Effect of cellulose nanofibrils on mechanical and electrical properties of metal ceramic heater

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The effect of cellulose nanofibrils (CNFs) on the mechanical properties of substrate of metal ceramic heater and electrical properties of electrically conductive layer were studied experimentally in a tube furnace at 1600 °C under reduced atmosphere. The alumina ceramics with 96 wt% of alumina and 4 wt% of sintering additives, namely SiO₂ and MgO were applied as the substrate. There was a noticeable rise in fracture toughness of alumina ceramics. The addition of 3 wt% of CNFs in ceramic had a significant effect on the improvement of fracture toughness. A $K_{IC}$ of 6.52 MPa·m$^{1/2}$ was achieved through the addition of 3 wt% CNFs. A considerable decrease in $K_{IC}$ was observed with addition beyond 3 wt% of CNFs. On the other hand, the relative density and bending strength had been steadily dropping with addition of CNFs. The bending strength was 296 MPa with no addition of CNFs. The bending strength of only 158 MPa was achieved with the addition of 5 wt% of CNFs. The sample with 1 wt% CNFs was selected as the substrate. The SiO₂ in the ceramic was reduced by pyrolysis of CNFs and formed W–Si solid solution. The temperature coefficient of resistance was decreased by the solution of Si into W.

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1. Introduction

Nowadays, the electrocaloric materials have been more widely adopted in people’s daily life and some of them are required to be with small volume and high efficiency. Of the many kinds of products that have been applied as electrocaloric materials, metal ceramic heater (MCH) has gained an appreciation for its high heat generation efficiency and excellent corrosion resistance. This electrocaloric material has been used in civilian facilities, medical facilities and military installation.1–4) Obviously, the customers are more interested in its safety, stability, durability and reliability.

Briefly, the MCH is the ceramic with surface metalization. The prepared metal slurry is printed on the surface of ceramic green body via stencil of designed circuit and the green body along with the metal layer after drying is covered by another ceramic green body. The ceramic green body is regarded as substrate of MCH. The two substrates and conductive layer form an indivisible whole after sintering at high temperature. The electrode wires are welded after that. The substrate is crucial to stability, durability and reliability of MCH product. Many kinds of ceramics can be chosen as the substrate. Alumina ceramic is the most common one that are applied as MCH substrate.

Aluminum ceramics, due to its high temperature resistance, abrasion resistance, corrosion resistance, high hardness, chemical stability and other excellent characteristics, are widely used in electrical device, wear-resisting parts, cutting tools and other fields. However, the alumina ceramics are very brittle. Many studies5)–9) have attempted to improve the stress concentration will result in catastrophic cracks. Consequently, low fracture toughness greatly limits its reliability in service. As a substrate, the fracture toughness of alumina is particularly important in the durability and reliability of MCH product. Since the conductive layer in MCH is only 10–20 μm in thickness, the cracks in the substrate will easily break the conductive circuit and then ruin the MCH.

Although many methods7)–9) have attempted to improve the fracture toughness of alumina ceramics, fiber toughening has been found to be an effective method of the melioration of fracture toughness. The crack initiation and propagation can be prevented by the fibers in ceramics. The mechanical mixing of the fibers with ceramics powders10),11) and in-situ synthesis of fibers12),13) in ceramics are the most common ways of fiber toughening. The
mechanical mixing is a simply and practical method of fiber introducing, but the chief objection to this method is non-uniform fibers distribution. On the other hand, the in-situ synthesis of fibers in ceramics can avoid problem of non-uniform mixing and effectively increase the fracture toughness of ceramics.

Cellulose nanoﬁbrils (CNFs) extracted from natural polymers are with high elastic modulus. The sustainable and renewable material has been applied in the melioration of ceramic fracture toughness.14) The carbothermal reduction was applied to form the silicon carbide by the combination of pyrolysis of CNFs and SiO2 in the ceramic. However, the research showed that with the increase of additional content of CNFs in ceramics, the fracture toughness increased with the unexpected decrease of bending strength. The ceramic with 96 wt% alumina content of that research focused on the ceramic with ternary system of Al2O3–SiO2–CaO. However, the alumina ceramics used as MCH substrates are always with Al2O3–SiO2–MgO system which is different from the previous research. The present study tries to introduce CNFs into substrate of MCH product in order to improve the fracture toughness of the substrates. The MCH substrates choose Al2O3–SiO2–MgO system in the present study.

Mechanical properties of MCH substrate and electrical properties of the conductive layer in MCH are two key factors to the product. Consequently, this work mainly focuses on the effect of CNFs on the mechanical properties of MCH substrate and the effect of CNFs on the electrical properties of conductive layer. The batch formula of ceramic with best additional number of CNFs will be decided after comprehensive evaluation. And then the selected ceramic will be employed as substrate of MCH sample. The electrical properties of MCH sample are evaluated after synthesis of MCH sample. The mechanism of the properties changing will be discussed in detail in the article.

2. Experiment

The fracture toughness of alumina ceramics was found to be increased by introduction of CNFs,14) and alumina ceramics are the most popular selections as substrate of MCH. Therefore, the experiment contains two parts. First, CNFs were introduced into alumina to enhance the mechanical property of the carrier. Second, metal slurry was prepared and then screen printed on a carrier with good mechanical property.

2.1 Sample preparation

In this study, alumina powders and sintering additives were applied as starting materials. The sintering additive was composed by MgO and SiO2 powders. The proportion of alumina was 96 wt% and the proportion of sintering additives was 4 wt%. The mass ratio of MgO and SiO2 at the eutectic point was determined to be 9:16 by the Mg–Si binary phase diagram. The purities of raw materials used in this study are listed in Table 1. CNFs were 4–10 nm in diameter and 1–3 μm in length. The CNFs were gradually introduced from 0 to 5 wt% in five increments of 1 wt% each, namely A0 to A5. Although CNFs have good dispersity in water, the dry powders are very easy to agglomerate. However, the uniform distribution of the CNFs in the ceramic must be ensured, thus, all raw materials including the CNFs were thoroughly wet-mixed in a planetary ball mill for 2 h according to the batch formula by using water as the ball-milling medium. The mixture was dried in oven at 100 °C for 24 h to remove the moisture. To avoid the influence by other agent, the mixed powders after drying were pelleted by adding 7 wt% of aqueous CNFs solution (1 wt% content of CNFs) and aged for 24 h. After that, the mixtures were then pressed into rectangular bars (37 mm × 6.5 mm × 6.5 mm) under a pressure of 40 MPa. The green bodies were dried at 100 °C for 24 h and then sintered in a horizontal tube furnace.

The metal slurry was prepared by mixing metal powders and organic carrier. The purities of raw materials used to form slurry are listed in Table 2. The metal powders were composed by 90 wt% of tungsten and 10 wt% of manganese. Since the screen-printing machine required the slurry with viscosity of 25 Pa·s, the mass ratio of the metal powders and the organic carrier was 9:1. The metal powders and organic carrier were thoroughly mixed in a planetary mill at 500 r/min for 6 h.

2.2 Experimental procedure

To gain an insight into the effect of CNFs on the alumina ceramics, a high temperature horizontal furnace with MoSi2 heating elements was introduced in the present experiment. As shown in Fig. 1, an alumina tube was employed as reaction chamber. The samples along with crucible were placed in the hot zone of the furnace. The reaction chamber was closed by stainless steel flanges at both ends. A B-type thermocouple was threaded through one of the flanges to measure the temperature of sample. The sintering temperature was set as 1600 °C. The reaction chamber was evacuated and flushed with experimental gas three times to ensure that most gas was experimental gas. The 99.99% argon gas was introduced into the reaction chamber to protect CNFs in the ceramics from oxidation.

| Table 1. Details of the materials used in MCH substrate |
| Ingredient | Purity | Manufacturer |
|---|---|---|
| α-Al2O3 | ≥99.99% | Sumitomo Chemical Co., Ltd., Japan |
| MgO AR, 98.0% | | Shanghai Macklin Biochemical Co., Ltd. |
| SiO2 | | Sinopharm Chemical Reagent Co., Ltd. |
| CNFs | 99.6% | Guilin Qhong Technology Co., Ltd. |

| Table 2. Raw materials of metal slurry |
| Materials | Purity (wt%) | Company |
|---|---|---|
| Tungsten powders | ≥99.90 | Shanghai Macklin Biochemical Co., Ltd. |
| Manganese powders | ≥99.90 | Shanghai Macklin Biochemical Co., Ltd. |
| Terpineol | | Sinopharm Chemical Reagent Co., Ltd. |
| Ethyl cellulose AR | | Sinopharm Chemical Reagent Co., Ltd. |
| Ethano | | Sinopharm Chemical Reagent Co., Ltd. |
According to a previous study, the heating rate near the thermal decomposition temperature of the CNFs exerts considerable influence on the morphology of the original shape. Consequently, 6 h were needed to heat the sample from room temperature to 600 °C. From 600 to 1600 °C, the heating rate kept at 4 °C/min. The sample was soaked at 1600 °C for two hours. Thereafter, the furnace was cooled down with 4 °C/min to protect the tube from thermal shock.

To prepare MCH sample, the heating circuit must be printed on the ceramic substrate, so carvings of conductive circle must be designed first. After the ceramic sample with great mechanical property was chosen, the sample mixture was pressed into a square with 20 mm in length and 1.5 mm in thickness. The designed circuit was printed on the ceramic substrate through the designed stencil by printing machine. The designed circuit and a sample photo after screen printing were presented in Fig. 2. Another ceramic without circuit was adhered on the substrate. The MCH green body was then placed in the same horizontal tube furnace for sintering. The same experimental procedure was applied to prepare the MCH sample. The experimental gas simulated the gas in industry, which was H₂ pass through warm water with temperature of 37 °C. After sintering, the nickel wires were welded in the joints. The photo of MCH product was presented in Fig. 3.

2.3 Characterization

Relative density was measured by AUY120 electronic analytical balance (Japanese Shimazu) through static weighing method. The bending strength of the samples after the experiment was evaluated through a three-point bending mode by using a computer-controlled electronic universal testing machine (REGER-4100, produced by Shenzhen Rui Geer, China). The fracture toughness was measured by indentation method. The sample surface was firstly polished and a micro-hardness tester (HVT-1000) was used to produce an indentation on the cone diamond head of the hardness tester on the polished surface with a load. The fracture toughness value \( K_{IC} \) was calculated based on indentation load \( P \) and indentation crack propagation length.

The resistance of the samples at different temperature points was measured by applying a DC low resistance tester (Jinhua Jinlitong Electronics Co., Ltd., China). The temperature coefficient of resistance (TCR) of the sample was calculated through Eq. (1).

\[
\alpha = \frac{R_1 - R_0}{R_0(T_1 - T_0)}
\]  

Where \( \alpha \) is TCR, \( R_1 \) and \( R_0 \) are the resistance of sample at temperature \( T_1 \) and \( T_0 \). \( T_0 \) is room temperature and \( T_1 \) is temperature of measurement.

After that the MCH specimen was analyzed by scanning electron microscopy (SEM) after Au–Pd coating. A field
emission scanning electron microscope (QUANTA FEG 450, US) with energy dispersive spectroscopy (EDS) was employed.

3. Results and discussion

3.1 Effect of CNFs on the mechanical properties of alumina substrate

Figure 4 presents the relative density and open porosity as function of CNFs content in alumina ceramics. A decrease in relative density and an increase in open porosity were observed. The CNFs are organic materials with high elastic modulus. On the other hand, the organic materials cannot be compatible with alumina powders. Consequently, the density of green body is hard to be granted via semi-dry pressing method. Figure 5 shows the mechanical properties as a function of additional CNFs in the samples. The low relative density is held responsible for the consequences of unacceptable bending strengths of alumina arising therefrom. However, the fracture toughness of alumina ceramics rises in the first stage, and then decreases. Sample A3 is with the highest fracture toughness of 6.52 MPa·m$^{1/2}$ but the bending strength of which is low.

The mechanical properties of alumina samples depend on its microstructure. Figure 6 shows the microstructure of sample A3 after sintered at 1600 °C. A fiber is found to be attached on two alumina grain boundaries. The fiber in present study was identified as SiC fiber according to the research. Figure 7 shows that CNFs have high aspect ratio and fiber network structure after high temperature pyrolysis. The CNFs provided fiber templates and SiC fiber was formed by carbothermal reduction. The microstructure of the sample can illustrate the improvement of fracture toughness. Definitely, the fiber is the kernel to the increasing of fracture toughness. The fibers can provide different means of energy dissipation in order to prevent crack propagation and absorb impact energy. On the other hand, the grain boundaries of particles do not contact with each other. However, the unexpected pores and defects in ceramic are another reason for the improvement of fracture toughness. CNFs are organic materials which are extracted from natural polymer and with high elastic modulus. The incompatibility of CNFs with alumina powders strongly prevents the aggregation of the alumina grains. Moreover, heat treatment will cause the emission of gas before the transformation of CNFs into carbon fibers. Pores will remain in the alumina specimen. These two behaviors bring the alumina specimen with low relative density and low bending strength. On the contrary, the defects are beneficial to the improvement of fracture toughness. Resistance to crack initiation and propagation...
is a critical factor in the melioration of fracture toughness. The previous study evidently showed that the pores at the crack front make the crack tip blunting. Consequently, the pores that remain in the alumina ceramics prevent the crack propagation.

However, the consistently decreasing of bending strength with additional content of CNFs in ceramics is understandable according to previous analysis. The trend of fracture toughness with addition of CNFs in Fig. 5 must be discussed here. The explanation is given as follows: although the pores prevent the crack propagation, the increased pores in ceramic greatly decline the hardness of sample. The fracture toughness is also strongly related to the hardness of sample. In present study, Vickers indentation fracture toughness (VIF) test was applied. Equations (2) and (3) were used to calculate the fracture toughness of ceramic samples.

\[
\frac{K_{IC}}{H_0^{1/2}} = \frac{H}{E\varphi} \left( \frac{c}{a} \right)^{-3/2} \left( \frac{c}{a} \geq 2.5 \right) - 0.129 \left( \frac{c - a}{a} \right)^{-1/2} \quad \left(0.25 \leq \frac{(c - a)}{a} \leq 2.5\right)
\]

where \( H \) is the Vickers hardness (GPa), \( K_{IC} \) is fracture toughness (MPa m\(^{1/2}\)), \( a \) is the half length of the indentation diagonal (mm), \( c \) is half length of the surface crack (mm), \( \varphi \) is the shape factor (\( \varphi = 3 \)), and \( E \) is the elastic modulus (\( E = 300 \) GPa).

As shown in Eqs. (2) (3), the fracture toughness depends on not only length of crack propagation but also hardness of specimen and diagonal of the indent. The defects can prevent the propagation of cracks, but they lower the hardness of ceramics at same time. Therefore, the consistently decreasing of hardness will cause reduction of the fracture toughness, because the low value of hardness enlarges the diagonal of the indent. Hence, the fracture toughness increased with the addition of CNFs but decreased sharply beyond 3 wt\%.

**Figure 8** shows morphologies of the specimens showing crack propagation after \( K_{IC} \) tests. The sample with a CNFs content of 1 wt\% has relatively small indentation size and obvious cracks. In contrast, the sample with a CNFs content of 3 wt\% has a large indentation size and no obvious cracks at the top of the indentation. The addition of CNFs has an effect on increasing the fracture toughness of the sample. However, it will decrease the hardness of the material to a certain extent. For MCH products, to sacrifice bending strength for improving fracture toughness is unacceptable. Considering both fracture toughness and bending strength of MCH substrate, sample A1 is selected as the substrate candidate.

### 3.2 Effect of CNFs on the TCR of MCH

The batch formula of sample A1 is employed as the substrate of MCH sample in present study. The MCH products are used as heating elements and the TCR curve is always applied to control the heating temperature. Consequently, the resistances of MCH samples at different temperature are essentially important, since TCR can be calculated by Eq. (1). After preparation of MCH samples, the resistances of the samples at different temperature are measured and linear relation is observed in **Figure 9**. The resistance of sample at room temperature is 3.04 and 8.21 \( \Omega \) is the resistance of sample at 500 °C. According to Eq. (1), the TCR of MCH sample is calculated as 3783 ppm/°C. On the other hand, the electrical properties of MCH are from the printing circuit. The conductive layer in present study is composed by W, Mn and organic carrier according to the composition of metal slurry.

Among those components of the conductive layer, elements W and Mn play different roles. W plays a role of electricity conduction and heat generation. Mn will be oxidized under \( H_2/O_2 \) atmosphere and the MnO makes the conductive layer combine with ceramic substrate. Therefore, only W participates in the conduction of electricity. However, the TCR of W is found to be 4800 ppm/°C. The TCR of the present MCH sample is lower than the value of pure W.

**Figure 10** shows the microstructure of MCH sample and its mapping results. The white phase in SEM picture is
The conductive layer and the rest dark part is alumina substrate. The element Si is clearly observed in the mapping results. EDS analysis shows that the content of Si is around 1 wt% in the conductive layer. The appearance of Si in the conductive layer proves that the formation of W–Si solid solution. The solid solution will influence the TCR and it is the main reason for the reduction of TCR value. The TCR of solid solution can be expressed as following Eq. (4):\(^{20}\)

\[
\alpha_s = \frac{\rho_0}{\rho_0 + \rho_1} \alpha
\]

Where \(\alpha_s\) is TCR of solid solution, \(\alpha\) is temperature coefficient of solvent in solid solution, \(\rho_0\) is resistivity of solvent in solid solution and \(\rho_1\) is the resistivity of solute in solid solution. Hence, the solute Si in W–Si solid solution makes TCR value of MCH sample lower than that of pure W.

It should be mentioned here that no Si or silicate compound is in the metal slurry and Si element only exists in the ceramic substrate as the form of SiO\(_2\). The formation of W–Si solid solution is explained as the reduction of SiO\(_2\) during the experimental procedure. Thermodynamically consideration shows that reaction (5) happens at temperature above 1500 °C according to the Gibbs energy of reaction.

\[
\text{SiO}_2 + 2\text{C} = \text{Si} + 2\text{CO} \\
\Delta G = 717550 - 369.18T \text{J/mol}
\]
Because carbon will be formed by pyrolysis of CNFs under the reduction atmosphere, the amorphous carbon reacts with SiO$_2$ at temperature above 1500 °C. Thus, the CNFs are the source for the formation of Si. Meanwhile, when Si is formed at above 1500 °C, the activity of pure Si is 1 and Si will dissolve spontaneously into W in order to lower the activity. Therefore, the W–Si solid solution is formed.

It must be noted that the metal slurry also contains organic carrier, so the organic carrier may also bring carbon during heat treatment. However, this point of view is untenable. The carrier is composed by 94 wt% of terpineol, 5 wt% of ethyl cellulose and 1 wt% of ethanol. The terpineol and ethanol are the organic materials which are easy to volatilize. Only 5 wt% of ethyl cellulose in organic carrier may transfer into carbon. As described in experiment part, the slurry only contains 10 wt% of organic carrier, so only 0.5 wt% of ethyl cellulose remains in the slurry. Because most weight will be lost during the pyrolysis and the weight of conductive layer is around 22 mg after printing, the carbon brought by the organic carrier can be ignored accordingly.

From product perspective, CNFs may not be a good option for MCH producing. Although the CNFs can somehow improve the fracture toughness of alumina ceramics, the unexpected decreasing of bending strength limits the effect on the improvement of mechanical properties. Additionally, the inevitable formation of W–Si solid solution by the reaction between pyrolysis of CNFs and SiO$_2$ in the alumina ceramics substrate brings the change in TCR of MCH product. Those shortcomings need to be considered at the same time.

4. Conclusions

The influence of CNFs on the mechanical properties and electrical properties of MCH sample were investigated by using a horizontal tube furnace at 1600 °C under protective atmosphere. The alumina ceramic was employed as MCH substrate. CNFs were applied to improve the fracture toughness of MCH substrate. Microstructure showed that the SiC fiber was formed in the sample. A significant increasing of fracture toughness was found with the addition of CNFs but a notable decrease in $K_{IC}$ was observed with addition beyond 3 wt% of CNFs in ceramics. A $K_{IC}$ value of 6.52 MPa$\cdot$m$^{1/2}$ was gained by the addition of 3 wt% CNFs. On the other hand, the downward trend in relative density brought the steadily dropping of bending strength with addition of CNFs content increasing. The bending strength of 296 MPa was observed without addition of CNFs. The increasing content of CNFs in the ceramic had serious implications for the bending strength of ceramics, which was lowered by around 50 wt%. Only 158 MPa in bending strength was achieved with the addition of 5 wt% of CNFs. The sample with 1 wt% CNFs was selected as MCH substrate after comprehensive consideration. After synthesis of MCH, the unexpected decline of TCR was observed. The TCR of 3784 ppm/°C was obtained. It was found that the SiO$_2$ in the ceramic was reduced by pyrolysis of CNFs and formed W–Si solid solution. The TCR value was decreased by the solution of Si into W. CNFs may not be a suitable additive for MCH substrate.

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