The Effect of TiO₂ Addition on the Characteristics of CuFe₂O₄ Ceramics for NTC Thermistors

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Abstract.

The effect of TiO₂ addition on the characteristics of CuFe₂O₄ ceramics for NTC thermistors has been studied. This study was to get an alternative NTC thermistor ceramic from CuFe₂O₄ based-one. The ceramics were produced by pressing a homogeneous mixture of CuO, Fe₃O₄ and TiO₂ (0, 0.25 and 0.75 w/o) powders in appropriate proportions to produce CuFe₂O₄ based ceramics and sintering the pressed powder at 1100°C for 2 hours in air. Electrical characterization was done by measuring electrical resistivity of the ceramics at various temperatures (25°C-100°C). Microstructure and structural analyses were also carried out by using optical microscopy and x-ray diffraction (XRD), respectively. The XRD analyses showed that the CuFe₂O₄ ceramic with and without TiO₂ addition are composed of two crystal structures i.e. cubic and tetragonal spinels. Microstructural data showed that all of the ceramics contain rounded grains and the second phase was segregated at grain boundaries. According to the electrical data, it was known that the TiO₂ addition increased the thermistor constant (B) and the room temperature electrical resistivity (ρRT). The value of B and ρRT of the produced CuFe₂O₄ ceramics fitted those for market requirement.

Key words: Thermistor, NTC, CuFe₂O₄, TiO₂.

I. INTRODUCTION

The NTC thermistors are widely used in the world due to their potential use in many sectors, 1) for many applications such as temperature measurement, circuit compensation, suppression of in rush-current, flow rate sensor and pressure sensor, 1), 2). It is well known that most NTC thermistors are produced from spinel ceramics based on transition metal oxides with general formula of AB₂O₄ where A is metal ion in tetrahedral position and B is metal ions in octahedral position, 3)-10). Many studies have been done to improve the characteristics of the spinel based-NTC thermistors, 6), 7), 11). However, the study on the effect of TiO₂ addition on the characteristics of CuFe₂O₄ spinel ceramics sintered at 1100°C for NTC thermistor has not been reported yet.

Many reports show that the CuFe₂O₄ ceramics can be applied as soft magnet, 12)-14) and catalyst, 15)-17), however, potentially; the CuFe₂O₄ ceramics have capability of being NTC thermistors too due to its semi conductive property. This ceramic is economically interesting because it may be produced using local abundant mineral, such as hematite and magnetite as a part of raw material. According to CuO-Fe₂O₃ phase diagram, 18), there is an area where the ceramic composing of CuO and Fe₂O₃ heated at 1100°C will have a microstructure containing liquid phase. In room temperature, the liquid phase will be a boundary material. This boundary material theoretically may affect the characteristics of the ceramics, especially the electrical characteristics. Since an additive of TiO₂ is added, the characteristics of the CuFe₂O₄ may change because two conditions may occur since the TiO₂ is added to the CuFe₂O₄. The conditions are the TiO₂ dissolves in the CuFe₂O₄ by substituting Cu ions or Fe ions (first) and the TiO₂ does not dissolve but segregated at grain boundaries and may react with the liquid phase that originally exists (second).

Since the first condition occurs, the CuFe₂O₄ ceramics may have a lower electrical resistivity when the substitution of Fe³⁺ and/or Cu²⁺ by Ti⁴⁺ ions creates free electron in the conduction band. Meanwhile, since the second one occurs, the electrical resistivity may be higher because the segregated TiO₂ may change the microstructure. This works is to know the effect of TiO₂ addition on the characteristics of the CuFe₂O₄ ceramics for NTC thermistors, especially the electrical characteristic based on the above-mentioned hypothesis.

II. METHODOLOGY

Powders of CuO, Fe₃O₄ and TiO₂ were weighed in appropriate proportions to fabricate TiO₂ added-CuFe₂O₄ ceramics where the TiO₂ were 0, 0.25 and 0.75 w/o (weight %) and mechanically mixed. The mixture of powders was calcined at 800°C for 2 hours. After calcination, the powder was crushed and sieved with a siever of < 38 μm. The sieved powder was then pressed with pressure of 3.9 ton/cm² into green pellets. The green pellets were sintered at 1100°C for 2 hours in air with heating and cooling rates of 6°C/minutes.
The crystal structure of the sintered pellets was analyzed with x-ray diffraction (XRD) using Kα radiation at 40KV and 30mA. The microstructure of the pellets was investigated by an optical microscope. Before optical investigation, the pellets were ground, polished, and etched. The opposite-side surfaces of the sintered pellets were coated with Ag paste. After the paste was dried at room temperature, the Ag coated-pellets were heated at 500°C for 10 minutes. The resistivity measurement was performed at various temperatures from 25°C to 100°C in steps of 5°C.

III. RESULTS

Fig.1, Fig.2, and Fig.3 show the XRD profile of CuFe₂O₄ ceramics added with 0, 0.25 and 0.75 w/o TiO₂, respectively. The pattern of Fig.1 contains peaks of cubic CuFe₂O₄ but at 2θ = 53.6° there is a peak of tetragonal one (after being compared to the XRD standard profile of cubic CuFe₂O₄ from JCPDS No. 25-0283 and of tetragonal CuFe₂O₄ from JCPDS No. 34-0425). The coexistence of cubic and tetragonal phases is clearly shown in Fig. 2 and Fig. 3. This feature suggests that the cooling rate during sintering was high enough (fast cooling). Goya and Rechenberg, 19) showed that CuFe₂O₄ crystallized to tetragonal spinel when it was cooled slowly from a high temperature. The feature of Fig. 2 and Fig. 3 shows that there is an effect of TiO₂ addition. The structure of the ceramics added with 0.25 w/o and 0.75 w/o is composed of two structures of cubic and tetragonal spinels. The effect seems to be complex as indicated by Fig. 3 that shows that at a high concentration of TiO₂ the ratio of cubic to tetragonal becomes higher (Bragg peak of 311 of cubic becomes higher than that of 211 tetragonal). However, it can be noticed that the addition of TiO₂ decreases the cooling rate.

There is an additional peak at 2θ about 40 (S) in the XRD pattern of CuFe₂O₄ ceramic without addition of TiO₂. This peak comes from a second phase. It may be the grain boundary material that melted during sintering. Compared to the pattern of standard CuO (JCPDS No. 05-0661), it is known that the additional peak (S) is the peak of CuO (200). The same peak and other additional peak cannot be observed in all TiO₂ added samples. It may be because, if any, the yield of the reaction between TiO₂ and CuO (original melted material) is in small concentration and may be due to the small concentration of added TiO₂ that is smaller that the precision limit of the x-ray diffractometer used. According to ionic radii data, there is a possibility that a part of the added TiO₂ dissolved in the CuFe₂O₄ spinel ceramic but it cannot be concluded from the XRD profiles in this works. The microstructure and electrical data may be used to evaluate whether a part of the TiO₂ added was dissolved or not.

Fig. 1. XRD profile of CuFe₂O₄ ceramic without TiO₂ (T means peak from tetragonal and S is peak from second phase).

Fig. 2. XRD profile of 0.25 w/o TiO₂ added-CuFe₂O₄ Ceramic (C means peak from cubic).

Fig. 3. XRD profile of 0.75 w/o TiO₂ added-CuFe₂O₄ Ceramic (C means peak from cubic).

Fig.4, Fig.5 and Fig. 6 are microstructures of the CuFe₂O₄ ceramics added with 0, 0.25 and 0.75 w/o TiO₂, respectively.
It is clearly seen that all ceramics have rounded grains, suggesting the present of liquid phase during sintering. The grains are relatively large, as the consequence of the liquid phase sintering. Based on CuO-Fe₂O₃ phase diagram, 18), the liquid phase is about 15 % of the ceramics. This amount is considerable and affected the grain growth during sintering significantly. This is the reason of large grain formation found. From Fig. 5, Fig. 6 and Fig. 7 it can be seen that the addition of TiO₂ decreases the grain size though it is not significant. It is can be seen also from those figures that the appearance of grain boundary material for the ceramic with and without TiO₂ is different, suggesting the different material. The grain material in the CuFe₂O₄ ceramic without TiO₂ addition is CuO, but that in the CuFe₂O₄ ceramic with TiO₂ addition may be reaction product of CuO and TiO₂ or other material. However, the absent of the additional peaks in the XRD patterns of TiO₂ added-samples may indicate that the main grain boundary material is the same structure with the matrix.

The electrical data of the TiO₂ added-CuFe₂O₄ ceramics is shown in Fig. 7 and Table 1.

\[ \rho = \rho_0 \exp \left( \frac{B}{T} \right) \]  

where, \( \rho = \) Electrical resistivity, \( \rho_0 = \) Electrical resistivity at infinite temperature, \( B \) is the thermistor constant and \( T \) is the temperature in Kelvin.
in our ceramics. In the samples containing TiO$_2$, this is the reason of the large grains formation found considerably promoted grain growth during sintering. This large amount of melted material is segregated and co-exists with the melted material at the grain boundaries. The segregated TiO$_2$ is likely to segregate at grain boundaries. The segregated TiO$_2$ may react with the original melted material but it cannot be known from the XRD profile. The segregated TiO$_2$ then inhibits the grain growth during sintering. This feature is in agreement with the data of microstructure showing that the grain size slightly decreases following the increase of the added TiO$_2$. The thickness of the grain boundary material found in CuFe$_2$O$_4$ ceramic (without TiO$_2$) is relatively thinner than the thickness of the grain boundary material found in those containing TiO$_2$. This is a factor that may affect the electrical characteristics of the ceramics.

The change of the electrical characteristics is controlled by the change of the microstructure that may change by the TiO$_2$ addition. Since the added TiO$_2$ dissolves in CuFe$_2$O$_4$ by substituting Cu and/or Fe following eq. 2 and 3, the room temperature resistivity ($\rho_{RT}$) and thermistor constant (B) should decrease. The increase ($\rho_{RT}$) and (B) as shown by our data indicates that the added TiO$_2$ is not dissolved in the CuFe$_2$O$_4$ and tends to segregate at the grain boundaries. The increase of the ($\rho_{RT}$) and (B) is mainly caused by decrease of grain size and the change of the feature of the grain boundary material.

Table 1. Electrical characteristics of the TiO$_2$ added-CuFe$_2$O$_4$ ceramics.

<table>
<thead>
<tr>
<th>No.</th>
<th>Additive of TiO$_2$(w/o)</th>
<th>B (°K)</th>
<th>$\alpha$ (%/°K)</th>
<th>$\rho_{RT}$ (Kohm-cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>0</td>
<td>2350</td>
<td>2.61</td>
<td>2.9</td>
</tr>
<tr>
<td>2.</td>
<td>0.25</td>
<td>3187</td>
<td>3.54</td>
<td>60.5</td>
</tr>
<tr>
<td>3.</td>
<td>0.75</td>
<td>4759</td>
<td>5.29</td>
<td>119.9</td>
</tr>
</tbody>
</table>

IV. DISCUSSION

The rounded grains of the ceramics are caused by melted material at the grains boundaries. According to the CuO-Fe$_2$O$_3$ phase diagram, the melted material contained by the CuFe$_2$O$_4$ without TiO$_2$ addition is about 15 mole %. This is a relatively large amount. This large amount of melted material considerably promoted grain growth during sintering. This is the reason of the large grains formation found in our ceramics. In the samples containing TiO$_2$, the TiO$_2$ may dissolve or segregate. Since there is no interaction between the original melted material and the TiO$_2$, and the TiO$_2$ is dissolved in the CuFe$_2$O$_4$ ceramic by substituting Fe$^{3+}$ or Cu$^{2+}$ following eq. 2 or 3, the electrical resistivity of the ceramic should be lower, and the microstructure will be the same with that of the CuFe$_2$O$_4$ ceramic. The feature of the grain boundary material in the samples added with TiO$_2$ (See Fig. 5 and 6) is different than that of the ceramic without TiO$_2$ addition (See Fig. 4). This indicates that the added TiO$_2$ is likely to segregate at grain boundaries. The segregated TiO$_2$ may react with the original melted material but it cannot be known from the XRD profile. The segregated TiO$_2$ then inhibits the grain growth during sintering. This feature is in agreement with the data of microstructure showing that the grain size slightly decreases following the increase of the added TiO$_2$. The thickness of the grain boundary material found in CuFe$_2$O$_4$ ceramic (without TiO$_2$) is relatively thinner than the thickness of the grain boundary material found in those containing TiO$_2$. This is a factor that may affect the electrical characteristics of the ceramics.

The ceramics containing small grains and much grain boundary material contains large grain boundary area. Because the grain boundaries act as a scattering center of charge carriers, the relative frequency of electron scattering increases, resulting in an increase in the room temperature resistivity and thermistor constant.

$$2\text{TiO}_2 = 2\text{Ti}^{4+}_\text{Fe} + 3\text{O}_2 + \frac{1}{2}\text{O}_2\text{gas} + 2\text{e} \quad (2)$$

$$\text{TiO}_2 = \text{Ti}^{2+}_\text{Cu} + \text{O}_2 + \frac{1}{2}\text{O}_2\text{gas} + 2\text{e} \quad (3)$$

where, $\text{Ti}^{4+}_\text{Fe} = \text{Ti}^{4+}$ ion occupies Fe sublattice, $\text{Ti}^{2+}_\text{Cu}$ = $\text{Ti}^{4+}$ ion occupies Cu sublattice, $\text{O}_2$ = Oxygen ion occupies oxygen sublattice, $\text{O}_2\text{gas}$ = Released oxygen gas and e = Released electron.

V. CONCLUSION

The CuFe$_2$O$_4$ ceramic can be applied as NTC thermistor. The grain size of the CuFe$_2$O$_4$ ceramics decreases by addition of TiO$_2$ because the added TiO$_2$ is segregated and co-exists with the melted material at grain boundaries and inhibits grain growth during sintering. The addition of TiO$_2$ increases the room temperature resistivity ($\rho_{RT}$) and the thermistor constant (B) as well as the sensitivity ($\alpha$) of the CuFe$_2$O$_4$ ceramics by changing the microstructure. The value of ($\rho_{RT}$), (B) and ($\alpha$) of the CuFe$_2$O$_4$ ceramics made in this work fits the market requirement.

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VI. REFERENCES

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