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著者	N Yoshikawa
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Microwave Processing of Metallic Materials

N. Yoshikawa

Graduate School of Environmental Studies, Dept. of Materials Science and Enginaeering,Tohoku University
6-6-02, aza-Aoba, Aramaki, Aoba-ku, Sendai, Japan, 980-8579

Corresponding author : yoshin@tohoku.ac.jp

Abstract

The author has performed experimental studies on microwave heating of metallic materials for these twenty years. In this report, it is intended to review the researches and discuss the future prospects on this subject, from the following three points of view: 1. Separated E(Electric)/H(magnetic) field heating in a single mode cavity contributed to understanding of the microwave heating mechanisms of various materials. It was demonstrated that heating behavior of metal film depends on the substrate normal direction with respect to the microwave oscillating magnetic field. 2. In heating of metal/ceramic composite materials, its effective permittivity values have to be determined. In relation with occurrence of conductivity percolation, some measurement data are presented exhibiting negative permittivity (real part), and possible interpretation of the composites' permittivity was discussed. 3. In microwave processing of materials, "non-thermal effect" has been proposed, so far. In this report, the non-thermal effect observed in annealing the Au thin film will be presented. And possible effect of magnetic resonance heating is proposed.

Key words : microwave, metal heating, electric field, magnetic field, permittivity, non-thermal effect

Introduction

Ever since discovery of microwave application to heating materials in 1940s [1], there are many researches and attempts performed for processing materials. One of the major applications is as a heat source of domestic microwave oven for cooking. It has been also applied for some industrial purposes, such as for drying leaves, timbers and roasting coffee beans etc. Because of its specific characteristics of rapid, internal and selective heating, its usage has been widely spread. For example, it has advantages of heating a cold food once stored in a refrigerator, immediately. Thick wet timbers can be dried from the internal area, within a shorter time than the general processes by hot air drying.

Different from the above heating applications, microwave application to metals has been less common, because metals reflects microwave, and a bulk metal cannot be heated effectively. This is related with a fact that the microwave penetration (skin) depth to metals is about or less than 1 microns, therefore heat generated on a surface thin layer is dissipated by heat conduction to the internal area and temperature of the whole metal bulk cannot be raised very much. Microwave heating can be applied to metal powders or films, having their scales of an order of their skin depth. Researches on microwave heating application to metal sintering has been paid attention at the end of '90s [2], and several attempts have been undertaken since then, such as for preparation of nano-grained metal sintered compacts [3], together with some theoretical studies. One of the another contribution to microwave metal heating researches is by the method of a separated electric (E-) and magnetic (H-) field heating in a microwave cavity [4]. In measurement of electron spin resonance (ESR), it is common to place a specimen in a magnetic field maximum position in a microwave cavity and use the microwave H-field, however, specific utilization of separated E- and H- field for heating materials is a relatively new method. In this study, the author's recent findings in separated E- and H- heating of metals is presented.

In an analysis of microwave heating of ceramics/metal composite materials, averaged (effective) physical properties of the composites are important parameters. In this study, the authors' measurement of average permittivity and conductivity of the composites will be presented, and it is intended to discuss their significance related with the heating mechanisms.

The authors have investigated the microwave heating of metal films and demonstrated its dependence of heating efficiency on directions of microwave magnetic field [5]. The detailed study on the metal films has revealed some specific phenomena of microstructural evolution in the film annealing processes. This findings are to be demonstrated as one on the non-thermal characteristics of microwave heating. And lastly, possibility of ferro magnetic resonance (FMR) heating application will be proposed.

Experimental

Specimens used for the experiments are reagent grade powder particles of metals, graphite and ceramics (cordierite, magnetite) having grain size between several hundred nanometer to ten microns. Au film is sputter-coated on SiO_2 substrates with variation of sputtering time for controlling the film thickness in a range of several ten to hundred nanometers, the substrates were cleansed with en ethyl alcohol under ultrasonic irradiation in advance. For the experiments of FMR heating, Fe foil (Johnson-Matthey, 130μm in thickness) was prepared. Microwave heating of the specimens was conducted using a single mode cavity (5.8GHz, TE103, P_{max} 700W(magnetron), 100W(solid state oscillator)) or a single mode wave guide applicator (2.45GHz, TE10, P_{max}2kW). Detail of the single mode applicator can be found elsewhere [5]. Temperature of the heating objects was measured by an optical method using a sapphire rod (Luxtron, PhotoriX system), the pyrometer has a lower temperature detection limit of 350°C. Measurement of complex permittivity of powder mixture was conducted using a vector network analyzer (VNA, Agilent E5062A) in a frequency range between 100MHz and 3GHz by a co-axial transmission method. External static magnetic field less than 4×10^5[A/m] was imposed to the microwave cavity with an electromagnet.

Results and Discussion

1. Microwave heating of metals in separated E- and H- field

In a microwave cavity, standing wave is generated and the distributions of E- and H- field are formed in different manners (Fig. 1). Namely, E-field maximum position is different from that of H-field by a quarter of the wave length (TE10 mode). Therefore, if a specimen (heating object) is small enough with respect to the field distribution, separated E- and H- field heating is possible. This heating method enables rapid and energy effective heating, because of the concentrated irradiation of either E- or H- field. In addition, it contributes to academic purposes of clarifying the heating mechanisms of materials, according to an equation of the microwave energy loss : P [J/m^3/s] (Eq. 1), where **E** and **H** are the electric and magnetic field vector, ω is an angular frequency and is equal to 2πf (f : frequency [s^{-1}]), ε" and μ" are imaginary parts of complex permittivity and magnetic permeability, respectively. And σ is an electric conductivity of material.

$$P = \left(\omega\varepsilon'' \left|\boldsymbol{E}\right|^2 + \omega\mu'' \left|\boldsymbol{H}\right|^2 + \sigma\left|\boldsymbol{E}\right|^2\right) / 2 \tag{1}$$

Dielectrics such as water, paper and some ceramics are heated well in E- field maximum position. On the other hand, metallic materials are better heated in H-field maximum position than in E- field (metal powder, for example [4]). It is rather natural, considering the induction current generated by an alternating magnetic field. However, the third term in right hand side of Eq. 1, which corresponds to the ohmic loss due to induction current, is not described as the contribution of alternating H-field. It is interpreted that there is a relationship between E- and H- field on metal surface. And the electromagnetic analysis has been performed by setting some boundary conditions.

Metal thin film can be heated well in H-field, however, our previous study has shown that heating behaviors are different when films are placed in different ways with respect to the oscillating microwave magnetic field [5]. It was pointed out that the best heating was obtained in the cases of film normal, parallel to the magnetic field direction (the Au film thickness is less than 1 micron, and microwave penetrates the film, and induction current is effectively generated in the whole volume of films, comparing with the other two configurations.). Therefore, H2 in Fig. 2(a) is the most effective configuration for generating the electric current on the surface.

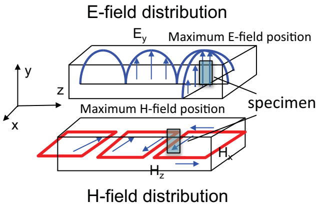


Fig. 1: Schematics of E- and H- field distributions in TE103 microwave cavity.

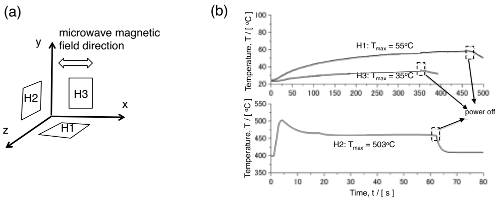


Fig. 2: (a) Three configurations (H1,H2, H3) of metal film on SiO_2 substrate with respect to the oscillating microwave magnetic field and (b) heating curves of Au films placed in the three configurations [5].

2. Physical properties of metal/ceramics composites

In analyzing microwave heating processes for fabricating metal/ceramics composite materials, it is required to measure their physical properties related with microwave energy loss. They are electric conductivity, permittivity and magnetic permeability. The latter two are complex values, but it is possible to use DC electric conductivity for the metals at microwave frequency. Specific features are demonstrated in the composites' permittivity.

Measured permittivity of graphite (C) and goethite (FeO(OH)) mixtures are shown in Fig. 3, as a function of frequency for different graphite compositions. When graphite content is low (Fig. 3(a)), both real and imaginary parts of permittivity exhibited positive values, however, the real part becomes negative (Fig. 3(b)) when graphite content increases and exceed the conductivity percolation value [6]. The same tendency was observed in the cases of Mo/cordierite ($Mg_2Al_4Si_5O_{18}$) mixtures. Fig. 4 indicates the Mo volume fraction dependence of (a) real and (b) imaginary parts of permittivity. The negative real part values appear in the conditions of largest grain size. As previously discussed [7], occurrence of negative real part permittivity is related with the formation of conduction path or percolation, namely at a composition when the whole composite body becomes conductive. However, it has to be noted that the permittivity measurement condition is sometimes out of the possible range of measurement, because of the conductivity. Therefore, the only positive values of graphite / FeO(OH) mixtures are plotted in Fig. 5, with fitting curves by a mixing law expressed by Eq. 2, which is based on the EMA (Effective Medium Approximation, symmetric composite configuration [7]). ε_1, ε_2 and ε_m are permittivity of phase 1, 2 (inclusion) and average (effective) permittivity of composite, respectively. f is a fraction of phase 2, and f_c is a fraction of percolation threshold. In the fitting procedure, complex permittivity of graphite has to be assumed. Two complex numbers having positive and negative real part values were input, for the trial fittings. It looks both of them fits the data well. The real part value influences the microwave penetration distance. And the imaginary part is closely related with the microwave heating characteristics. All the values of imaginary parts increased as an increase of both graphite and Mo fractions. Nevertheless, it has to be noted that when conductor fraction is low, large heating rate is not attained, because of low loss, and in conditions of large fraction of conductor conditions, in which whole body becomes metallic, and heating rate decreased, as well. This is because of decrease in penetration distance (δ) of the composite body according to Eq. 3.

$$f\frac{\varepsilon_2-\varepsilon_m}{\varepsilon_2+A\varepsilon_m}+(1-f)\frac{\varepsilon_1-\varepsilon_m}{\varepsilon_1+A\varepsilon_m}=0 \quad , \quad A=(1-f_c)/f_c \qquad (2)$$

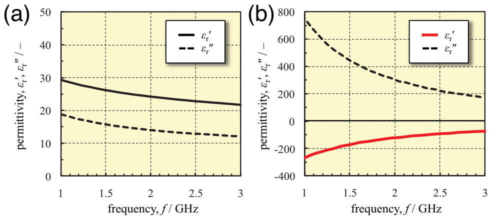


Fig. 3: Real and imaginary parts of permittivity as a function of frequency for graphite/goethite mixtures of graphite (a) 8.2%, and (b) 11.2% [6].

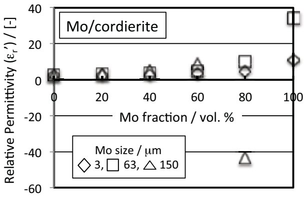
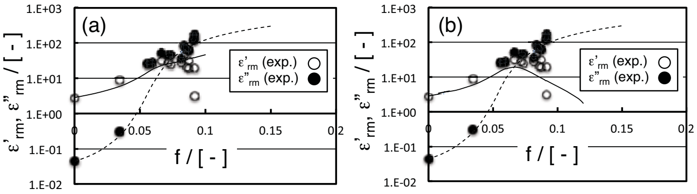


Fig. 4: Permittivity of Mo / cordierite powder mixtures having various particle sizes, plotted as a function of Mo volume fraction,



$$\delta=\sqrt{\frac{2}{\sigma\omega\mu}} \qquad (3)$$

Fig. 5: Measured complex permittivity of FeO(OH) / C powder mixtures plotted as a function of C volume fraction, real (solid line) and imaginary (dotted line) are fitted by (a) 1060-3568i and (b) -73-3350i using Eq. 2.

3. Specific phenomena by microwave heating of metallic materials

There are many reports, proposing so-called “microwave non-thermal effects”. Some of them are the phenomena, which are not interpreted in terms of temperature at which they would occur. For example, they claim enhancement of kinetics of reaction, sintering and some mass transport etc. However, some of reports may contain experimental results due to erroneous temperature reading. For example, temperature measurement under microwave irradiation is not necessarily easy, such as a thermocouple being heated and playing a role of antenna, and thus an erroneous reading may occur. The optical method is the most effective for the temperature measurements, however, setting of the emissivity is not necessarily straightforward.

In this report, microwave annealing process of Au thin film (~20nm) deposited on SiO_2 substrates is presented as an example. Same optical method (pyrometer using a sapphire rod, because of no influence by microwave irradiation) was employed for the measurement of temperature both in microwave and conventional (electric furnace) heating. Because microwave heating in separated H-field takes place very rapidly, microwave power was switched off immediately, after temperature reached the predetermined value. In the conventional heating, electric furnace temperature was controlled at the predetermined value, and the specimen film (on the substrate) and pyrometer rod was inserted into the furnace, together and then removed, imitating the same temperature history as that of microwave heating. AFM photographs of the film surface are depicted in Fig. 6 for comparing the two heating methods. It can be seen that the microwave heating brought about more flat surface and connecting of grains. It is anticipated that the surface diffusion is enhanced by microwave irradiation, not by thermal effect but by some effect due to inhomogeneous distribution of surface electric current, which could function together with microwave magnetic field. This phenomenon is under investigation for clarifying as an electromagnetic field effect.

Lastly, it would be of significance to introduce one of our findings [8] on the microwave magnetic heating mechanism. Fig. 7 demonstrates a heating curve, specimen temperature is indicated by a left vertical axis. A Fe sheet is placed in a magnetic field maximum position, and started at 480°C by an ordinary microwave heating. When a slowly varying external magnetic field (H^{ext}) is applied after 200s (the magnitude of H^{ext} is expressed by a right vertical axis) perpendicular to the microwave (oscillating) magnetic field, temperature increased and experienced a temperature peak, at about 230s, then decreased even when H^{ext} was kept increasing, however, after about 450s when H^{ext} is decreased, the temperature peak appeared again at 650s, the two peaks corresponding to H^{ext} equal to 0.08[T] (6.4×10^4 [A/m]). This phenomenon is due to ferro-magnetic resonance (FMR). So far, the authors examined not only iron but also other ferro (ferri) magnetic materials, no particular difference has been observed in microstructural difference from the ordinary microwave heating or conventional heating. However, the temperature increase caused by FMR is due to an acquisition of microwave energy by electron spins of their simultaneous precession motion (precession frequency equal to microwave frequency), then the energy transferred to the lattice of the materials and was detected as a temperature increase. It is expected that the microwave energy once received by spin motions could cause some effect before transfer to the lattice or could transfer in different ways to lattice. Further investigation is being carried out.

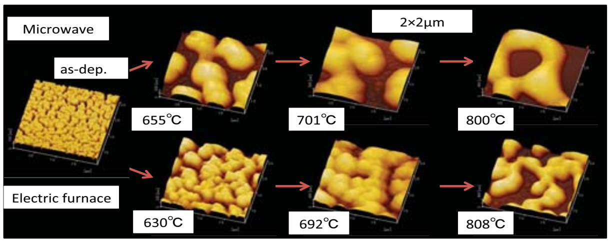


Fig. 6: Comparison of microstructural evolution between microwave and conventional heating in annealing of Au thin film, observed with AFM.

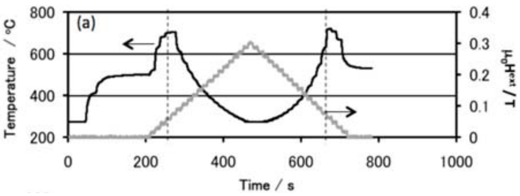


Fig. 7: Heating curve (black line) under imposition of slowly varying external magnetic field (glay line) [8].

Conclusions

Microwave heating of metallic materials has not been a major processes applied to their fabrication. However, since the beginning of this century, its applications to sintering of metal powder and to annealing metal thin films are being performed. In addition, method of separated E/H field microwave heating contributed to understanding the role of microwave magnetic field for metallic materials. This report started with describing the present author's recent studies and introduced some topics on negative permittivity of metallic materials and some specific phenomena related with the so-called "microwave non-thermal effect".

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