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Temperature dependence and shape effect in high-temperature microwave heating of nickel oxide powders

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ABSTRACT

The temperature dependence of microwave absorption was investigated for $Ni_{1-y}O$ particles over the frequency range 2.0–13.5 GHz and temperature range 25–1000 °C. Using a coaxial transmission line method with a network analyzer, both the real and imaginary parts of the relative permittivity (ε'_r and ε''_r, respectively) and permeability (μ'_r and μ''_r, respectively) were measured; finding that both are largely dependent on the temperature at all frequencies. Furthermore, permeability loss factors related to shape effects were observed at high frequencies, indicating an increase in the microwave-absorption properties. A modified form of Mie's theory was applied to discuss these effects, wherein a spherical model demonstrating a close fit to the shape effect data suggests a more complex microwave-absorption behavior at increased temperature.

1. Introduction

The use of microwaves (MW) has been extensively studied as an alternative means of supplying energy in applications such as chemical reduction and heating [1–5]. For example, Ishizaki and Nagata [2] constructed a high-power (120 kW), continuous 2.45-GHz MW furnace. Similarly, Peng et al. [3] constructed a 915-MHz, 225-kW MW furnace to scale up steel production. In the field of organic chemistry, Verma et al. have reported MW-enhanced reactions of ammonium molybdate with H_2O_2 that have significant potential for the pretreatment of woody biomass by enzymatic saccharification [4]. In addition, Yamaguchi et al. have demonstrated the successful fabrication of face-centered cubic (fcc) Ni nanoparticles within an extremely short duration by means of an MW-assisted intramolecular reduction of Ni^{2+} ions contained in a formate complex with long-chain amine ligands [5]. In all these processes, the use of MW irradiation provided excellent energy control, as well as many advantages over conventional methods, such as speed, product selectivity, and greater efficiency.

The use of MW heating for the synthesis of $Ni_{1-y}O$ has previously been demonstrated by many researchers [5–8]. For instance, Lai et al. synthesized a mixed-valence nickel oxide by precipitation from an aqueous solution of nickel nitrate and sodium hydroxide, and by oxidation with sodium hypochlorite [6]; the time required for phenol degradation being greatly reduced in either instance by MW irradiation. Wang et al. also took advantage of MW irradiation in their synthesis of Ni_xO via the decomposition of basic nickel carbonate ($mNi(OH)_2 \cdot nNiCO_3 \cdot xH_2O$), because $Ni_{1-y}O$ is a good absorber of MWs [7]. Once again, the use of MW heating enabled excellent control over the energy delivered to the processes and rapid production, with Yoshikawa et al. also reporting a rapid carbothermic reduction of $Ni_{1-y}O$ [8]. In this, a powdered mixture of $Ni_{1-y}O$ and graphite was heated by a single-mode MW applicator at 2.45 GHz, with the magnetic component of the MWs reported to enhance the reaction rate. Consequently, processes employing $Ni_{1-y}O$-MW combinations as a basic system for the fabrication of catalytic agents have shown great benefits in terms of speed and efficiency.

Despite all this, the temperature dependence of the MW-absorption properties of $Ni_{1-y}O$ particles requires further investigation to adequately establish the chemical concepts for each process because $Ni_{1-y}O$ powders of various particles shapes were employed in obtaining more efficient reaction rates. In particular, the permittivity and permeability of $Ni_{1-y}O$ particles at a given MW frequency (which define its MW-absorption properties) are

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expected to be largely dependent on the temperature given the measurements obtained from other materials [9–11]. Moreover, because the MW-absorption properties of $Ni_{1-y}O$ particles greatly influences their thermal distribution at a microscopic scale (which is known as selective heating), and because the chemical reaction by MW heating induces the anomalous behavior, the permittivity and permeability are important considerations for the design of chemical processes. The effect of the particle shape also needs to be taken into account, with $Ni_{1-y}O$ expected to behave similarly to semimetal particles at temperatures of around 1000 °C based on its electrical conductivity ($\sigma = 263\ S\ cm^{-1}$). Furthermore, because metal particles heated by polaritons at MW frequencies change their absorption properties in relation to their shape, the absorption properties of $Ni_{1-y}O$ particles are often very different from those of a single crystal, as reported by Rao et al. [12].

In the present study, the temperature dependence of the MW-absorption properties of $Ni_{1-y}O$ (i.e., permittivity and permeability) is experimentally investigated at frequencies within the range 2.0–13.5 GHz and temperatures between 25 and 1000 °C. Because the energy transfer from MW to particles is largely dependent on their electrical conductivity and shape, the effect of the latter is also explored by comparing the experimentally obtained data with theoretical predictions based on Mie's theory.

2. Experimental procedure

For this study, a $Ni_{1-y}O$ powder comprising 6×10^{-1}-μm-diameter particles with a relative density of 4.80 g cm^{-3} was used (Supplemental Data 1). The real and imaginary parts of the relative permittivity (ε'_r and ε''_r, respectively) and permeability (μ'_r and μ''_r, respectively) were measured across the temperature range 25–1000 °C and the MW-frequency range 2.0–13.5 GHz using a coaxial transmission line method with a network analyzer (Agilent Technologies, N5230A), coaxial cables, and an APC7 coaxial sample holder (Fig. 1).

During the measurement, the temperature was increased at a rate of 10 °C/min using an electric resistance furnace, during which the transmission and reflection (S parameters) of the irradiated MWs were measured approximately every 50 °C. The network analyzer had an output power of ca. 1 mW, requiring approximately 2 s for each measurement. The complex permittivity and permeability were calculated from the S parameters using an algorithm of the Nicolson–Ross model [13,14]; air being used as a reference for calibration.

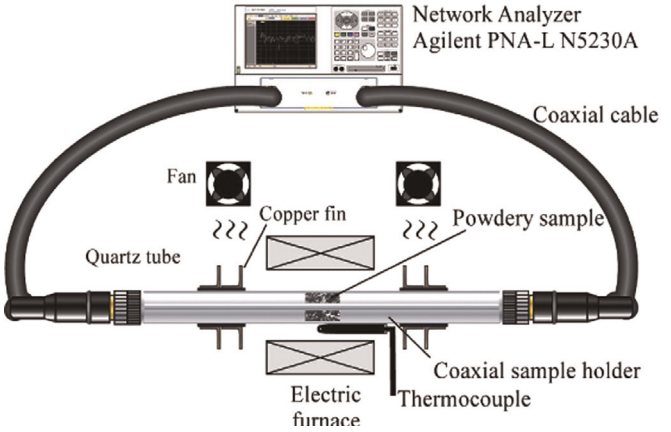

Fig. 1. Experimental setup used for measuring relative permittivity. An R-type thermocouple is attached to the 300-mm-long SUS316L stainless steel sample holder by Pt wire. The apparent temperature (T_{app}) varies almost linearly with the true temperature (T_{true}) according to $T_{app} = T_{true} \times 1.0313 + 43.237$, which was used to correct the temperature for all data.

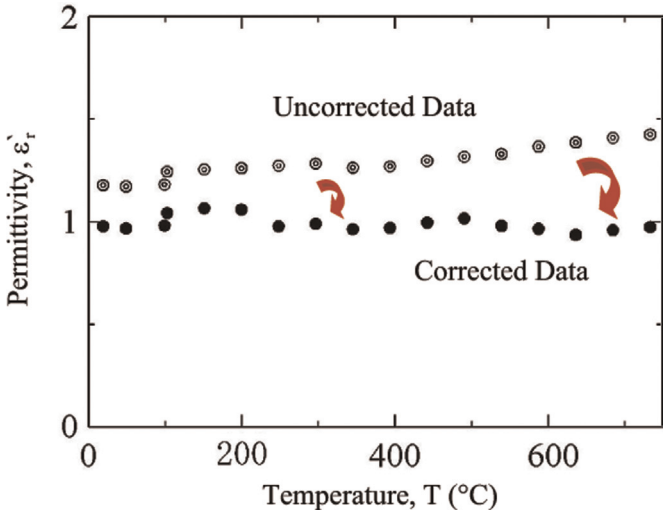

Fig. 2. Real part of permittivity for air, as calculated using the Nicolson–Ross model. In the absence of $Ni_{1-y}O$ inside the sample holder, the permittivity should be 1. Assuming that thermal expansion lengthens the sample holder, the change of length can therefore be estimated to maintain the accuracy of the measurement according to $L = 1.6 \times 10^{-3}T + 300.83$; where L is the estimated length at temperature T.

When the coaxial sample holder is heated its length is increased by thermal expansion, thus affecting the accuracy of the measurement. These differences between actual and measured permittivity were shown to be quite large at frequencies in the region 7–13.5 GHz, and at high temperature. A difference of 10 GHz was therefore used as a reference frequency to determine the length of the sample holder (see Fig. 2).

The true temperature of the $Ni_{1-y}O$ was estimated from preliminary experiments. In these, the temperature was measured with a thermocouple attached to the outer wall of the sample holder, as opposed to a thermocouple embedded in the sample. Furthermore, the apparent and true temperatures were measured simultaneously during the heating cycle of the pre-experiment by using thermocouples attached to the outer wall of the holder and embedded in the sample to calibrate the temperature. The measured temperatures, therefore, represent an apparent temperature, from which the true temperature of the $Ni_{1-y}O$ was estimated.

3. Results and discussion

3.1. Temperature dependence of the absorption properties of $Ni_{1-y}O$

As shown in Fig. 3, the relative complex permittivity (ε'_r and ε''_r) of a $Ni_{1-y}O$ powder is largely dependent on the sample temperature at frequencies of 2.45–12.5 GHz, with ε''_r increasing with temperature at all frequencies due to the fact that ceramics are highly conductive at high temperature [12]. Furthermore, if it is assumed that the permittivity of the $Ni_{1-y}O$ powder is $\varepsilon_r \approx (\sigma/\omega)i$ (where σ is the static electrical conductivity and ω is angular frequency), then the fact that electrical conductivity increases exponentially means that ε_r will exhibit a similar behavior; which is typical for the MW absorption of metal oxides [9,15].

The relative complex permittivity (ε'_r and ε''_r) of $Ni_{1-y}O$, however, exhibits a very different behavior to that observed with other powdered ceramic materials (magnetite and hematite) at high temperature using a coaxial transmission line method [9,15]. Specifically, the relative complex permittivity of magnetite powders increases with temperature up to 600 °C, but decreases