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Improvement of Humidity Sensitivity of Woodceramics by Metal Doping

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Electrical properties of woodceramics (WCMs) doped with various metals have been investigated. The samples were prepared by dipping the WCMs into solution of metal compounds of various concentrations. After the dip, those were annealed in vacuum at 600°C. When the resistance of WCMs becomes lower than that without metal doping, the resistance change ratio to humidity change becomes larger since the metal doped WCMs enlarge the ability of water absorption. The resistance response of WCMs doped with chromium to humidity is improved compared to that without doping. The metal doping technique is useful to control the resistance of WCMs for making reliable and improving the sensitivity to humidity.
Key words: woodceramics, humidity sensor, porous carbon, electrical properties, metal doping

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 in 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 them has 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 the use at lower temperatures because of 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 -12]. 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 to form 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 (ecomaterials) designed for minimizing the environmental impacts. It is reported that the electrical resistance of WCMs decreases with increasing humidity and the change of resistance on humidity is caused by the absorption of water molecules at the porous surface [8 -12].

In commercially used sensors, magnesium or tin are doped for the purpose of improvement of the sensitivity. It is known that titanium and nickel make a hydrophilic group on the surface of materials by photocatalyst action. Thus, the improvement sensitivity of humidity is expected by doping metals into WCMs. Furthermore, WCMs can be fabricated from various woody materials so that metal doping technology becomes important for equalizing of WCMs resistance. In this paper, the electrical characteristics of WCMs doped with various metals have been studied and the validity of metal doping technique is discussed.

2. EXPERIMENTAL

Medium-density fiber board (MDF hereafter) 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 600°C in a vacuum furnace to form WCMs. In order to dope

Table 1 Metal compounds used for doping in WCMs.

Metals	Metal Compound	Chemical Fomula
Cr	Chromium Acetate	$(CH_3COO)_3Cr$
Zn	Zinc Acetate	$(CH_3COO)_2Zn$
Ti	Titanium (III) Chloride	$TiCl_4$ (liq.)
Ni	Nickel(II) Chloride	NiCl
Zr	Zirconium Oxychloride	$ZrOCl_2$
Sn	Tin(II) Aetate	$(CH_3COO)_2Sn$
Li	Lithium Percholorate	$LiCl_4$

metals into WCMs, they were dipped into the solution with metal compounds shown in table 1 at various concentrations for 24 or 48 hours. After drying the samples, they were annealed at 600°C for 10 min in vacuum furnace. Aluminum was evaporated in a high-vacuum onto the WCMs surface to make ohmic contacts as electrodes. The space between the electrodes was 3 mm. In order to remove physical strain of the specimens during the fabrication and for reproducibility of measurements, the samples were subjected to a forming by a current of 10 mA for 30 min. Electrical resistance were measured in the chamber where humidity was controlled in the range between 5 and 80%RH by introducing steam and dry nitrogen gas.

3. RESULTS AND DISCUSSION

Metal concentration dependence of electrical resistance at the humidity of 5%RH for WCMs doped with Cr and Zn is shown in Fig.1. The slashed region in Fig.1 indicates the resistance for WCMs without metal doping. The resistance for WCMs dipped in the solution for 24 and 48 hours shows the same tendency so that the amount of metals incorporated at WCMs surface is saturated less than 24 hours dipping. The way of resistance change is different between Cr doping and Zn doping. As the metal concentration increases, the resistance increases for Cr doping; on the other hand the resistance decreases for Zn with concentration. It seems that Cr and Zn atoms are adsorbed at different sites of WCMs surface. The resistance for WCMs doped with low concentration of Cr and Zn indicates lower values. However, that doped with high concentration of Cr indicates larger values compared to that without metal doping. Low concentration of Cr and Zn atoms absorbed at a part of the sites to emit carriers which contribute to current. High concentration Cr is absorbed at all sites which

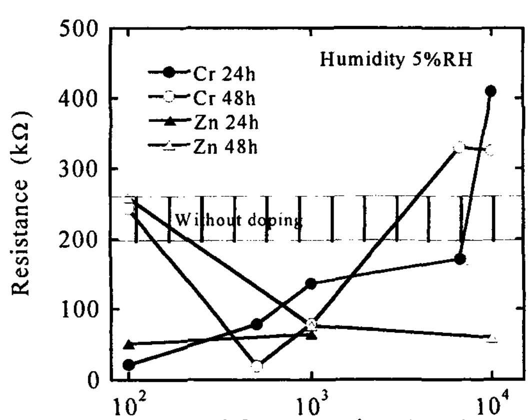

Fig.1 Metal concentration dependence of electrical resistance for WCMs doped with Cr and Zn.

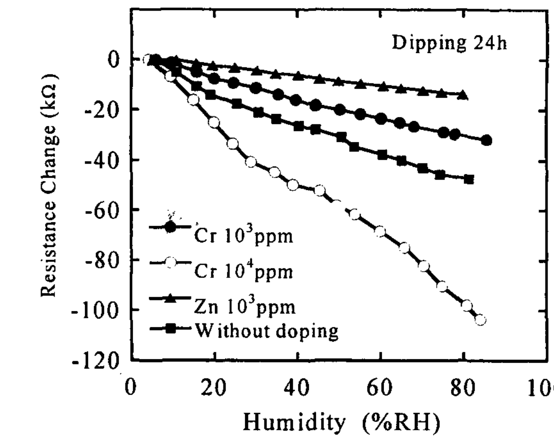

Fig.2 Humidity dependence of resistance change for WCMs doped with Cr and Zn.

Table 2 Resistance at 5%RH and resistamce change (5% -> 80%RH) for WCMs.

Sample	Resistance at 5%RH (kΩ)	Resistance Change at 5%RH -> 80%RH (kΩ)
Zn 10^3ppm	64	14
Cr 10^3ppm	136	32
Without doping	194	47
Cr 10^4ppm	409	104

captures carriers.

Figure 2 represents the humidity dependence of resistance change for WCMs doped with Zn and Cr where the resistance was subtracted by that at 5%RH. The resistance at humidity of 5%RH and the resistance change for the humidity change from 5 to 80%RH are summarized in table 2. As the humidity increases from 5 to 80%RH, the resistance decreases due to the absorption of water molecules at the porous WCMs surface, yielding H_3O^+ and OH^- ions. The amount of resistance change is larger for the WCMs with larger resistance at humidity of 5%RH. Figure 3 shows the humidity dependence of resistance normalized by the resistance at humidity of 5%RH. Although the amount of resistance change depends on the resistance at humidity of 5%RH, the change ratio shows almost the same values in all WCMs.

It is assumed that the resistance of WCMs is shown by

$$R_0 + \Delta R = \frac{1}{(n_0 + \Delta n) q \mu} \cdot A \qquad (1),$$

where R_0 and n_0 are the resistance and carrier concentration at humidity of 5%RH, ΔR and Δn are changes of resistance and carrier concentration for the humidity change, μ is mobility of carriers, q is

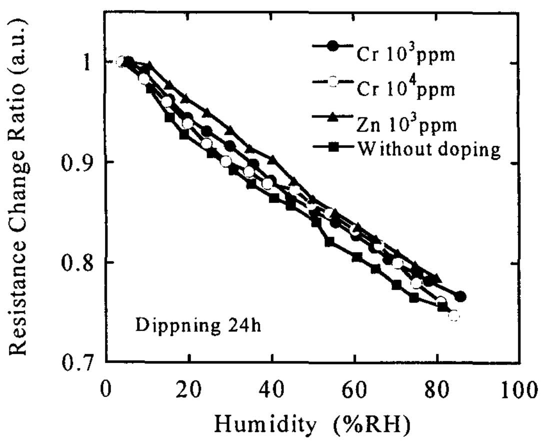

Fig.3 Humidity dependence of normalized resistance for WCMs doped with Cr and Zn.

electric charge and A is constant formula factor. When the increase of carrier concentration (Δn) only depends on humidity, the resistance change (ΔR) and the change ratio ($R_0 + \Delta R/R_0$) become large where R_0 is large, while those are small where R_0 is small.

Figure 4 shows resistance change ratio for the humidity change form 5 to 70%RH versus resistance at humidity of 5%RH. The slashed region in Fig.4 is calculated from eq. (1) using Δn obtained from the results of WCMs without metal doping. It is clearly observed that the data points of WCMs which has lower resistance due to metal doping exist at lower part of the region, while and that which have larger resistance exist at the upper part of the region. These results suggest that the WCMs with lower resistance than the slashed region have a large ability for absorption of water and indicate a large change of resistance to humidity.

Resistance change ratio of WCMs doped with various metals for humidity change from 5 to 80%RH versus the resistance at humidity of 5%RH is shown

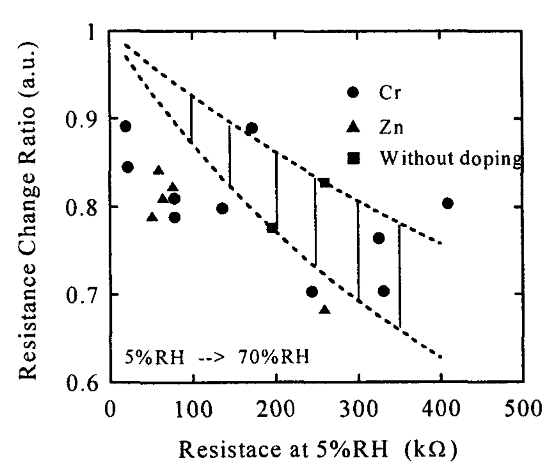

Fig.4 Resistance change ratio at humidity change from 5%RH to 70%RH v.s. resistance at 5%RH.

in Fig.5, where the metal concentration is 10^3ppm with the dipping time of 24 hours in metal compound solution. The slashed region is calculated from eq. (1). The resistance for WCMs doped with Li, Ni, Zn, Ti and Cr become lower, while that doped with Sn and Zr become larger than that without doping. Therefore, the absorption site of metals on WCMs surface seems to be different among metals. Li, Ni, Zn, Ti and Cr make their resistance low and enlarge the ability of water absorption caused by the large change ratio of resistance. On the contrary, Sn and Zr make resistance high and weaken the ability of absorption.

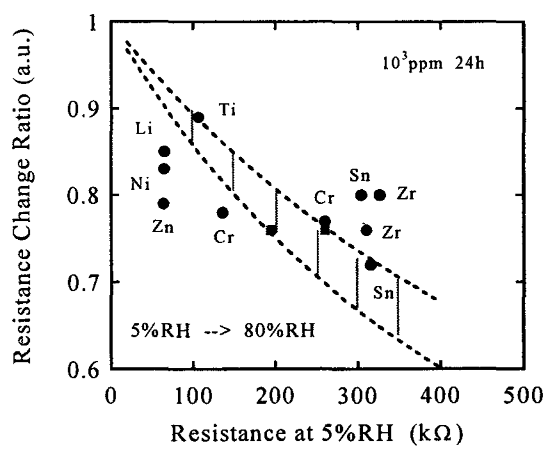

Fig.5 Resistance change ratio at humidity change from 5%RH to 80%RH v.s. resistance at 5%RH for WCMs doped with various metals.

Time response of electrical resistance for WCMs doped with Cr and without metal doping at humidity change from 5%RH to 80%RH is shown in Fig.6, where the response can be classified into two components. The response of exponential transition with two components in Fig.1 is expressed by

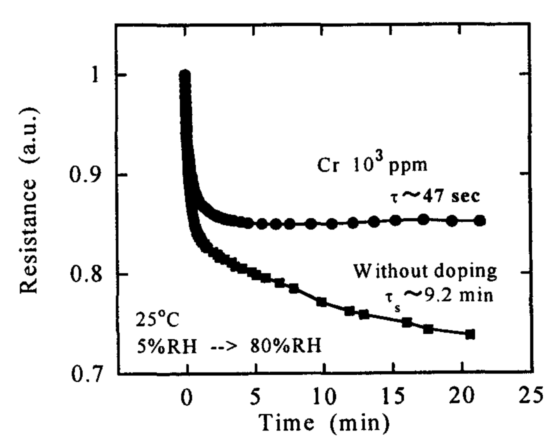

Fig.6 Time responce of electrical resistance for WCMs at humidity change from 5%RH to 80%RH.

$$R(t)-R(\infty)=A\exp\left(-\frac{t}{\tau_s}\right)+B\exp\left(-\frac{t}{\tau_f}\right) \quad (2),$$

where R(t) is resistance at time t after exposed to humidity change, A and B are constants, and t_s and t_f are the time constant of slow and fast responses, respectively. The time constants have been determined from Fig. 6 using eq. (2), yielding t_s = 9.2 min, t_f = 75 s for WCMs without metal doping and t_f = 47 s for WCMs doped with Cr. It is noted the time constant t_s has been improved by doping Cr into WCMs.

4. CONCLUSION

The electrical characteristic of WCMs doped with various metals has been studied. The resistance depends on not only the kind of metal also the concentration of the metal. When the resistance of WCMs becomes lower than that without metal doping, the resistance change ratio to the humidity change becomes larger than that predicted by eq. (1), since the metals doped into WCMs enlarge the ability of water absorption. The resistance response of WCMs doped with Cr to humidity change is improved. Therefore, the metal doping is useful technique to control the resistance of WCMs for making reliable and improving the sensitivity to humidity. A further investigation is needed to understand where metal is absorbed and reacted on the WCMs surface.

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