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Microstructural and electrical properties of $Y_{0.2}Al_{0.1}Mn_{0.27-x}Fe_{0.16}Ni_{0.27-x}(Cr_{2x})o_y$ for NTC thermistors

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Abstract

Mixtures of refractory oxides and transition metal oxides for yttrium–aluminum–manganese–iron–nickel–chromium–oxygen (Y–Al–Mn–Fe–Ni–Cr–O) systems were prepared using normal ceramic processes, for use as negative temperature coefficient (NTC) thermistors to measure a wide temperature range. Platinum–rhodium (Pt–Rh) alloy electrodes were inserted into the body during the formation process to increase the reliability at high temperatures and decrease the contact resistance. The properties of the thermistors were analyzed by X-ray diffraction (XRD), scanning electron microscopy (SEM), and resistance measurements. The shrinkage rate, grain size, and density of the specimens doped with Cr_2O_3 were higher than those of non-doped specimens. The crystallinity of the grains decreased with the addition of 0.006 mol of Cr_2O_3. The grain size increased with Cr_2O_3. The resistance behaviors were similar for the two specimens, but the values were higher with the Cr_2O_3. The *B* constant value (the coefficient of temperature sensitivity) was 3636 K for the non-doped specimen and 3876 K for the specimen doped with 0.006 mol of Cr_2O_3 across a temperature range of 0–600 °C. The specimens exhibited a linear relationship between their electrical resistance and reciprocal temperature over a wide temperature range, indicating NTC thermistor characteristics. The mixtures of refractory oxides and transition metal oxides extended the measurement range from 0 °C to 600 °C, and the addition of Cr_2O_3 increased the resistance and the B constant in the doped sample.

Keywords: NTC thermistor; Ceramic materials; Microstructure; Temperature-resistance

1. Introduction

Negative temperature coefficient (NTC) thermistors are thermally sensitive resistors that have a decreasing resistance with increasing temperature [1–4]. NTC thermistors are mainly used in electronics for the suppression of in-rush current, for measurement and control of temperature, or as compensation for other circuit elements [5–6].

The measurement range of common ceramic thermistors is limited because their coefficient of temperature sensitivity (*B* constant) is usually high. Thus, thermistors are classified as either for room temperature applications below 100 °C and for medium temperature applications between 100 °C and 300 °C.

In particular, the thermistor applications involving automobiles and spaceships require a wide measurement range from room temperature to very high temperatures. Thermistors for these applications must display a resistance value of hundreds of k Ω at room temperature and several tens of Ω at 900°C. To enable these goals, studies on thermistors must focus on discovering materials that have a low *B* constant, a linear response over a wide temperature range, and stable properties and phases at high temperatures.

Previous studies on NTC thermistors were predominantly focused on spinel structure with a formula of AB_2O_4 or spinel-like structures. The common materials for ceramic thermistor is the transition metal oxides such as Mn_3O_4, Co_3O_4, Fe_2O_3 and NiO. However, the thermistors based on spinel structure and transition metal oxides is generally limited to temperatures below 200 °C [7–12]. Feltz and Polzl proposed a system of iron–nickel–manganese–oxygen ($Fe_xNi_yMn_{3-x-y}O_4$) compositions based on the

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spinel structure for high temperature applications [13]. However, the B constants for these are not stable for temperatures below 400 °C, which limits their applicable temperature range. For special high-temperature applications, zirconium dioxide (ZrO_2) and yttrium oxide (Y_2O_3) thermistors could be used; these thermistors are also limited to use at high temperature above 500 °C because of their excessively high resistance at temperatures below 300 °C.

Varghese et al. studied the microstructure and electrical properties of the nickel–manganese–chromium-iron ($Ni_{0.75}Mn_{(2.25-x-y)}Cr_xFe_y$) system, i.e., a surplus of B elements for the AB_2O_4 spinel structure [14]. The effect of microstructure and electrical properties on aluminum oxide (Al_2O_3) inclusion for a manganese–nickel–cobalt–aluminum–oxygen ($Mn_{0.37}Ni_{0.3}Co_{0.33-x}Al_xO_4$) system was studied by Park and Han [15]. In this study, the NTC properties were just measured from room temperature to 140 °C.

Y_2O_3 and Al_2O_3 are well known refractory materials with high resistance values at high temperatures. The transition metal oxides, such as MnO_2, Fe_2O_3, NiO, and Cr_2O_3, are materials commonly used in room temperature thermistors. Thus, it could be possible to create a thermistor that covers a wide temperature range using a mixture of transition metal oxides and refractory materials. Such mixtures facilitate an expanded selection of new compositions with the desirable electrical properties to measure a wide temperature range. In this study, the microstructural and electrical properties of a yttrium–aluminum–manganese–iron–nickel–chromium–oxygen (Y–Al–Mn–Fe–Ni–Cr–O) system for NTC thermistors were studied to widen the measurement range from room temperature to 600 °C.

2. Experimental

Y_2O_3, Al_2O_3, MnO_2, Fe_2O_3, NiO, and Cr_2O_3 powders with high-purity ($\geq$ 99.5%) were used as the chemical reagents to establish thermistors that cover a wide temperature range. These powders were weighed to meet the compositions of $Y_{0.2}Al_{0.1}Mn_{0.27-x}Fe_{0.16}Ni_{0.27-x}(Cr_{2x})O_y$ where $x=0$ or 0.006. A wet-blending was performed by ball milling of the weighed powder mixtures for 12 h. The wet-blended mixtures were dried at 120 °C for 24 h. The mixture was subsequently calcined at 1200 °C at a heating rate of a 5 °C/min for a dwell time of 2 h.

The calcined mass was again crushed and pulverized to obtain the fine powders. The fine powders to make a green specimen were pressed at 120 MPa into a rectangular mold. The size of green specimen was 2 mm × 1.5 mm × 2 mm, and it had a pair of inserted platinum–rhodium alloy (Pt–Rh, 13 wt%) wires as electrodes, as shown in Fig. 1. The diameter of the Pt–Rh electrodes was 0.3 mm. The distance between the two wires and their insertion depth into the specimen were both 1 mm. The fine powders were also used to make a green disk specimen with 12 mm diameter and 3 mm thickness to measure a linear shrinkage and an apparent density.

The green specimens and the Pt–Rh metal electrodes were co-sintered at 1400 °C for 1 h in air. The crystal structure of each of the as-sintered specimens was analyzed by X-ray diffraction (XRD; Rigaku DMAX 2500) using a Cu-Kα (0.15406 nm) radiation source at 40 kV and 25 mA. The XRD patterns were obtained over a 2θ scan range of 25–55°. The microstructure and the grain size of the fractured specimens were investigated using a field-emission scanning electron microscope (FESEM; Hitachi S-4700). The electrical resistance as a function of temperature was measured from −40 °C to 900 °C using a digital multimeter (Hewlett Packard HP 34401B).

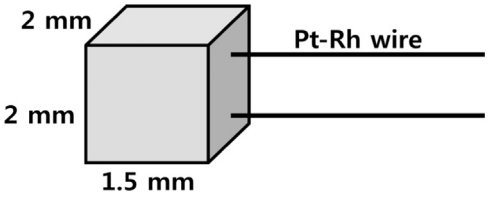

Fig. 1. Schematic of sample dimensions and location of the electrodes inserted into the sample.

Table 1
Linear shrinkage, average grain size, and apparent density characteristics after sintering at 1400 °C for 1 h.

Composition	Linear shrinkage (%)	Average grain size (μm)	Apparent density (g/cm^3)
$Y_{0.2}Al_{0.1}Mn_{0.27}Fe_{0.16}Ni_{0.27}O_y$	18.3	1.16	4.22
$Y_{0.2}Al_{0.1}Mn_{0.264}Fe_{0.16}Ni_{0.264}Cr_{0.012}O_y$	20.2	2.18	4.34

3. Results and discussion

The analysis results of the macro- and micro-structures after sintering are summarized in Table 1. The linear shrinkage and average grain size are 18.3% and 1.16 μm for $Y_{0.2}Al_{0.1}Mn_{0.27}Fe_{0.16}Ni_{0.27}O_y$, respectively, and 20.2% and 2.18 μm for $Y_{0.2}Al_{0.1}Mn_{0.264}Fe_{0.16}Ni_{0.264}Cr_{0.012}O_y$, respectively. Their apparent densities are 4.22 g/cm^3 for the $Y_{0.2}Al_{0.1}Mn_{0.27}Fe_{0.16}Ni_{0.27}O_y$ and 4.34 g/cm^3 for the $Y_{0.2}Al_{0.1}Mn_{0.264}Fe_{0.16}Ni_{0.264}Cr_{0.012}O_y$. The linear shrinkage percentage was obtained from a direct diameter reading using vernier calipers and the following equation:

$$LS = \frac{(D_g - D_s)}{D_g} \times 100 \quad (1)$$

where D_g and D_s are the diameters of the green disk specimen (12 mm) and the sintered disk specimen, respectively.

The shrinkage rates of these specimens are very high because ceramic sintering shrinkage usually ranges from 10% to 20%. The Cr_2O_3 doped specimen corresponds to an enhanced, high densification sintering effect as the high degree of shrinkage produces a high density. The shrinkage rate, grain size, and density of the Cr_2O_3 doped samples are higher than those of the non-doped specimens, and demonstrated that the Cr_2O_3 could act as a dopant as well as a sintering aid, even with a small quantity of 0.006 mol.