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Effect of sintering temperature on humidity sensitivity of a MgCr₂O₄-TiO₂ ceramics sensor

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Porous 80 MgCr₂O₄–20TiO₂ ceramics were investigated as humidity sensors. The ceramics sensors were obtained by cold isostatic pressing and sintering of the fine MgCr₂O₄ and TiO₂ powders synthesized by sol-gel methods. The effects of sintering temperature on the humidity sensitivity were studied by measuring the electrical resistance in different relative humidities (R.H.) at 27 °C. The results indicated that the calcining temperature obviously affected the resistance variation of the sensor in the range of 11.3-84.7% RH. The resistance variation was small at a calcining temperature of 600 °C for 2 h. With an increase in the calcining temperature, the resistance variation increased to a maximum of 1.49×10^5 % at 800 °C for 2 h, but decreased to 7.41 × 10⁴% and 4.07 × 10⁴% at 1000 °C for 2 h and 1200 °C for 2 h respectively. Resistance variations of 90% between 11.3% RH and 84.7% RH can be performed in 25 s and 50 s for the humidity adsorption and humidity desorption respectively. The completed response times are 55 s and 90 s for the adsorption and desorption respectively. The large sensitivity and swift response of 80MgCr₂O₄–20TiO₂ ceramics to humidity are suitable for humidity sensing applications.

Key words: MgCr₂O₄-TiO₂, sol-gel method, ceramics sensor, sintering temperature, humidity sensitivity, response time.

Introduction

MgCr₂O₄-TiO₂ ceramics have been investigated by different authors as a possible candidate for humidity measurement devices [1-4]. Reproducible results, good sensitivity and short response time have been observed with these materials. MgCr₂O₄-TiO₂ ceramics with a molar ratio of 80:20 especially possess a relatively low resistance and higher humidity sensitivity. Over the years a great many sensing methods have been developed for measuring a variety of humidity-related parameters. Each of these has unique advantages and limitations and is suitable only in certain applications. The range of applications in humidity measurements is increasing with time as new requirements of the effects of humidity on quality, cost, safety, comfort, and human health. The humidity sensitivity property of ceramics sensor is associated with their specific surface area and surface hydroxyl groups, which mainly depend on the grain size, microstucture and sintering process.

 $MgCr_2O_4$ -TiO₂ ceramics as a sensor were currently prepared by a solid reaction method at high temperature. This method has disadvantages of high synthesis temperature, poor chemical homogeneity and contamination by components, influencing negatively the sensing layer behavior. Some wet chemical method should allow the syntheses of $MgCr_2O_4$ and TiO₂ fine powders at a lower temperature. These wet chemical methods can provide a smaller particle size, a more uniform content distribution and a better microstructural control than the solid chemical reaction. In this paper we present the synthesis of the MgCr₂O₄ and TiO₂ fine powders by sol-gel methods and the effect of sintering temperature on humidity sensitivity of the $80MgCr_2O_4$ – $20TiO_2$ ceramics sensor.

Experimental Sections

For the preparation of the MgCr₂O₄ powder, the chromium chlorite hexahydrate (CrCl₃6H₂O) and magnesium sulphate (MgSO₄) were dissolved in a solution of methanol and water at valume ratio of 1:1 at a composition of MgCr₂O₄. 1 mol% excess chromium chlorite was added to compensate for the chromium loss during firing. Citric acid (CA) and ethylene glycols at a molar ratio of CA : EG : $(Cr^{3+}+Mg^{2+}) =$ 1:5:1 were added to this solution with constant stirring. The resultant stable precursor solution was a green-colored transparent resin with concentrations of 0.05 M and 0.101 M for Mg²⁺ and Cr³⁺ respectively. The precursor was dried successively at 90 °C, 100 °C, 120 °C, and 170 °C for 12 h, 2 h, 12 h, and 1 h, respectively. During the initial stage of the drying, higher temperature made the solution cloudy. So the slow drying schedule was used to dry the solution. The solution then remainted transparent during the drying. The color of the solution changed from green to deep green successively. The dried precursor was calcined at 900 °C for 6 h.

To synthesize the TiO_2 powder, an appropriate amount of titanium butoxide ($TiC_{16}H_{36}O_4$) was dissolved in anhydrous ethanol and stabilized with a little acetylaccetone and the pH adjusted to 5 with HCl with constant stirring

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and stable for a period of 3 days. The concentration of Ti^{4+} ions in the solution was 0.1 M. The solution was then dried for 48 h at 60-80 °C. The color of the gel was changed from yellowish to yellow. The solution remainted transparent during the drying. The as-dried precursor was calcined for 1 h at 400 °C in air.

The MgCr₂O₄ and TiO₂ powders at a molar ratio of 80 : 20 were mixed with an appropriate aqueous solution of polyvinyl alcohol. The mixture was stirred for 2 h. Samples were formed. By cold isostatic pressing at about 100 Pa. The as-pressed samples were heated to sintering temperature in two stages. In the first stage the sample was heated from room temperature to 500 °C at a heating rate of 2 K·minute⁻¹. In the second stage the sample was heated from 500 °C to the sintering temperatures of 600 °C, 800 °C, 1000 °C, and 1200 °C at a heating rate of 10 K·minute⁻¹, respectively. The sintering was preformed for 2 h for all the samples. Cooling procedures were conducted in the furnace.

The phase identifications of the powders were conducted at room temperature using X-Ray diffractometer (XRD, CuK_{α 1}, $\lambda = 0.15406$ nm, Model No. D/Max-2200PC, Rigaku, Japan). The phase and the particle sizes of the powders and sensor were determined with the Jade5 analysis software provided with the X-Ray diffractometer. Scanning electron microscopy (SEM, Model No: JXM-6700F, Japan) was used to study the surface morphology and grain size of the sensors.

The sintered samples had a diameter of 12 mm and a thickness of 1.5 mm. Both sides of the samples were painted with silver wires with a silver paste. The samples were then dried in an oven at 800 °C for 0.5 h. The humidity sensitivity of the films were tested by measuring the DC electrical resistance of the sample in small sealed glass chambers containing super-saturation solutions of LiClH₂O, Mg(NO₃)₂6H₂O, NaCl, and KCl. Super-saturation solutions of LiClH₂O, Mg(NO₃)₂6H₂O, NaCl, KCl can produce equilibrium atmospheres with relative humidities of 11.30, 52.96, 75.30, and 84.70%RH in a sealed chamber at a testing temperature of 27 °C (standard published by NBS of USA in 1977). The measurement of the response time was carried out between two relative humidities of 11.30 and 84.70%RH, by recording resistances at different adsorption or/and desorption times after changing the film from one humidity condition to another.

Result and Disscussion

The TG/DSC curves of the $ZnCr_2O_4$ precursor prepared by a similar method indicated that a remarkable exothermic peak appears at 882.5 °C [7]. Thus a calcining temperature of 900 °C was used to calcine of the MgCr₂O₄ powder in this study. Fig. 1 shows the XRD spectra of the MgCr₂O₄ and TiO₂ powders, which indicate that the MgCr₂O₄ powder is of a single-phase cubic spinel structure, and that the TiO₂ powder consists of anatase with a little rutile. The average particle sizes determined by XRD analysis were about

Fig. 1. XRD patterns of MgCr₂O₇ and TiO₂ powder ceramics.

30.2 nm and 12.1 nm for the MgCr₂O₄ and TiO₂ powders respectively. Fig. 2 shows SEM micrographs of the sintered samples, which indicate that the disk sample surfaces consist of small grains of ~50-150 nm and a few large grains of ~1.5 μ m and had a porous morphology. With an increase in the calcining temperature, it can be seen that the grain size slightly increased and some grains were linked together with each other (Fig. 2(c) and 2(d)). This linked grain texture could have resulted from melting and/or crystal growth.

The weight losses of the $80MgCr_2O_4-20TiO_2$ sensors in the range of the high temperature calcining were determined by measuring the weight of sensors before and after calcining at various temperatures. The weight of samples decreased from 0.7890 g to 0.7882 g, 0.7869 g, 0.7861 g, and 0.7853 g when calcining samples at 600 °C, 800 °C, 1000 °C, 1200 °C for 2 h, respectively. These weight losses of the sensors should have resulted from volatilizations of water, the organic binder polyvinyl alcohol and Cr ions.

It is well known that MgCr₂O₄ –TiO₂ is a humiditysensitive material. Fig. 3 shows the resistances of 80MgCr₂O₄ –20TiO₂ ceramic sensors as a function of the relative humidity. The sensors show a significant response to water vapor and were found to be sensitive to humidity. The calcining temperature obviously affected the humidity sensitivity of the sensor. The resistance variation with the humidity is very small for the sensor calcined at 600 °C. With an increase in the calcining temperature to 800 °C, the resistance variation in the 11.3-84.7% RH range increased to a maximum value of 1.49×10^{-50} . However, the resistance variation decreased to 7.41×10^{40} and 4.07×10^{40} with a further increase in the calcining temperature to 1000 °C and 1200 °C.

To explain the humidity sensitivity of these ceramics sensors we first consider the interaction of water with the $MgCr_2O_4$ –TiO₂ surface. Calcined $MgCr_2O_4$ and TiO₂ powder surfaces are hydroxylated when in contact with molecular water in air. The titanium and chromium cations





Fig. 2. SEM micrographs of MgCr₂O₇-TiO₂ ceramic samples sintered at (a) 600 °C, (b) 800 °C, (c) 1000 °C and (d) 1200 °C.



Fig. 3. Resistance variations of MgCr₂O₇-TiO₂ sensors sintered at different temperatures as a function of the relative humidity.

possess a larger electronegativity. These surface cations exposured to air have a strong attrataction for OH^- ions carried with a negative charge in air. This makes the hydroxylating process of surface cations combining with $OH^$ ion very easy and hydroxyl groups are formed numerously on the MgCr₂O₄ and TiO₂ surface. The fully-hydroxylated surface is hydrophilic and able to adsorb water by Hbonds. This is similar to the hydroxylating process and water adsorption on silica surfaces as assumed by Hair [8]. The adsorbed water can reduced the resistance of the two powders at a high relative humidity. For the sintered sample, a calcining temperature of 600 °C would not be enough to fully decompose the polyvinyl alcohol and remove its decomposition products from the powders surfaces, which would hinder the humidity sensitivity of the sensor. At a calcining temperature higher than 600 °C, the polyvinyl alcohol and its decomposition products would be fully removed, and a new fresh surface would perhaps be formed on the powders and become rehydroxylated. These processes make the humidity sensitivity appear intense. Alternately, the volatilizations of water, the organic binder polyvinyl alcohol and Cr ions with the calcination increase the porosity and thus the humidity sensitivity of the sensors. However, with a further increase in the calcining temperature to 1000 °C and 1200 °C, the linking between grains and the increase in grain size decrease the porosity and specific surface area of the sensors, which results in a decrease of the humidity sensitivity of the sensors

The dynamic adsorption-desorption curve is shown in Fig. 4 for the sensor sintered at 800 °C. The resistance variation of the sensor between a relative humidity of 11.31 and 84.70%RH reached 90% in 25 s and 50 s, a variation of 100% needed relatively long times of about 55 s and 90 s to accur, for the humidity adsorption and desorption



Fig. 4. Time response curves of the $MgCr_2O_7$ -TiO₂ sensor between two relative humidities of 11.3% R. H. and 84.7% R. H.

respectively. It is obvious that the humidity desorption process is slower than humidity adsorption on the $80MgCr_2O_4-20TiO_2$ sensor, which can be explained as follows. The surface hydroxyl groups are combined with adsorbed water molecules. The adsorbed water molecules are also combined with each other by H-bonds. Some energy is needed to break up these H-bonds to desorb the adsorbed water molecules in comparison with the adsorption process of water molecules.

The MgCr₂O₄–TiO₂ sensors can respond to water vapor at room temperature. This indicates that the mechansim of resistance change is not chem.-adsorption and chem. -desorption of water molecules on the MgCr₂O₄–TiO₂ sensors. This is because room temperature does not provide enough energy for chem.-adsorption and chem.-desorption that is usually associated with high activition energies. It is well known that H-bonds and relative weak intermolecular forces exist in between water molecules, which are lower than chemical bond in energy. The mechanism of humidity sensitivity is obviously adsorption and desorption of water molecules due to H-bonds and relatively weak intermolecular forces.

Conclusions

 $80MgCr_2O_4-20TiO_2$ sensors were prepared with MgCr_2O_4 and TiO_2 fine powders synthesized with a sol-gel processes at low temperature. Humidity sensitivity of the sensors was tested by measuring the DC resistance of the sensors at different relative humidities. The sintering temperature obviously affected the humidity sensitivity of the sensors. The sensor sintered at 800 °C possessed the maximum resistance variation of 1.49×10^{5} % over the range of 11.3-84.70% R.H. The resistance variations of 90% between 11.3% R. H and 84.7% R. H were accomplished in short response times of 25 s and 50 s for humidity adsorption and humidity desorption. The large sensitivity and swift response to water vapor make the sensor very suitable for humidity sensors applications.

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