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Preparation of Mn–Co–Ni mono-phase spinel oxide by oxidation of rock salt-type oxide

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Preparation of a mono-phase spinel from a ternary system Mn–Co–Ni oxide with a molar ratio of 3.0:1.9:1.1 was investigated. It was found that the oxidation profile of a rock salt-type oxide, which was formed at 1400 °C, was the most significant factor. As a result, the perfect mono-phase specimen was obtained by water quenching the rock salt-type oxide and then heat treating to oxidize it for more than 3 h at 1000 °C.

1. Introduction

A negative temperature coefficient (NTC) thermistor material, composed of the ternary system Mn–Co–Ni oxide with molar ratio of 3.0:1.9:1.1, has been studied and changes in crystal structure and electrical properties occurring during the firing processes of sintering, cooling-down and annealing have been reported [1–5]. The phase relations of the oxide were interpreted as follows. The cubic spinel is stable below 1040 °C, and at 1400 °C the rock salt type structure is also stable [4]. For consolidation of the system, a sintering temperature of 1400 °C was used generally. After sintering, phase separation occurs during cooling from 1400 °C to 1000 °C. Recovery to the single phase from the separated phase is difficult, as was clearly found in previous papers [2, 3, 5]. Therefore, preparation of a mono-phase cubic spinel during the cooling process has not yet been attained.

On the other hand, the change in electrical properties was ascertained to depend on the existence ratio of each crystal [5]. However, the contributions of each crystal to the electrical properties were obscure, because the mono-phase could not be obtained.

The formation of mono-phase crystal is considered to be very important for estimating the intrinsic electrical conductivity and also for elucidating the conduction mechanism. In addition, this would lead to the development of electrically stable thermistor elements with high yield.

The present study was performed to synthesize a mono-phase cubic spinel from the oxide prepared at 1400 °C. In the preliminary study, we found that "1000 °C oxidation" for the sintered specimen is a break-through condition. In this study, oxidation of the rock salt-type oxide at 1000 °C was especially investigated.

2. Experimental procedure

Manganese, cobalt and nickel nitrates were weighed in a molar ratio of 3.0:1.9:1.1 and well mixed. The composition was close to that of a thermistor currently on the market. To produce a starting oxide, the mixture was preheated at 1000 °C for 3 h. All experiments in this study were conducted in air.

Two kinds of heating profile experiments were attempted in order to obtain mono-phase cubic spinel from rock salt-type oxide.

1. The starting oxide was heated from room temperature to 1000 °C for 1 h and then was further heated to 1400 °C for 1 h to produce a rock salt-type oxide. After firing at 1400 °C for 3 h, the specimen was cooled to 1000 °C over 5 min, 1 and 12 h, respectively. The specimen was oxidized for 24 h at 1000 °C, and then quenched by dropping into water.
2. After the starting oxide was fired at 1400 °C under the same heating programme, the specimen was water quenched, and then heat treated to oxidize the rock salt-type oxide into cubic spinel at 1000 °C. The oxidized specimen was then water quenched as in procedure 1.

The specimens prepared in these manners were pulverized and analysed by X-ray diffraction.

3. Results and discussion

Fig. 1 shows the X-ray diffraction patterns of specimens which were heat treated at 1000 °C for 24 h after firing at 1400 °C, followed by cooling to 1000 °C (heating profile 1). In the figure, (a–c) are the profiles of specimens at the cooling rates of 80 °C min^{-1}, 400 and 33 °C h^{-1} to 1000 °C, respectively. In all specimens, weak peaks of rock salt-type structure were observed with the main peaks of cubic spinel. From these results, it is clear that as the cooling time becomes shorter the peak intensity of the cubic spinel increases and that of the rock salt-type oxide decreases. In a previous paper, the authors reported that the phase separation occurred in the oxide fired above 1040 °C [4]. In addition, according to our experience, the separated phase was apparently irreversible even though it was reheated at 1000 °C for more than 3

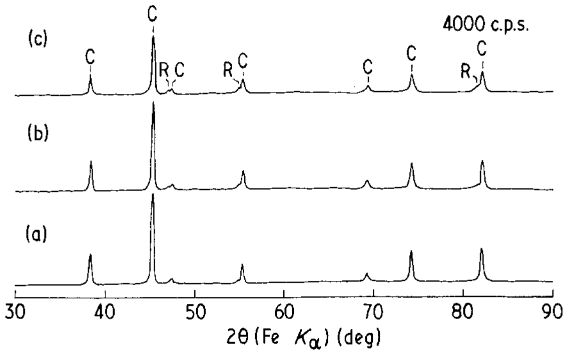

Figure 1 X-ray diffraction patterns of specimens heat treated at 1000 °C for 24 h after firing at 1400 °C. Cooling rate to 1000 °C: (a) 80 °C min^{-1}, (b) 400 °C h^{-1}, (c) 33 °C h^{-1}.

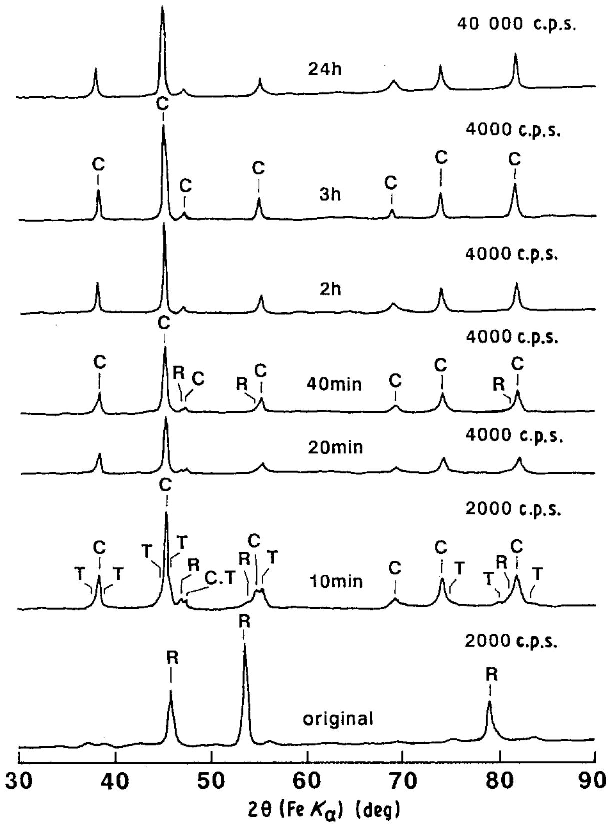

Figure 2 X-ray diffraction patterns of specimens heat treated for different times at 1000 °C after firing at 1400 °C and then water quenching. C, cubic spinel; T, tetragonal spinel; R, rock salt.

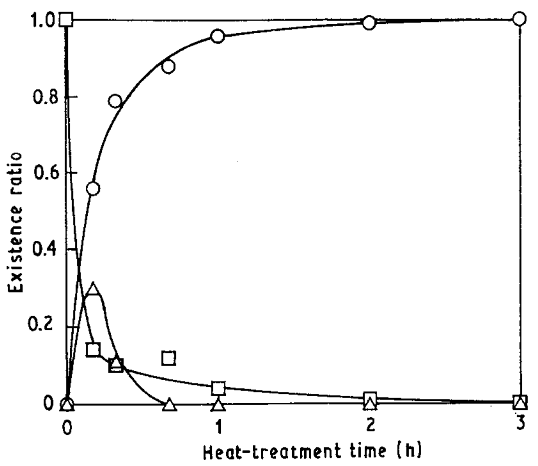

Figure 3 Existence ratio of each crystal as a function of the heat-treatment time. (○) cubic spinel, (△) tetragonal spinel, (□) rock salt.

days. Therefore, it can be considered that the rate of cooling from 1400 °C to 1000 °C should be as high as possible. In this experiment, cooling rates of more than 80 °C min^{-1} could not be attained because of the limit of the temperature control of the furnace. For this reason, another method of reheating the oxide at 1000 °C, such as heating profile 2, was investigated, i.e. first firing at 1400 °C for 3 h and then water quenching. These results are shown in Fig. 2. The quenched specimen after 1400 °C firing shows a profile of rock salt-type structure, which is coincident with the results of the experiment described in a previous paper [4]. This result confirms that the stable phase at 1400 °C is rock salt-type structure. Three kinds of crystal phases, rock salt, cubic and tetragonal spinels, coexist in the specimen heat treated for 10 or 20 min. On the other hand, the specimen heat-treated for 40 min has two kinds of crystal, cubic spinel and rock salt-type structure, eliminating the tetragonal spinel. In the specimen heat treated for 3 h, the crystal is only cubic spinel structure. The specimen heat treated for 24 h is also the same as that heat treated for 3 h.

Fig. 3 shows the relationship between heat-treatment time and crystal existence ratio calculated from the integrated peak intensity. In this calculation, each intensity was acquired by separating peaks of (3 1 1) in cubic spinel, (3 1 1) in tetragonal spinel and (2 0 0) in rock salt-type structure [5]. The peak areas of tetragonal spinel assigned (3 1 1) and (1 1 3), were also summed to investigate a multiplicity factor [6]. As shown in Fig. 3, it is clearly recognized that the crystal change, that is, oxidation from the lower oxide to the higher oxide, is very rapid, and that the crystal approaches the stable phase at 1000 °C within 1 h. After 3 h, the crystal phase is composed of only the cubic spinel structure. Consequently, the results of Figs 2 and 3 suggest that a perfect mono-phase cubic spinel can be obtained through heat treating the rock salt-type oxide for more than 3 h at 1000 °C. The mechanism of the mono-phase cubic spinel formation is now under investigation by micro-analysis.

The oxidation method investigated in this study may be widely used in the formation of other mono-phase spinels.

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