Transactions of the Materials Research Society of Japan 25 [3] 705-708 (2000)

Electrical and Capacitive Properties of Woodceramics for Humidity Sensor

Kazuhiko Kakishita, Toshikazu Suda and Hideaki Irisawa*
Polytechnic University, Department of Electronic Engineering,
4-1-1 Hashimotodai, Sagamihara, Kanagawa 229-1196, Japan
Fax: 81-42-763-9096, e-mail: kakisita@uitec.ac.jp
** Sanriki Corporation*
2-7-6 Omori-naka, Ohta-ku, Tokyo 143-0014, Japan
Fax:03-3763-8415, e-mail: eclipse@mx1.alpha-web.ne.jp

Electrical properties of woodceramics have been studied aiming at the usage for humidity sensor. Electrical resistance of woodceramics indicates the negative-temperature coefficient and the B constant of 6×10^2K as thermistor has been derived from the temperature dependence of resistivity. Relative humidity dependence of the electrical resistance for woodceramics with large surface area shows an excellently linear relationship in the range 15 - 70%RH measured. There occurs distribution of density in woodceramics: we found that electrical permittivity is correlated with the density.

Key words: woodceramics, humidity sensor, porous carbon, electrical properties, density distribution

1. INTRODUCTION

Sensing and controlling environmental humidity is receiving a great attention for industrial processes and also human comfort. In recent years the use of humidity control systems has increased in the quality control of production processes and a wide variety of industries. A large number of ceramic, polymeric, and composite sensors have been investigated as sensing elements [1 - 5]. Since each of these have advantages and limitations, no single device can be considered to be universally applicable as a humidity sensor.

Ceramic humidity sensors have shown advantages over polymer sensors in terms of their mechanical strength, resistance to chemical attack, and their thermal and physical stability [3, 5]. Polymers are inherently less robust than ceramics, and are limited to lower temperatures in usage with slow response, long-term drift, and hysteresis. Woodceramics (WCMs hereafter) are new porous ceramic materials and have recently shown a strong promise of constituting the next generation of industrial materials [6, 7]. The WCMs are drawing particularly strong attention as ecomaterials of low cost with the prominent characteristics of lightness, hardness, porosity, corrosion resistance, and heat resistance. The WCMs are fabricated by sintering woody materials impregnated with phenolic resin forming glassy carbon. It is noteworthy that WCMs can be fabricated from wood waste, waste papers, sawdust, telephone books and so on, thereby WCMs are environment conscious materials designed for minimizing the environmental impacts. When WCMs is used as sensors at commercial base, the problem of uniformity of WCMs should be taken into consideration. It is likely that there occurs distribution of the density because the size is subjected to shrink and the phenolic resin becomes gas phase during the sintering.

In this paper we report on the electrical properties of WCMs, particularly humidity and temperature dependence of electrical resistance. The distribution of density in bulk wood ceramics and the electrical permittivity were also measured, and were discussed.

2. EXPERIMENTAL

Medium-density fiber board (MDF hereafter) made from pinus radiata was used to manufacture WCMs. The MDF was impregnated with phenolic resin using an ultrasonic impregnation system [7]. After the impregnated MDF was dried at 135°C, it was sintered at 650°C (for electrical resistance measurements) and 500°C (for density distribution measurements) in a vacuum furnace to form WCMs. After cutting the WCMs to desired size, aluminum or gold was evaporated in vacuum onto the WCMs to make ohmic contacts as electrodes for measuring electrical characteristics. In order to remove strain of the specimens and for reproducibility of measurements, the specimens were annealed at 300°C for 30 min and then subjected to the current of 10 mA for 90 min. Electrical and humidity dependences of WCMs were measured in the chamber equipped with the Peltier stage to control the specimen temperature. Humidity was controlled by supplying wet and dry nitrogen gas by either bubbling the gas through water or passing it. The electrical resistance were measured by flowing a constant DC current of 1 mA between two electrodes and detecting potential yielded. The density distribution in WCMs was measured by X-ray TV system (SHIMAZU SMX-130). Electrical permittivity was derived from electrical capacitance measured using the sandwich-type electrode with 1 cm^2 area. Frequency for capacitance measurement were varied from 1 kHz to 100 kHz at 1 V applied.

3. RESULTS AND DISCUSSION

3.1 Temperature dependence of electrical resistance

Temperature dependence of the electrical resistance has been measured at temperatures from 25°C to 65°C for the WCM specimens at the relative humidity of 40%RH when varied thicknesses (1, 3 and 5 mm with cross section 6 x 4 mm^2), and are shown in Fig. 1 and Fig. 2. The resistance decreases with increasing temperature; indicating the negative temperature coefficients like semiconductor.

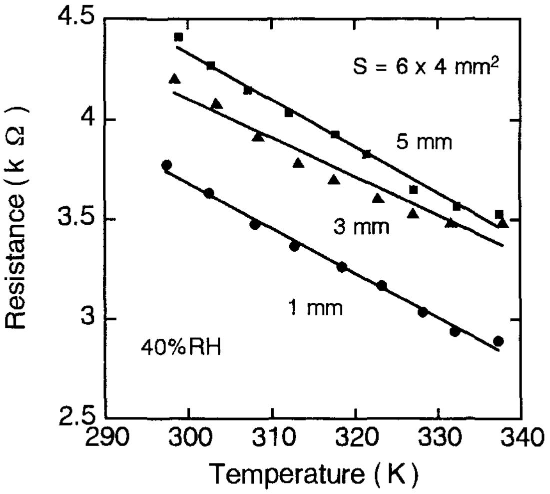


Fig1 Electrical resistance versus temperature at relative humidity of 40%RH for typical WCMs.

In general, electronic conduction and ionic conduction exist simultaneously in porous ceramics [12]. At low humidity, electronic conduction plays a major role, while ionic conduction plays a major role at high humidity. At medium humidity, there is a transition from electronic to ionic conduction. The resistances measured at 40%RH in Fig. 1, are the results given by the sum of electronic and ionic conduction.

The B value of thermistor is expressed by

$$B = \frac{\ln R_1 - \ln R_2}{1/T_1 - 1/T_2} \quad (1),$$

where R_1 and R_2 are the resistance at the absolute temperature T_1 and T_2, respectively. From Arrhenius plots of the electrical resistance shown in Fig. 2, the B values have been derived and show about 6x10^{2}K irrespective of the size of WCMs. This value is large enough as thermistor for commercial use.

3.2 Humidity dependence of electrical resistance

Humidity dependence of the electrical resistance is presented in Fig. 3 for the WCM specimens with various thickness (cross section 6 x 8 mm^2) at room temperature. The data have been taken after 5 min when the each humidity value has been obtained. The ordinate is shown here in relative resistance in order to facilitate the comparison with each other. It should be noted that the resistance change of WCMs with thickness thicker than 4 mm indicates a good linear relationship with humidity, whereas that with thickness thinner than 2 mm indicates a rise at low humidity range. It is suggested that the resistance change depends on the total surface area of WCM

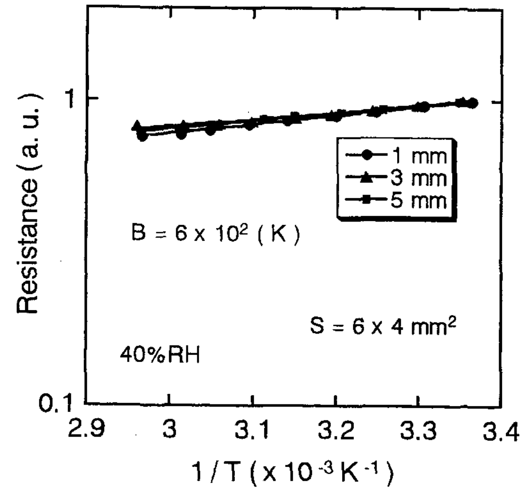


Fig.2 Arrhenius plots of elecrical resistance for WCMs.

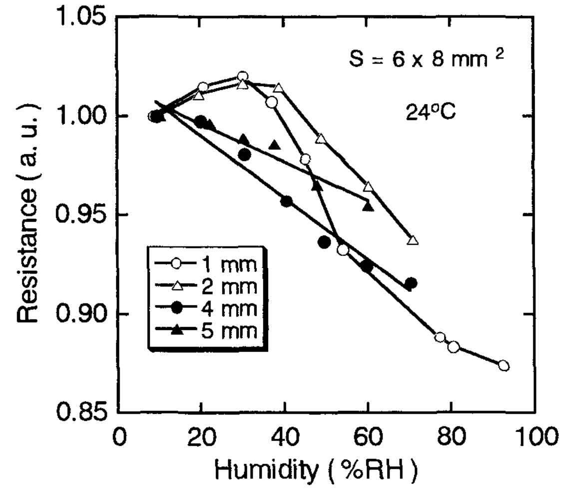
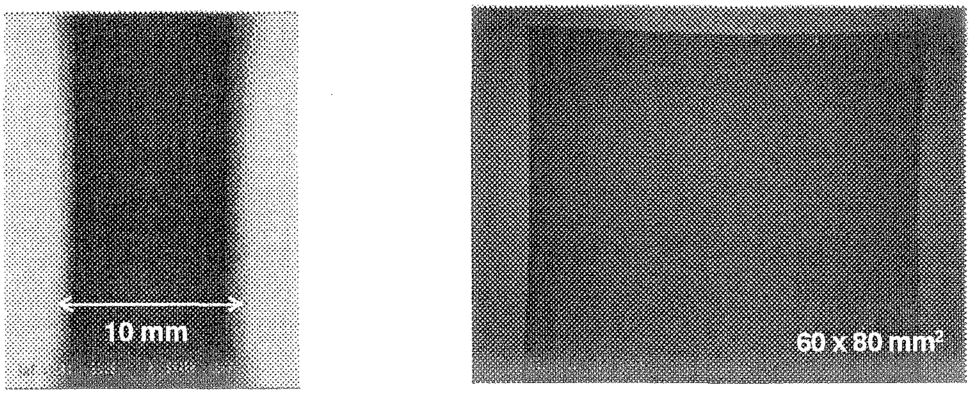


Fig.3 Relative humidity dependence of electrical resistance at 24°C.



(a) cross sectional view (b) plane view

Fig.4 X-ray transmission photograph of woodceramics sinetered at 500°C.

specimen, since the change of resistance on humidity is caused by the adsorption of water molecules at the porous surface. The adsorption of water molecules at the WCMs surface, could give rise to donor-like surface states [13], although the details of the process are not well understood. In addition, chemisorption, physisorption, and/or capillary condensation of water molecules within the pore structure lead to the dissociation of water molecules, yielding hydronium (H_3O^+) and hydroxyl (OH^-) ions [3]. These ions may attach to the surface at cationic or anionic sites. With application of an electric field, ions move to alternate sites, causing a reduced resistance. Consequently, the resistance decreases with humidity.

3.3 Distribution of density and electrical permittivity

X-ray transmission photographs are presented in Fig.4 for WCM specimen with 60 x 80 x 10 mm^3 sintered at 500°C. The MDF has a layered structure of woody fiber as clearly observed in Fig.4(a). During the sintering the phenolic resin changes into glassy carbon, thereby reinforcing the cell walls of wood cellulose. The glassy carbon has superior properties of corrosion resistance, mechanical strength, and suppresses the fissures and warps, retaining several of charcoal properties such as porosity, lightness, and so on. Black region can be observed at the periphery of the specimens as shown in Fig4(b), which means the density is high at the periphery.

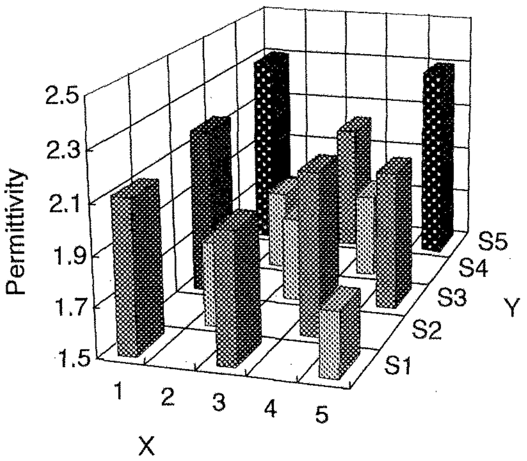


Fig.5 Permittivity distribution of bulk woodceramics mesured at 100 kHz.

Figure 5 shows the permittivity distribution of the same specimen. Permittivity is derived from the electrical capacitance measured at a frequency of 100 kHz. The average values of permittivity inside and outside of the specimen are about 1.9 and 2.1, respectively. That is, there is a difference in the permittivity between the periphery and inside. As a result, the density and permittivity are correlated each other. It is necessary to fabricate WCMs with uniform density for the commercial use. It is suggested that the permittivity measurement is the effective method to evaluate the density distribution.

The permittivity of WCMs increased form about 6 to 2 as the measurement frequency was decreased from 1 kHz to 100 kHz. This result suggests that WCMs have a long dipole moment and is consistent with the condensed aromatic ring structure of WCMs.

4. CONCLUSION

Electrical properties and distribution of density and permittivity of WCMs fabricated at 500°C and 650°C have been evaluated. The B constant of 6x10^{2}K as thermistor was derived from the temperature dependence of resistivity which is large enough for thermistor of commercial use. Relative humidity dependence of the electrical resistance for woodceramics with large surface area shows an excellently linear relationship in the range 15 - 70%RH measured. There occurs distribution of density and electrical capacitance where these two factors are correlated each other. The permittivity of woodceramics increased as frequency was decreased.

It seems that the woodceramics is a suitable candidate for use as a humidity sensor and also temperature sensor at low cost. Additional challenges remain to realize better sensitivity in practical application.

ACKNOWLEDGMENTS

The authors are indebted to Dr. T. Okabe of Industrial Research Institute of Aomori Prefecture for many helpful discussions and to Mr. T. Maehara at Sanriki Co. for fabrication of WCMs. We also wish to express our appreciation to Ms. Y. Kadowaki, Mr. M. Morita, Ms. Y. Suzuki and Mr. N. Morita for technical assistance.

References

[1] N. Yamazoe and Y. Shimizu, Sens. Actuators 10(1986), 379 - 398.
[2] B. M. Kulwicki, J. Am. Ceram. Soc., 74(1991), 697 - 708.
[3] H. Arai and T. Seiyama, “Sensors: A Comprehensive Survey”, Ed. By W. Goepel, J.Hesse, and J. H. Zemel, V CH Publishers, Weinheim (1992) Vol. 3, pp. 981 - 1012.
[4] J. G. Fagan and V. R. W. Amarakoon, Am. Ceram. Soc. Bull. 72m(1993), 119 - 130 .
[5] E. Traversa, Sens. Actuators B23(1995), 135 - 156.
[6] T. Okabe, K. Saito, and K. Hokkirigawa, J. Porous Mat., 2(1996), 207 -213.
[7] T. Okabe, K. Saito, M. Fushitani, and M. Otsuka, J. Porous Mat., 2(1996), 223 - 228.
[8] M. M. Tang and R. Bacon, Carbon, 2(1964), 211 -220.
[9] C. Morterra and M. J. D. Low, Carbon, 21(1983), 283 - 288.
[10] K. Ouchi and H. Honda, Fuel, 38,(1959) 429 - 443.
[11] Y. Yamashita and K. Ouchi, Carbon, 19(1981)., 89 - 94
[12] H. T. Sun, M. T. Wu, P. Li, and X. Yao, Sens. Actuators, 19(1989), 61 - 70.
[13] S. Suehara, T. Hatano, and A. Nukui, Appl. Surf. Sci. 100/101(1996), 252 -255.

(Received December 16, 1999; Accepted March 30, 2000)