Microwave Sintering Study of NiCuZn Ferrite Ceramics and Devices
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Studies on the sintering behavior, including densification and grain growth of NiCuZn ferrite ceramics were carried out in a microwave field of 2.45 GHz. Compared to conventional sintering, the shrinkage curves of a NiCuZn ferrite system processed by microwave sintering were observed to have shifted towards approximately 100°C lower temperatures. From the analysis of shrinkage data, it was found that the effective activation energy for diffusion under the microwave sintering was lower than that observed under conventional sintering. In addition, pressed toroidal inductors and multilayer chip inductors (MLCI) have also been sintered by the microwave processing. Although heating rate of the microwave sintering was faster than that of the conventional sintering, the microwave sintered samples were found to be without any visible cracks. The total sintering time was reduced significantly in comparison with the conventional sintering. In both the sintered toroidal and MLCI samples, comparable magnetic properties were obtained. [DOI: 10.1143/JJAP.41.86]
KEYWORDS: NiCuZn ferrite, microwave sintering, densification, grain growth, activation energy

1. Introduction
Microwave sintering of electronic ceramics has attracted a lot of interest because it has several advantages over the conventional sintering which include lower sintering temperature, reduced sintering time, and more uniform microstructures.1,2 In this microwave sintering study, NiCuZn ferrite system was selected owing to its use in both discrete chip inductors and integrated passive devices.2,3 Further, the NiCuZn ferrite's magnetic properties are very sensitive to microstructure as well as the chemical composition.4-12 Recently, microwave sintering of NiCuZn ferrite multilayer chip inductor and multilayer ceramic capacitors were reported.13,14 In all these studies, susceptor were used, and the multilayer structure ceramic devices were sintered at lower temperatures under microwave processing compared to the conventional processing. These materials had much shorter sintering time, and comparable electrical properties were obtained.

The objective of this paper is to relate accurate temperature measurements to a detailed analysis of the densification kinetics. And once optimal conditions were determined, microwave sintering of toroidal and multilayer chip inductors (MLCI) ferrites were compared to conventional processing.

2. Experimental Procedure
In this study, a modified microwave oven (Panasonic, 1440 Watts, 2.45 GHz) was used to sinter NiCuZn ferrite. Figure 1(a) shows the experimental settings in the microwave oven and (b) the thermocouple assembly. The general configuration of the microwave furnace has been described elsewhere.15 Temperature was measured using a shielded thermocouple. Stainless steel and platinum foil design were used to avoid microwave interference with the thermocouple electro motive force (EMF) signal. Details of the temperature measurement in the microwave oven will be discussed later. In the case of conventional sintering, a conventional box type furnace was used. The NiCuZn ferrite powder used in this study has the chemical composition of Fe2O3 : NiO : CuO : ZnO = 48 : 23 : 15 : 14 (mol%). The specific surface area of the powder was 7.48 m^2 g^-1. Circular disks (diameter 13 mm, thickness 2.2 mm) were made by uniaxial pressing at 98 MPa without binder. In order to measure the temperature dependence of shrinkage, the diameter of the disk samples were measured before and after sintering. Shrinkage was calculated by [(D0 - D)/D0] x 100 (%), where D0 is the diameter of green sample and D is the diameter of sintered sample. The microwave heating profile was controlled by a proportional integral derivative (PID) controller (Eurotherm 2404). To study the densification under constant heating rate, sintering was carried out under both microwave and conventional processing with a constant heating rate of 5°C/min. At the maximum temperature, the samples were held for 1 min, and cooled to room temperature with a cooling rate of 15°C/min. To study the isothermal sintering at each temperature, samples were taken to the maximum temperature with a heating rate of 5°C/min, then held from 1 min to 12 h for both microwave and conventional sintering, and cooled to room temperature with a cooling rate of 15°C/min.

The magnetic properties were determined for toroidal disks with the following dimensions (outer diameter 12 mm, inner diameter 6 mm, thickness 3 mm) and from MLCI devices (3.5 x 1.6 x 1.2 mm). In the case of microwave sintering, the samples were sintered with a heating rate of 25°C/min, and held at the maximum temperature (937°C for toroidal disks, 885°C for MLCI) for 20 min in the microwave oven, then cooled to room temperature with a cooling rate of 15°C/min. In the case of conventional sintering, the samples were sintered with a heating rate of 5°C/min, and held at the maximum temperature (950°C for toroidal disks, 900°C for MLCI) for 20 min, then cooled to room temperature with a cooling rate of 15°C/min. The difference of these sintering conditions were heating rate and sintering temperature. The frequency dependence of initial permeability and loss factor were determined using LCR meter (HP4194A) at room temperature. Characterization of microstructure was carried out using a scanning electron microscope (Hitachi 3500N). To determine the grain size of the NiCuZn ferrite, each sample was polished and then etched to reveal the grain size and microstructure. Chemical etching was carried out using 2% hydrofluoric acid solution.
and soaking for 1–3 days. The grain size was determined by the linear intercept method.

3. Results and Discussion

3.1 Self Heating by Microwave Radiation

It is well known that certain materials can absorb microwave efficiently\textsuperscript{16–18} and the nature of this microwave/material interaction is a function of permittivity, permeability, and conductivity of the sample. Previous research has shown that the primary coupling to the microwave energy is governed by induction.\textsuperscript{19} Therefore, a common practice in microwave sintering of low absorbing ceramic materials is to preheat the sample using a susceptor,\textsuperscript{20–22} allowing the sample to be heated until the intrinsic permittivity is sufficient to achieve direct coupling with the microwave energy. As shown in Fig. 1(a), MoSi$_2$ was used as susceptor to preheat the samples, and ZrO$_2$ and insulation around the sample prevent the heat dissipation from sample. In order to determine the ability of the sample to undergo self heating via microwave absorption, the system was exposed to microwave radiation both with and without a ferrite sample.

After an induction period at 1200 watts of 2.45 GHz microwave radiation, the temperature of the NiCuZn ferrite experienced a thermal runaway above 300°C. Fig 2 shows the temperature differences between the NiCuZn ferrite sample in the oven and the control (no sample). From these results, it was confirmed that NiCuZn sample absorbed microwave efficiently and could possibly undergo a self heating of the sample in microwave radiation.

3.2 Temperature measurements

Under conventional sintering, the thermocouple is in equilibrium with the sample and with each system under investigation to define the temperature. In the case of microwave sintering, samples can be self heated and also the thermocouple itself can become an effective antenna perturbing the field and discharging to ground sample. In this study, the thermocouple junction was fixed just above the sample (1–2 mm from the sample surface) to control sample temperature in the microwave oven. Under these situations, the thermocouple always indicates inaccurate temperatures of both the sample and the system.\textsuperscript{23–24} Therefore, it was important to understand the cooling rate and then determine the sintering temperature by time extrapolation.\textsuperscript{25}

For each sintering temperature in the 500–950°C range, the same shape and sized circular disk samples were sintered at a heating rate of 25°C/min and held at the maximum temperature for 1 min in the microwave oven. Then the microwave power was turned off and the thermocouple junction was quickly brought in contact with the surface of the sample. The time dependence of temperature was recorded after making contact. Figure 3 shows the time dependence of sample surface temperature after microwave power was turned off at each sintering temperature (solid line). At the beginning, the temperature went up to establish a quasi thermal equilibrium state, and after 30–50 s, it reached a maximum temperature and was started cooling down. Each cooling curve was extrapolated to time zero so that we could estimate the temperature of the sample surface during microwave sintering. The temperature of the thermocouple in microwave radiation and the extrapolated temperature including the statistical error calculated from the least squares method are shown in Table 1.

According to Birnboim \textit{et al.},\textsuperscript{26} who studied the
Fig. 3. Time dependence of temperature after microwave power off. (Solid line: Temperature of thermocouple, Dashed line: Extrapolated lines calculated from cooling curves.)

Table 1. Measurement of extrapolated sample temperature.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Extrapolated Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>500</td>
<td>515 ± 0.32</td>
</tr>
<tr>
<td>600</td>
<td>617 ± 0.48</td>
</tr>
<tr>
<td>700</td>
<td>719 ± 0.43</td>
</tr>
<tr>
<td>800</td>
<td>826 ± 0.61</td>
</tr>
<tr>
<td>850</td>
<td>885 ± 0.48</td>
</tr>
<tr>
<td>900</td>
<td>937 ± 0.74</td>
</tr>
<tr>
<td>950</td>
<td>985 ± 0.74</td>
</tr>
</tbody>
</table>

microwave sintering of ZnO, a large temperature difference between the surface and core (inner part) of sample was observed, especially in the case of 2.45 GHz microwave radiation. To confirm the temperature difference in the sintered NiCuZn ferrite, the microstructures of both the surface and inner part were observed. Figure 4 shows the fractured surface of a sample sintered at 885°C under the microwave processing, where no significant differences of microstructure could be detected between surface [that is, below 200 μm from the surface, Fig. 4(b)] and inner part [Fig. 4(c)]. As the sample size was relatively small, the temperature difference in the inner part and outer part was considered to be minimal. Thus, it was concluded that the extrapolated temperature represents the temperature of the bulk sample during microwave sintering. Therefore in this study, we used the extrapolated temperature to represent the sample temperature during microwave sintering.

3.3 Densification study at constant heating rate

Generally, it has been reported that the onset of shrinkage under microwave sintering shifts towards lower temperatures compared to that of conventional sintering. This phenomena is often referred to as the "microwave effect", which is often questioned because of the high heating rate. The sintering mechanism can change and is equivalent to a simple "Fast Firing". Figure 5 shows the temperature dependence of shrinkage curve of NiCuZn ferrite sintered under the microwave and conventional processing. The conventional sintering at 5°C/min showed a higher densification curve. So there appears to be no evidence for a "fast firing" processing, and this experiment supports a "microwave effect" in the densification at constant heating rate. To calculate effective activation energy of diffusion at constant heating rate, a method used by Young and Cutler was used. In this method, the temperature dependence of shrinkage was divided into grain

Fig. 4. Fractured surface of NiCuZn ferrite sintered under microwave processing at 885°C. (a) Lower magnification view of the sample surface. (b) 200μm below the surface. (c) Core (inner part).

Fig. 5. Temperature dependence of shrinkage in NiCuZn ferrite for both microwave and conventional sintering.
boundary diffusion [eq. (1)] and volume diffusion [eq. (2)]. These are expressed as
\[ \frac{d(\Delta L/L_0)}{dT} = \left[ 2.14 \times \Omega D_b RT \right] \frac{1}{(ka^4cQ)^{1/3}} \times \left[ \frac{Q}{(3RT^2)} \right] \exp \left[ -\frac{Q}{(3RT)} \right], \] (1)
\[ \frac{d(\Delta L/L_0)}{dT} = \left[ 5.34 \times \Omega D_v RT \right] \frac{1}{(ka^4cQ)^{1/2}} \times \left[ \frac{Q}{(2RT^2)} \right] \exp \left[ -\frac{Q}{(2RT)} \right], \] (2)
where
\[ \Delta L = L - L_0 \]: the change in the length of sample (m),
\[ L_0 \]: initial sample length (m),
\[ L \]: sintered sample length (m),
\[ \gamma \]: surface energy (J m\(^{-2}\)),
\[ \Omega \]: vacancy volume (m\(^3\)),
\[ b \]: effective grain boundary width (m),
\[ D_b \]: grain boundary diffusion coefficient (m\(^2\) s\(^{-1}\)),
\[ D_v \]: volume diffusion coefficient (m\(^2\) s\(^{-1}\)),
\[ T \]: temperature (K),
\[ k \]: Boltzmann constant (J K\(^{-1}\)),
\[ R \]: gas constant (J mol\(^{-1}\) K\(^{-1}\)),
\[ a \]: particle radius (m),
\[ c \]: heating rate (K s\(^{-1}\)),
and
\[ Q \]: activation energy (J).

According to Young and Cutler, the temperature dependence of \( \exp \left[ -\frac{Q}{(RT)} \right] \) dominates all other temperature dependent parameters, so that \( \ln[\Delta L/(L_0T)] - T^{-1} \) plots can be fitted by a linear relation, with the slope equivalent to the effective activation energy of diffusion.

Figure 6 shows the calculation of the effective activation energy at constant heating rate. From these lines, the effective activation energy for diffusion and the statistical error of energy value were calculated by least squares method as follows.
\[ \ln[\Delta L/(L_0T)] = (1.9331 \pm 0.2565) \]

![Graph showing relationship between ln(ΔL/(L₀T)) and T⁻¹.](image)

Figure 6. Relationship between ln(ΔL/(L₀T)) and T⁻¹. (The slope of each line represents activation energy for diffusion.)

Activation energy \( nQ = 61 \pm 2.33 \text{ kJ mol}^{-1} \) (microwave).
\[ \ln[\Delta L/(L_0T)] = (7.3075 \pm 0.9997) \]
\[ + (-14172 \pm 1098.8)T^{-1}. \] (3)

Activation energy \( nQ = 118 \pm 9.15 \text{ kJ mol}^{-1} \) (conventional).

From eqs. (1) and (2), \( n \) represents the driving mechanism for diffusion that is, \( n = 1/3 \) for grain boundary diffusion, \( n = 1/2 \) for volume diffusion. Although it was impossible to identify the diffusion mechanism just from the data, the effective activation energy for diffusion during the microwave sintering was found half as large as that for conventional sintering case. This result suggests that sintering was promoted by microwave radiation and the "microwave effect" could be real. Figure 7 shows fractured surfaces of samples sintered under both microwave and conventional processing. It was observed that the rate of initial neck growth was promoted by microwave radiation significantly.

3.4 Isothermal grain growth

Isothermal grain growth study was performed under both microwave and conventional sintering. Generally, isothermal grain growth kinetics is given by eqs. (5) and (6),
\[ G^2 = aKt, \] (5)
\[ K = \exp \left[ -\frac{Q}{(RT)} \right], \] (6)

where \( G \), \( t \), \( Q \), \( R \), \( T \), and \( a \) are grain size, time, activation energy, gas constant, temperature, a constant, respectively.

Figure 8 shows the microstructure of NiCuZn ferrite sintered at 937°C under the microwave processing, and at 950°C under the conventional processing. Figure 9 shows the time dependence of grain growth for NiCuZn ferrite at each sintering temperature. From Fig. 9, activation energies of grain growth under isothermal condition were determined. Taking the logarithm of both sides in eq. (6), we obtain
\[ 3 \ln(G) = \ln(a) - \frac{Q}{(RT)} + \ln t, \]
\[ = D' + \ln t. \] (7)

Figure 10 shows the relationship between \( D' \) and \( T^{-1} \) with each line fitted using least squares method. From the slope of the lines, the activation energy for isothermal grain growth was calculated as follows,

Microwave sintering: \( \bar{Q} = 640 \pm 164 \text{ kJ mol}^{-1} \),
Conventional sintering: \( \bar{Q} = 463 \pm 1.78 \text{ kJ mol}^{-1} \).

The error of activation energy was again calculated from the least squares fitting. Contrary to reported microwave sintering grain growth studies, \( \bar{Q} \) the activation energy for microwave sintering is larger than that for conventional case. These results suggest that grain growth under isothermal sintering was not promoted by microwave radiation.

Generally, the driving force of grain growth is inversely proportional to the grain size. In Fig. 10, it is noted that the grain size at the starting point of isothermal condition under the microwave sintering was always larger than under the conventional sintering. Contrary to the Al₂O₃ microwave
Fig. 7. Fractured surface of NiCuZn ferrite sintered under microwave [(a1)–(a3)], and conventional [(b1)–(b3)] processing.

Fig. 8. Microstructures of NiCuZn ferrite sintered under microwave processing [at 937°C, (a1)–(a3)], and conventional processing [at 950°C, (b1)–(b3)].

Fig. 9. Time dependencies of grain growth under isothermal condition. (Solid line: Microwave sintering; Dashed line: Conventional sintering.)

Fig. 10. Activation energy of grain growth under isothermal conditions for both microwave and conventional sintering.
sintering results,\textsuperscript{36} it was considered that NiCuZn ferrite absorbed microwave energy more efficiently, so that diffusion and grain growth could be promoted for a shorter time by the microwave radiation.

The local temperature differences at pores and interfaces in the earlier stage of sintering are considered to be the origin of the "microwave effect".\textsuperscript{37,38} The microwave radiation effect on grain growth is expected to be smaller than the effect on densification in the case of densified sample as these interfaces disappear in the later stage of sintering. As a consequence, enhanced grain growth is not observed with isothermal microwave sintering.

3.5 Microwave sintering of bulk type inductor and multilayer chip inductor

From the results of sintering studies, enhanced densification was confirmed in the NiCuZn ferrite sintered under microwave processing. However, these may have differences in residual stress and the magnetic properties. Figure 11 shows the initial permeability ($\mu_i$) and quality factor ($Q = (\tan \delta)^{-1}$) of toroidal samples sintered under both microwave and conventional processing. Figure 12 shows the microstructure of these samples. It was thought that the comparable magnetic properties of NiCuZn ferrite sintered under microwave processing resulted from the similar microstructure.

Using the same heating rate, holding time, and cooling rate conditions, MLCI samples were sintered under microwave processing. Figure 13 shows the inductance ($L$) and quality factor of MLCI sintered under both microwave and conventional processing. Figure 14 shows the external appearance and fractured surface of these samples. The property of the MLCI sintered under microwave processing

![Graph showing frequency dependence of initial permeability and quality factor for NiCuZn ferrite toroidal sintered under microwave and conventional processing.](image)

Fig. 11. Frequency dependence of initial permeability ($\mu_i$) and quality factor ($Q$) for NiCuZn ferrite toroidal sintered under microwave (at 937°C, solid line), and conventional processing (at 950°C, dashed line).

![Microstructure images of NiCuZn ferrites sintered under microwave and conventional processing.](image)

Fig. 12. Microstructure of NiCuZn ferrites sintered under microwave [at 937°C, (a)], and conventional processing [at 950°C, (b)].

![External appearance and fractured surface images of MLCI sintered under microwave and conventional processing.](image)

Fig. 13. Frequency dependence of inductance ($L$) and $Q$ for MLCI sintered under microwave (at 885°C), and conventional (at 900°C) processing.

![External appearance and fractured surface images of MLCI.](image)

Fig. 14. External appearance and fractured surface of MLCI sintered under microwave processing [at 885°C, (a1)–(a3)], and conventional processing [at 900°C, (b1)–(b3)] (a1) and (b1): External appearance of sintered MLCI. (a2) and (b2): Fractured surface of inner electrode part of sintered MLCI. (a3) and (b3): Fractured surface of sintered MLCI.
was found to be comparable to that for conventional processing case owing to the similar microstructure as shown in Fig. 14.

Because of multilayer structure and high heating rate sintering, the samples had a possibility to delaminate between the electrodes and the ferrite, especially when the binder of green MLCI sample was burnt out. However no delaminations were found. In addition, in the case of MLCI sintering, it was needed to sinter electrode (Ag) and ferrite at the same time. From the difference of microwave coupling between electrode and ferrite, local temperature difference appeared under microwave sintering. Figure 15 shows the back scattering electron (BSE) and composition images of vicinity of electrode in MLCI sintered under both microwave and conventional processing at the same temperature. It was observed that electrode (Ag) melted and diffused into the ferrite material under microwave sintering. Therefore, to fully control the microwave sintering, it is needed to measure the local temperature difference in the sample.

4. Conclusions

In this study, the sintering behavior including densification and grain growth, of NiCuZn ferrites in a microwave field of 2.45 GHz was carried out. It was verified that densification of NiCuZn ferrites was significantly promoted by microwave processing. The effective activation energy for diffusion during microwave sintering was half of conventional sintering case. On the other hand, the microwave sintering showed little effect on the activation energy for isothermal grain growth in NiCuZn ferrites. In addition, their toroidal inductors and MLCI have been sintered under microwave processing without causing cracks or delamination, and demonstrated similar properties to conventionally sintered ferrites.

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