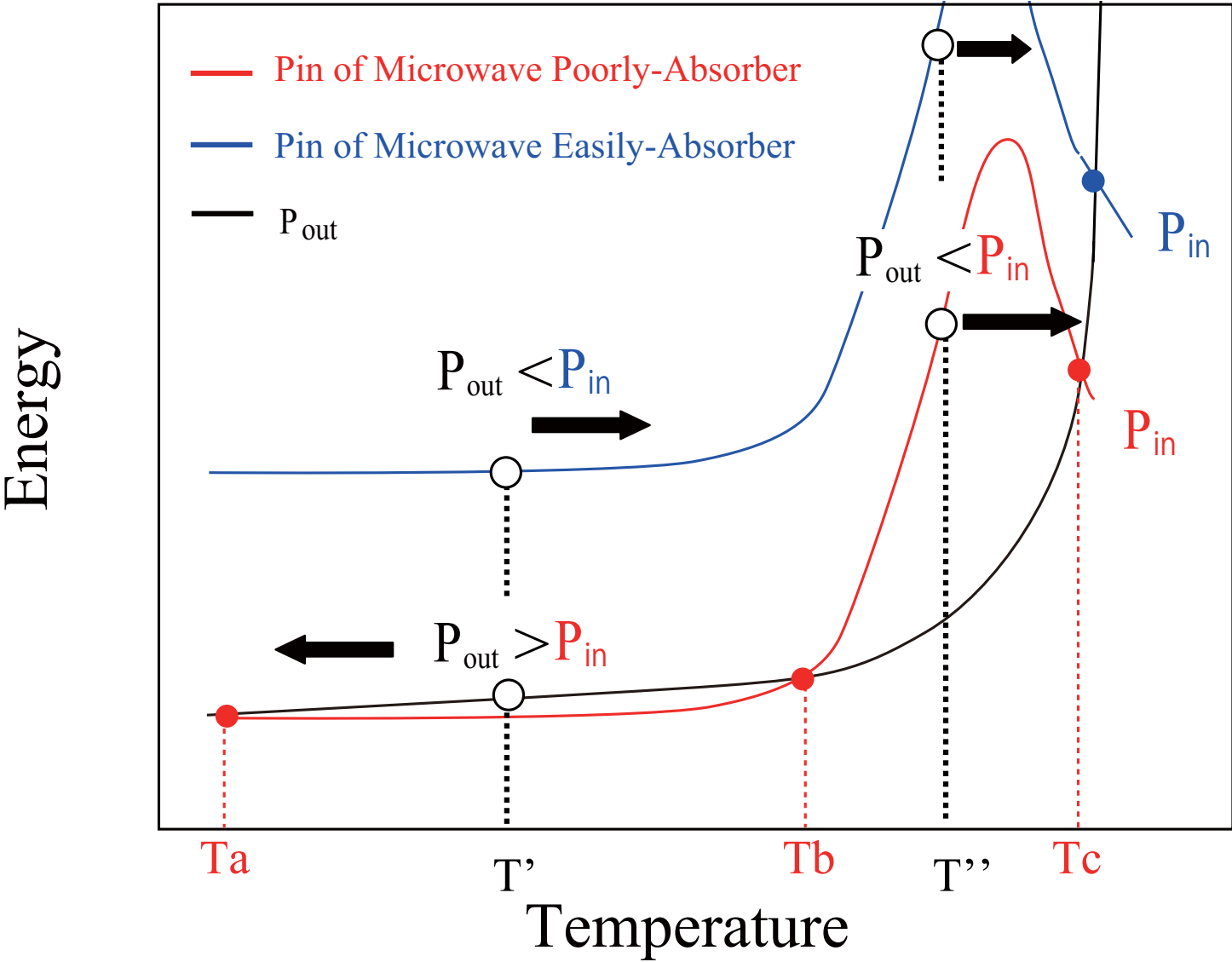Fig. 3 Kashimura et al.

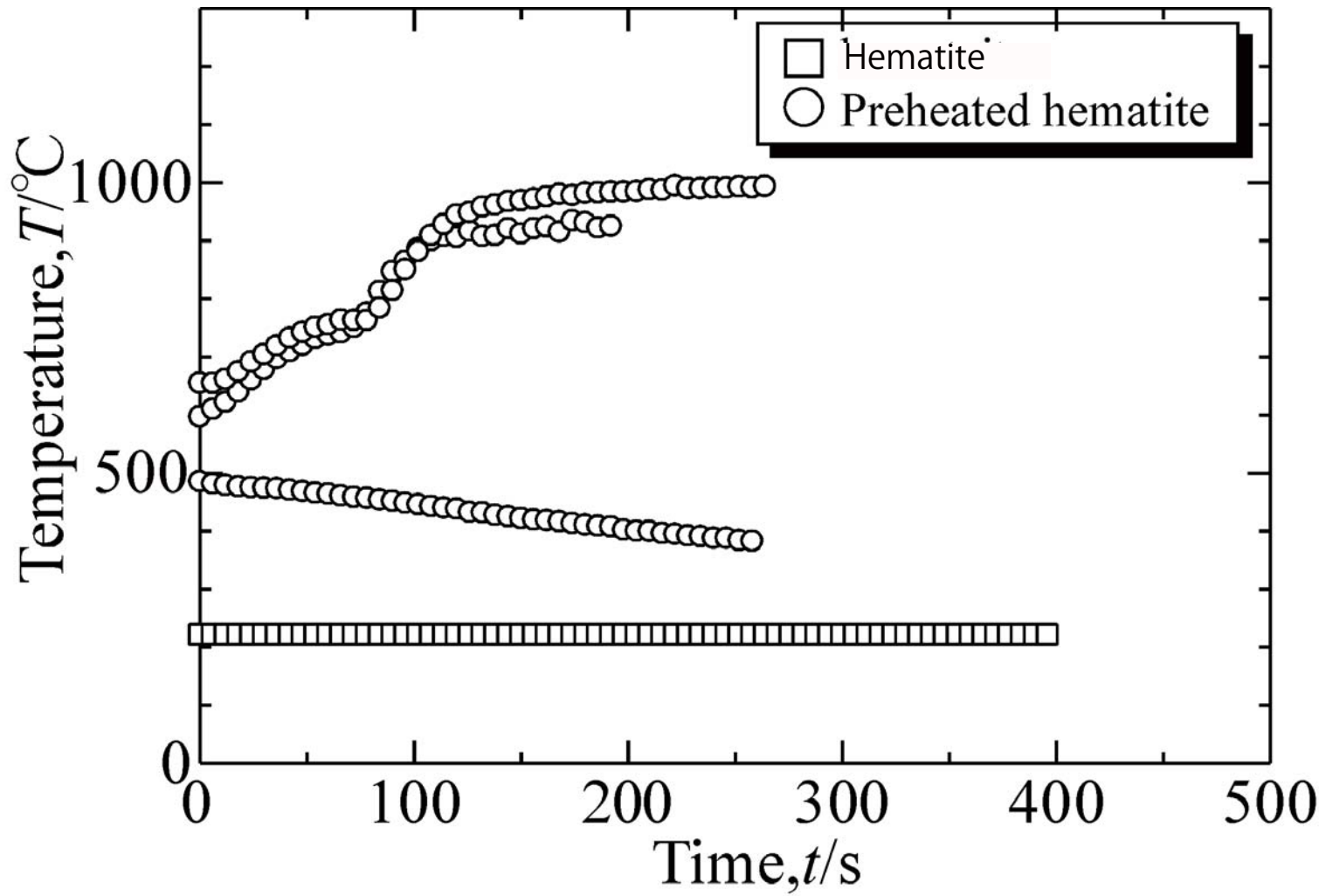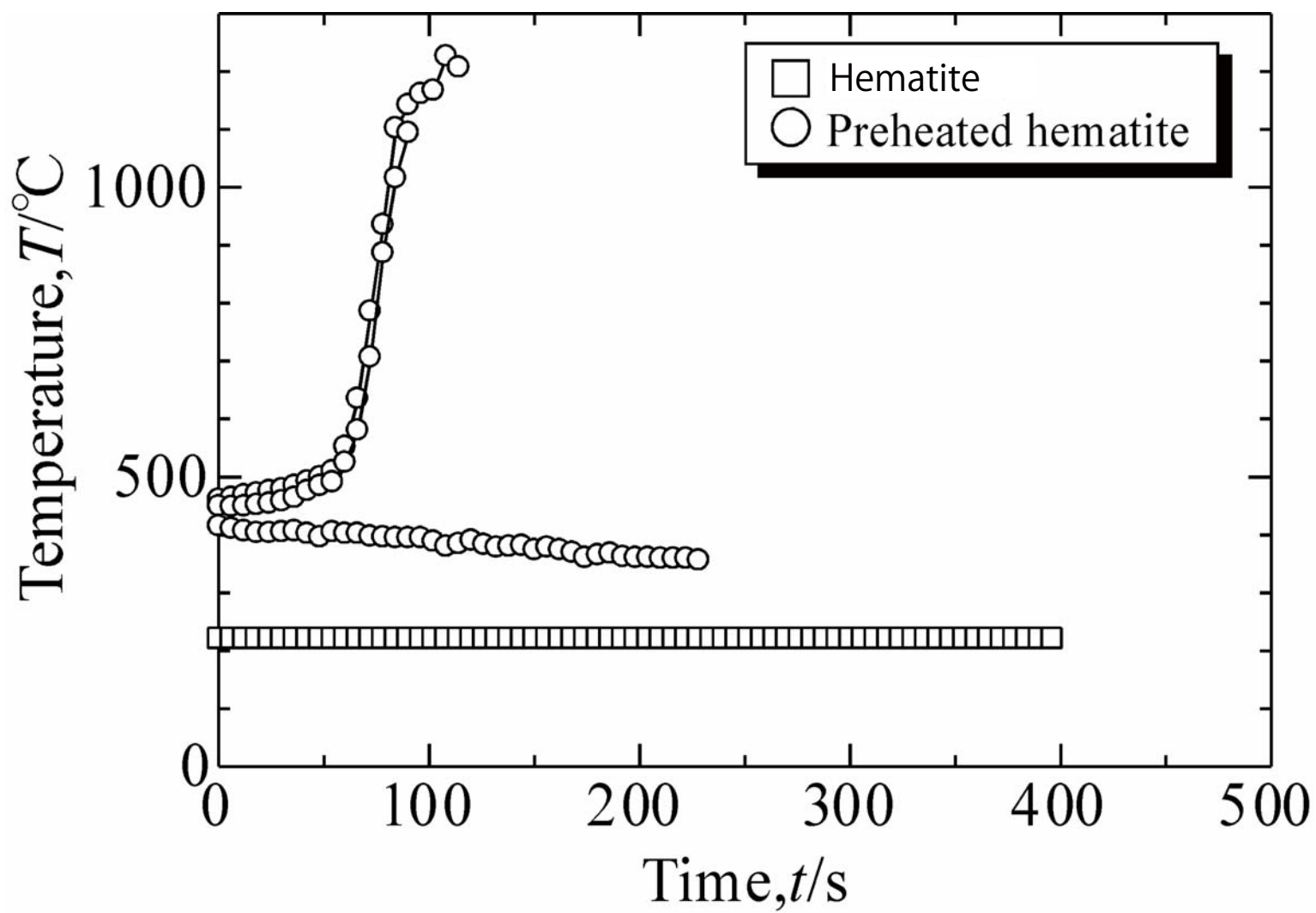# Figure 4 Kashimura et al.

Figure 5 (a) Kashimura et al.

Figure 5 (b) Kashimura et al.

Kashimura et al. Supplemental Data