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SCIENCE DIRECT
Sensors and Actuators A 120 (2005) 337–342
SENSORS AND ACTUATORS A PHYSICAL
www.elsevier.com/locate/sna

Characterization of transition metal oxide ceramic material for continuous thermocouple and its use as NTC fire wire sensor

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Received 25 November 2003; received in revised form 22 November 2004; accepted 12 December 2004
Available online 25 January 2005

Abstract

The ceramic powder prepared from the mixture of Mn_3O_4 and La_2O_3 have been characterized for NTC behavior and the same have been used as CT^2C (continuous thermocouple) sensor in the form of a thin metal cable to detect over-heating. These materials have mega ohm resistance at room temperature and showed exponential drop in resistance with the rise in temperature over a temperature range of 100–400 °C. It has been observed that as the concentration of La_2O_3 increases from 0 to 10% the NTC behavior drops from (400–260 °C) ±10%. The material was pressed into pellets and sintered at 700 °C for 3 h resulting in good bonding strength. Electrical characterization of the material was done by measuring the resistance over a temperature range of 100–400 °C. The material showed reproducible NTC characteristics over the temperature range 400, 370, 340, 280, and 260 °C with decreasing thermistor constant values (B = 9588, 9210, 8500, 5170, 3330 K^{-1}) and activation energy (ΔE = 826, 794, 733, 445, 287 meV), respectively. The decrease in activation energy of the ceramic powder with increase in La_2O_3 concentration makes it possible to fabricate thermal sensors which can be used in different temperature ranges. The microstructure was studied using SEM and evidence of a sintered body with grain size around 1 μm was observed in the material. XRD analysis indicated the single-phase tetragonal structure of the ceramic material. The process of using this ceramic material for fabrication of 10 ft continuous fire wire sensor has been explained.

Keywords: NTC; Thermal sensor; Ceramic material

1. Introduction

Thermistor materials are very attractive in micro-electronic and opto-electronic systems because of their unique thermo-electrical properties [1,2]. Negative temperature coefficient (NTC) thermistors are temperature sensitive resistors, whose resistance decreases with the increase in temperature. The dependence of resistance on temperature approximately follows an exponential law [3–7]. The NTC property of these materials makes them well suited for use as thermistors in temperature sensing applications and continuous over-heat detection systems [7]. Manganese based spinel semi-conducting ceramics have been studied as NTC thermistors since they possess interesting electrical properties [8–13]. The current study investigates the NTC behavior of a Mn_3O_4 and La_2O_3 powder mixture over a temperature range 100–400 °C. This ceramic powder has also been used for the fabrication of a sensor up to 10 ft length and has been characterized for thermal behaviour. With the increase in temperature of the sensor body the resistance of embedded thermistors decreases. This resistance change can be then converted into voltage or current signal [5,6]. The properties used to characterize NTC materials, are the material constant (B) and the temperature coefficient (α). X-ray diffraction (XRD), scanning electron microscopy (SEM) has been used to examine the structure of the material.

2. Experimental

2.1. Preparation of ceramic material

The chemicals used are manganese dioxide (MnO_2) of Loba chemicals (AR Grade), lanthanum oxide (La_2O_3), wax,

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doi:10.1016/j.sna.2004.12.014

and stearic acid of SD Fine chemicals. All the chemicals are used in their pure form without further purification. MnO_2 was converted to Mn_3O_4 by keeping it in a silica crucible at 1000 °C for different intervals of time up to 20 h however it has been observed that 8 h are sufficient for its complete conversion. Mn_3O_4 and La_2O_3 were mixed together in the stoichiometric weight percentage as per in Table 1 and ball milled using a planetary ball miller (Retsch PM 100) for about 6 h to homogenize the distribution of the two materials and reduce the particle size to a minimum size. This homogenized powder was then mixed with wax and stearic acid 0.5% each, and again grinded for 0.5 h to improve the flow ability of powder inside the pipe. The microstructure of as prepared and sintered sample was observed by scanning electron microscope (JEOL, JSM 840A). Rigaku, Dmax IIIC Diffractometer was used for XRD analysis including phase identification with Cu Kα; radiation ($\lambda = 1.5406$ Å). TCR measurements were made by two-probe method using Protek 506 digital multimeter with RS-232 interface. The muffle furnace having temperature range ambient to 1200 °C with Digital Temperature Controller (ATC-151) was used.

2.2. Fabrication of pellets for NTC characteristics

Each of the ceramic powder prepared as in Table 1 was used to make the thermistor assembly. Two thermocouple wires chromel and alumel each of 0.3 mm diameter were placed in to two drilled holes of the lower ram of the die plug. 5 gm of ceramic powder was placed in the die block with a plunger on the top of the die. Cold pressing of the powder was done at 5 t load. The lower ram was ejected from the die body after the compaction of the powder. The thermistor consisting of sensing wire assembly was then carefully removed. Each assembly was then subjected to combined calcination and sintering cycle in an air fired high temperature furnace, in which the temperature is controlled by temperature controller with an accuracy of ±2 °C. The temperature of each test sample was increased from ambient to 400 °C at a rate of 10 °C min^{-1} which has held constant for 2 h, followed by ramping the temperature to 700 °C at the rate of 20 °C min^{-1}. These test samples were sintered at 700 °C for about 3 h. The samples were then allowed to reach the ambient with in the muffle. Each of The sintered samples is 15.1 mm thick and 8.0 mm in diameter. Initial heating was carried out at 400 °C for the removal of organic vapours. For NTC characterization of these pellets chromel and alumel lead wires were used to connect the thermistor to a Protek 506 digital multimeter.

Table 1
Composition of ceramic materials

Sample	La_2O_3 (wt.%)	Mn_3O_4 (wt.%)
M0	–	100.0
M1	2.5	97.5
M2	5.0	95.0
M3	7.5	92.5
M4	10.0	90.0

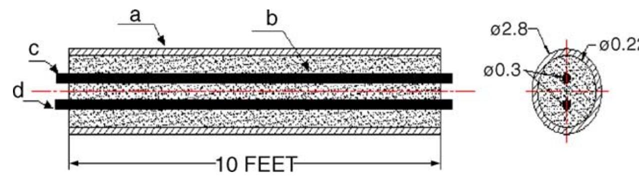

Fig. 1. Schematic diagram of 10 ft long sensor: (a) 316 stainless steel tube o.d. 2.8 mm and wall thickness 0.22 mm; (b), ceramic powder; (c) chromel; (d) alumel, sensing wires of diameter 0.3 mm.

Each sample was then kept in the furnace and the temperature was raised from ambient to 400 °C and the resistance values were recorded after every 20 °C rise in temperature.

2.3. Fabrication of 10 ft sensor

The schematic diagram of 10 ft long sensor is shown in Fig. 1. The fabrication of these sensors was carried out using stainless steel tubes (SS 316) of 3.5 mm uniform diameter. Each tube was mounted on 50 mm thick wooden former, which have semi-cylinderical slot to hold the tube firmly (Fig. 2). Both the sensing wires c and d (chromel and alumel)

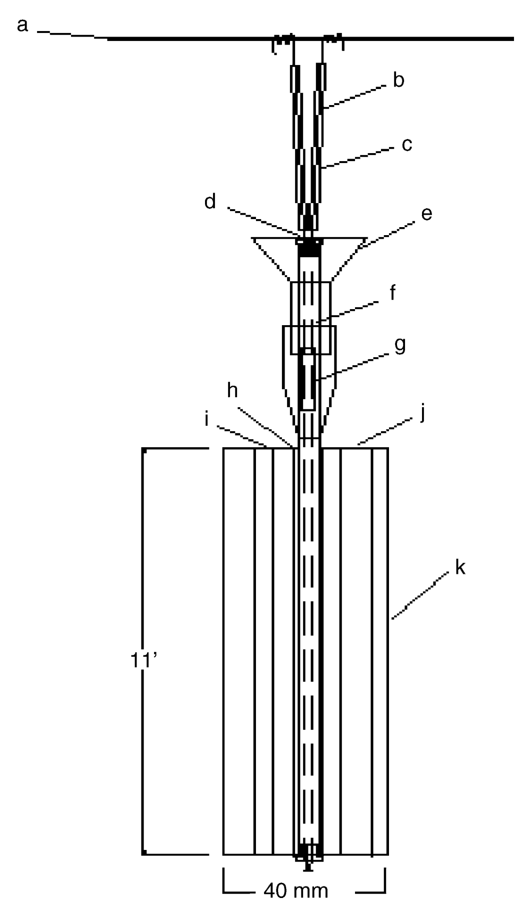

Fig. 2. Diagram for ceramic powder filling technique: (a) rod; (b) wires; (c) capillary; (d) manderal; (e) funnel; (f) Ø3.5 pipe; (g) window; (h) semicircular slot of Ø3.0 mm; (i) semicircular slot of Ø0.3 mm; (j) semicircular slot of Ø4.0 mm; (k) split type grooved wooden block.