Synthesis of ceramic powders based on manganese, cobalt and nickel oxides

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Abstract: $Mn_xCo_yNi_zO_t$ ceramic powders were prepared by mixing and heat treating the oxides at temperatures in the 1200-1300 °C range for thermistor fabrication. Slurries containing the powders dissolved in water with organic binder and deflocculant were atomized in a spray dryer to get fine and homogeneous powder particles for pressing and sintering large quantities of pellets. The distribution of particle size of powders was determined by laser scattering, the density of the sintered pellets by hydrostatic (Archimedes) technique, and the electrical behavior in the room temperature-200 °C by a two-probe method. The results show that the synthesis processing and the homogenization by spray dryer are important for the fabrication of large quantities of similar ceramic thermistors with narrow distribution of electrical response.
keywords: NTC, thermistor, ceramic powder synthesis

Introduction

Ceramic sensors find many applications in several areas. ZrO_2-based polycrystalline ceramics are the main component of oxygen sensors for many applications in steel making industry for monitoring oxygen dissolved in molten steels and in the automotive industry for adjusting the air-fuel ratio in combustion engines [1, 2]. Rare-earth doped barium cerates have been proposed as hydrogen sensors [3]. Many reports may be found on the use of $ZrTiO_4$, $MgAl_2O_4$ and $MgFe_2O_4$ as humidity sensing ceramics [4, 5].

Negative temperature coefficient (NTC) thermistors are resistors used in temperature sensing devices in electrical appliances and in vehicles. Their electrical resistance decreases upon heating [6]. Their basic composition contains manganese, cobalt and nickel oxides with the spinel structure of general formula AB_2O_4 [7-9]. The synthesis of these compounds is done by simply mixing thoroughly the oxides in the desired stoichiometry, adding suitable organic compounds (binders, deffloculators and plastifyers) to have a homogeneous slurry for spray drying to obtain flowable powders for compaction and sintering. Many parameters affect the final electrical behavior of the NTC compound. In this contribution, three different routes are followed for the preparation of one of the NTC compounds of the Mn-Co-Ni phase diagram. A routine procedure is proposed for preparing large quantities of powders for a pilot plant production of NTC thermistors.

Experimental

The following raw materials were used for the synthesis of the NTC powders by different routes: NiO, $NiCO_3$, MnO_2, $Mn(CO_3)_2$ and Co_3O_4. For the solid state synthesis the three oxides were thoroughly mixed in an agate mortar. A slurry was prepared by adding polyethylene glycol and stearic acid to a water solution of the powders for spray drying (Niro atomizer operating at 200-300 °C) to produce a homogeneous mixture for pressing and sintering. The powders were pressed to cylindrical pellets (10 mm x 2 mm) and sintered in the temperature range 1200 - 1300 °C. For the polymeric precursor (Pechini) technique the nitrates of the oxides were obtained by adding HNO_3 and heating. The stoichiometric contents of the metal nitrates were mixed and ethylene glycol was added (60:40 vol.% proportion) under continuous mixing under heating. Afterwards citric acid is added up to a gel formation. Heating the gel at 80 °C produces a polymeric resin, which under calcination in the 500-700 °C range yields the thermistor oxide powder. For the carbonate precursor technique, Ni, Mn and Co carbonates were mixed, pressed to pellets and heat treated at 1200 °C. That procedure was followed twice with intermediate grindings for homogenization purposes.

Thermal analysis of the powders were carried out in a Netzsch STA 409E simultaneous thermal analyzer in the 25 °C-1100 °C range with a 10 degree/min heating rate under synthetic air.

X-ray diffraction measurements were performed in a Bruker-AXS D8 Advance diffractometer operating at 40 kV-40 mA with Cu-kα radiation.

The morphology of the powders was studied by scanning electron microscopy with a Philips XL30 SEM with EDX analysis.

Electrical resistivity measurements were carried out. The sintered thermistor pellets were placed in a sample chamber which could be heated from RT to 150 °C. Dc electrical measurements of the thermistors were performed in that temperature range in a homemade sample chamber; Hewlett Packard and Fluke multimeters were used for evaluating the temperature and the electrical resistance, respectively.

Results and Discussion

Fig. 1 shows the thermogravimetric and the differential thermal analysis results of the precursor prepared by the polymeric precursor technique. The reaction is complete at approximately 400 °C with a total mass loss of 80%.

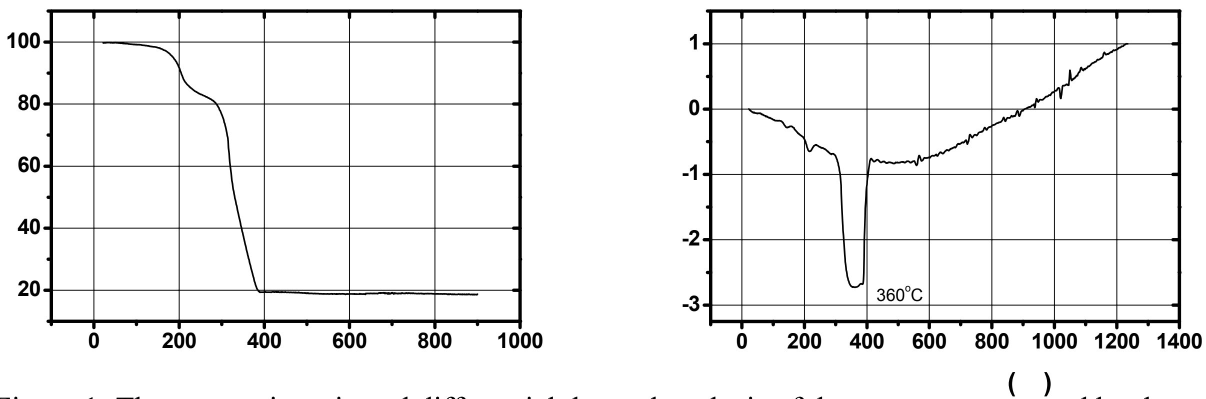

Figure 1: Thermogravimetric and differential thermal analysis of the precursor prepared by the polymeric (Pechini) precursor route.

Figure 2 shows the X-Ray diffraction patterns of the powders prepared according to the three routes: mixing of oxides, mixing of carbonates and polymeric precursor technique. All routes lead to single phase NTC thermistors irrespective of the powder synthesis followed for obtaining the NTC powders. The main diffraction lines are identified as a spinel type compound.

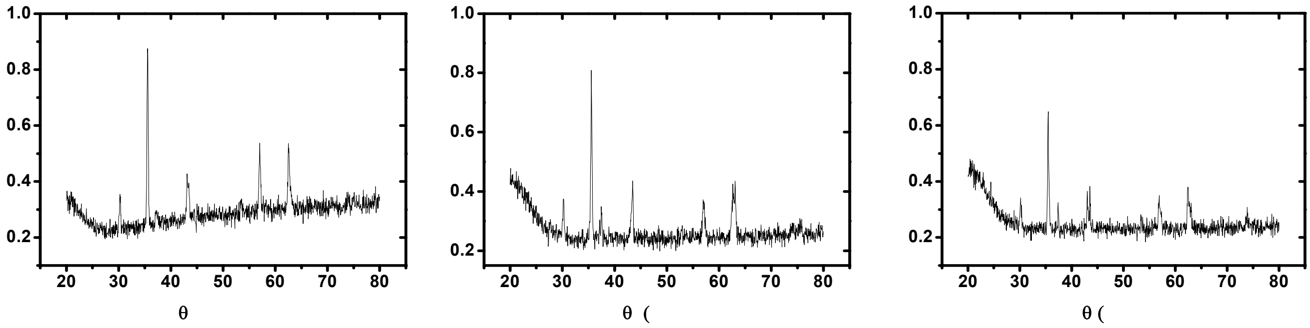

Figure 2: X-Ray diffraction patterns of Ni-Mn-Co thermistors sintered pellets prepared from powders synthesized following three different routes. See text for details.

The electrical behavior of the sintered pellets was analyzed by two-probe dc measurements in the 20 °C - 150 °C range. The NTC typical curves are shown in Figures 3 and 4: the electrical resistivity decreases for increasing temperature. The range studied is found to be suitable for application in domestic appliances (water heaters, toasters, etc) and the automotive industry (cars, buses, trucks, etc.).

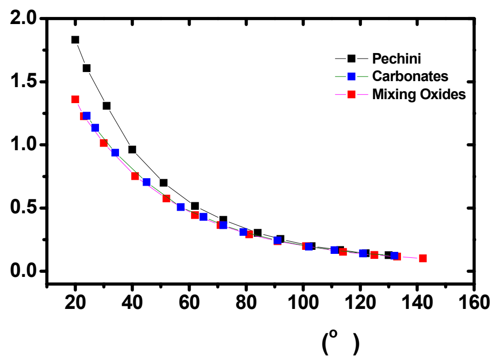

Figure 3: NTC behavior of Ni-Mn-Co (1:2:5) oxide sintered pellets. Powders prepared by the Pechini technique and by oxide and carbonate mixing techniques.

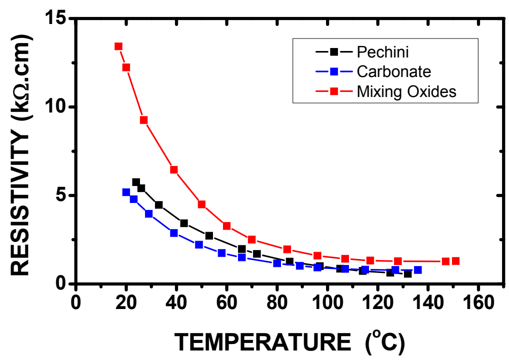

Figure 3: NTC behavior of Ni-Mn (1:2) oxide sintered pellets. Powders prepared by the Pechini technique and by oxide and carbonate mixing techniques.

Figure 3 shows that the electrical response does not vary for pellets prepared from powders with composition Ni-Mn-Co (1:2:5), obtained by mixing oxides and by mixing carbonates. Powders prepared by the polymeric precursor technique, on the other hand, show the best results: a higher value of the B coefficient in the 20 °C - 80 °C range (Cf. Figure 3).

Figure 3 shows the electrical response of pellets prepared from powders with composition Ni-Mn (1:2). Here, the mixing of oxides technique gives apparently the best result. Their higher values of electrical resistivity are probably due to a contribution of the porosity of the sintered specimens. Pellets prepared by mixing of carbonates and by the Pechini technique show similar behavior (Cf. Figure 3).

Figure 4 shows the effect of addition of chromium oxide to the Ni-Mn (1:2) composition. The B coefficient increases for increasing amounts of Cr_2O_3 addition to the powders prior to sintering. The reasons for this behavior are probably a chromium oxide resistive second phase inclusion or an increase of the porosity, or both. This behavior requires further studies.

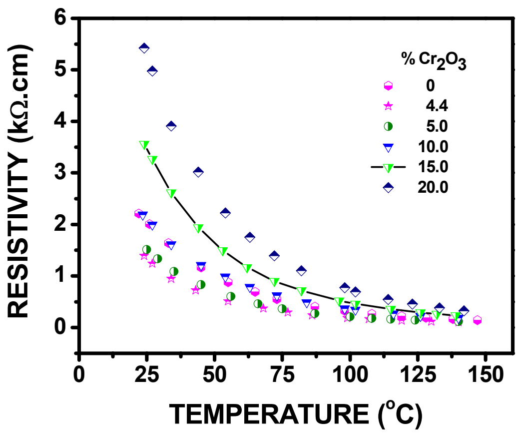

Figure 4: Dependence of the electrical resistivity of Ni-Mn (1:2) sintered pellets on temperature for different Cr_2O_3 additions.

The results of a scanning electron microscopy analysis of the powders prepared by the three different routes are shown in Figure 5. Powders after the polymeric precursor technique are finer than powders prepared by mixing the oxides, as expected. The EDS analysis of these powders show an even distribution of the precursor elements, Mn, Co and Ni. Powders prepared by the carbonate mixing route present large (average size 10 µm) spherical particles with Co preferentially located at the outer shells of the particles.

With the whole experimental procedure established, from the synthesis of powders via three different routes, the use of the spray dryer for making the powder particles flowable, the pelletizing of the powders using an high speed automatic pressing machine, sintering, application of electrodes for the electrical measurements, a protocol for fabrication of NTC thermistors are shown in Figure 6.

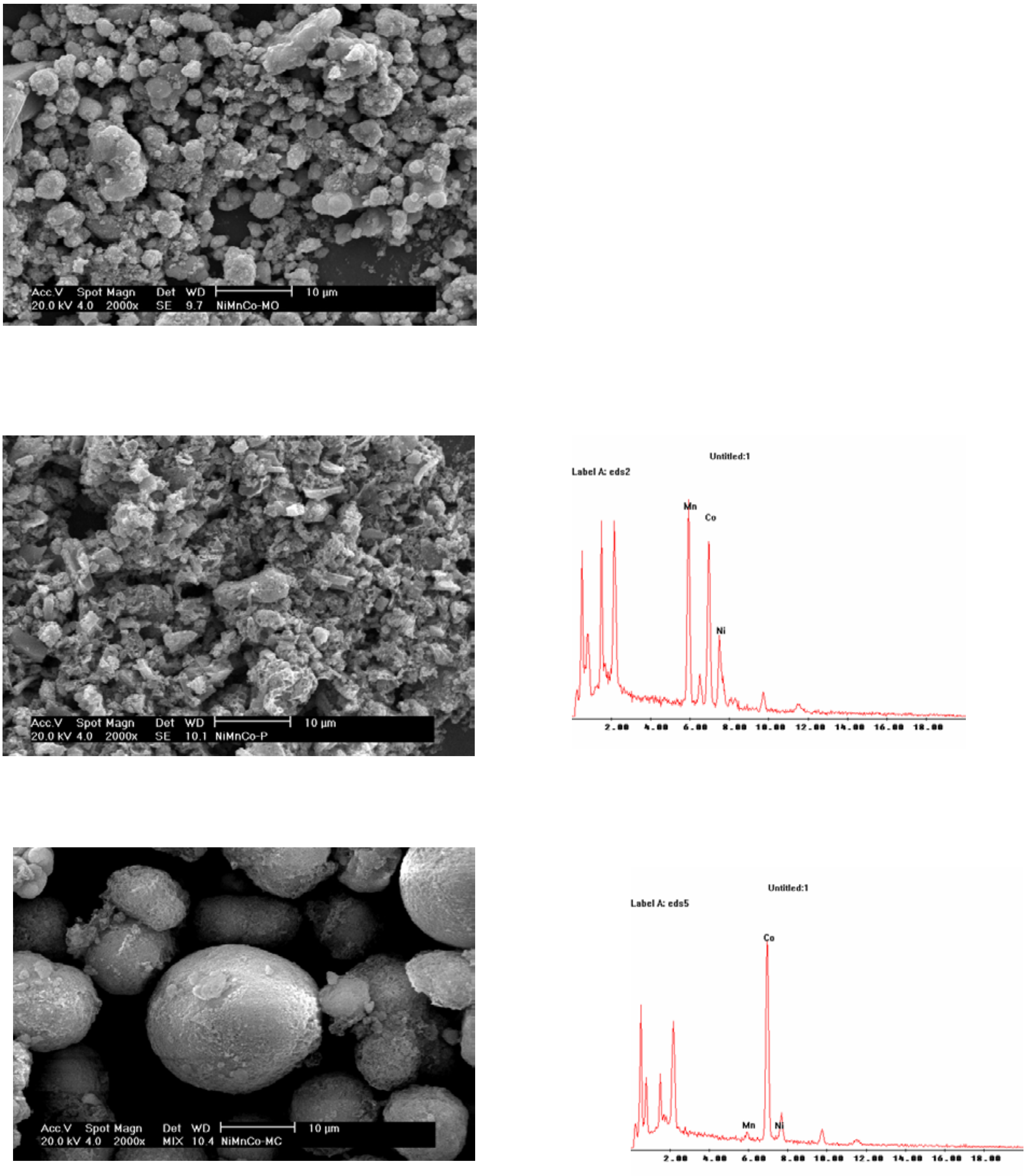

Figure 5: Scanning electron microscopy micrographs of Mn-Ni-Co powders prepared by three different routes: top - mixing of oxides, medium - polymeric precursor technique, and bottom - mixing of carbonates. At the right side, corresponding EDS analysis are shown.

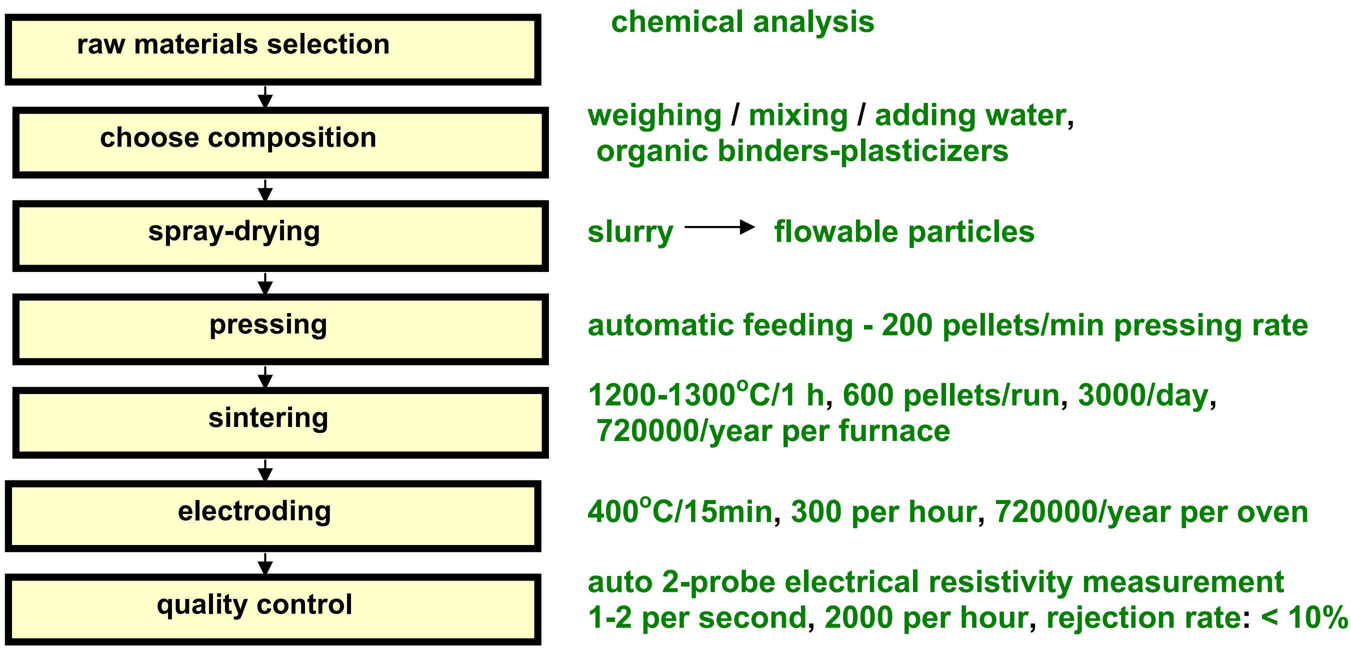

Figure 6: Proposed experimental sequence for producing large quantities of NTC thermistors.

Conclusions

- All routes, mixing of oxides, mixing of carbonates and polymeric precursor, produce single phase spinel oxides with NTC thermistor behavior.
- Chromium oxide additions increase the electrical resistivity and may be used to produce NTC thermistors with different electrical responses.
- Homogeneity of the powders is better achieved by the polymeric precursor technique.
- An industrial flowchart has been established for mass production of high quality temperature sensors for the automotive industry.

Acknowledgements

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