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Geometrical and Electrical Properties of NTC Polycrystalline Thermistors vs. Changes of Sintering Parameters

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Abstract:
NTC thermistor powder was made of a Mn, Ni, Fe and Co oxide mixture, calcinated at 1050°C / 60 min. The powder was milled in a ball mill down to an average particle diameter of 0.9 μm. Small disc shaped pills of the powder obtained were made by pressing with a pressure of 2.5 MPa. The pills were sintered in the temperature range of 900-1400 °C for 30-240 min. The volume and specific volume resistivity change were measured as a function of sintering conditions. Microstructure development was observed using a SEM microscope. Using the results obtained, optimization of sintering parameters was performed in order to determine optimal electrical properties of the selected thermistor composition.
Keywords: *$(Mn,Ni,Fe,Co)_3O_4$, NTC thermistor, Volume resistivity, Microstructure.*

Introduction

NTC thermistors based on Mn, Ni, Fe and Co oxides are produced all over the world and applied in electronic devices and sensors for temperature measuring, control or compensation, time delay, voltage regulation and surge suppression [1-4]. The purpose of this investigation was optimization of electrical properties of the selected thermistor compositions by changing the sintering parameters.

Complex AB_2O_4 e.g. spinel $(Ni,Mn,Fe,Co)_3O_4$ as a low resistivity thermistor composition (see fig.1) [5] was selected for preparation of a new thermistor paste due to the gentle slope of the thermistor B-factor (NTC exponential factor B). The main idea was to make a nanometric NTC paste with superior characteristics to the previous NTC 3K3 paste [6]. As formation of a liquid spinel phase is expected above 1550°C [5] sintering in a wide range from 900 to 1400 °C with different time durations from 30 to 240 min was performed in order to define resistivity and specific volume resistivity as a result of changes in the microstructure such as growth of polycrystalline grains, sub-grain structure and porosity.

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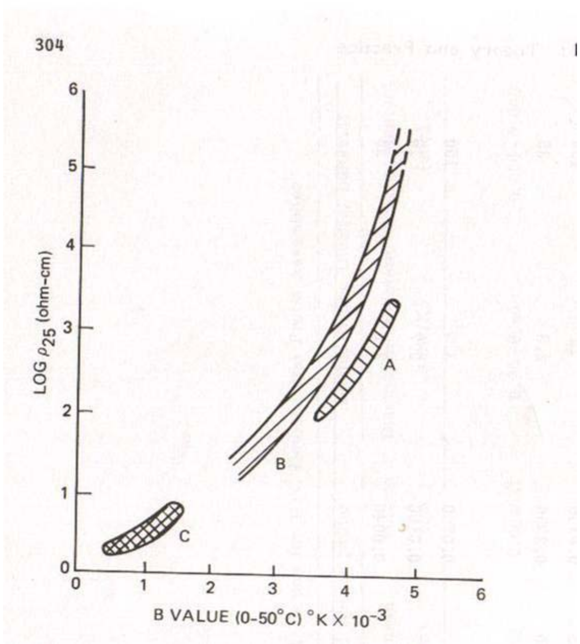


Fig. 1 Relationship between resistivity and exponential B-value for three classes of thermistor compositions : A - Li doped (Mn,Ni,Co) – oxides, B - $(Ni,Mn)_3O_4$, $(Ni,Mn,Co)_3O_4$, complex $(Ni,Mn,Fe,Co)_3O_4$, C-$(Fe,Ti)_2O_3$

Experimental

NTC thermistor powder was prepared of a Mn, Ni and Co –oxides mixture using a classical powder preparing procedure such as calcinating and ball milling. The composition comprising of Mn:Ni oxides in the ratio 4 : 1 and a small amount of Fe and CoO oxides was calcinated at 1050°C for an hour. EDS analysis of SEM micrographs (fig. 2) showed that the sintered thermistor comprised of 51.12 Mn, 19.01 Ni, 0.85 Fe, 0.58 Co and 28.43 O. After vibratory, ball and ultra fast milling an average powder particle size of 0.9 μm was achieved.

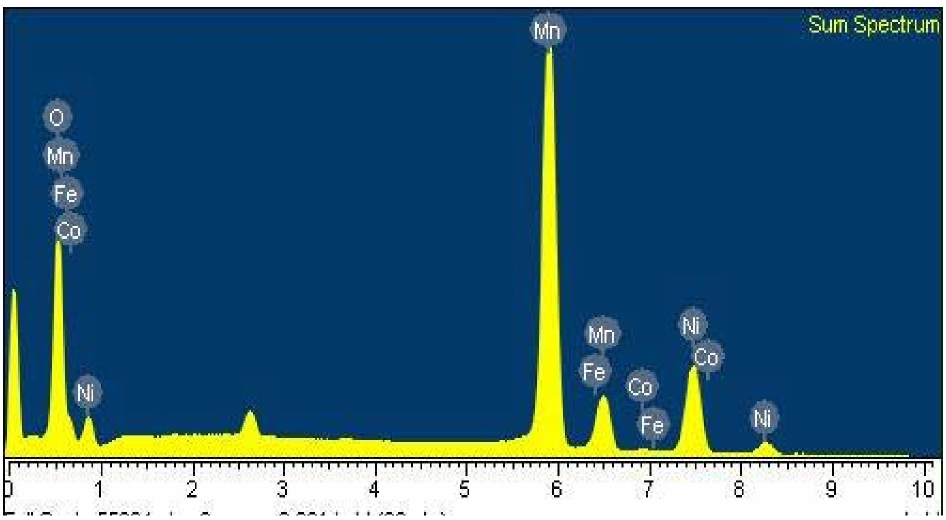


Fig. 2 EDS digram of NTC thermistor based on Mn,Ni,Fe,Co- oxides.

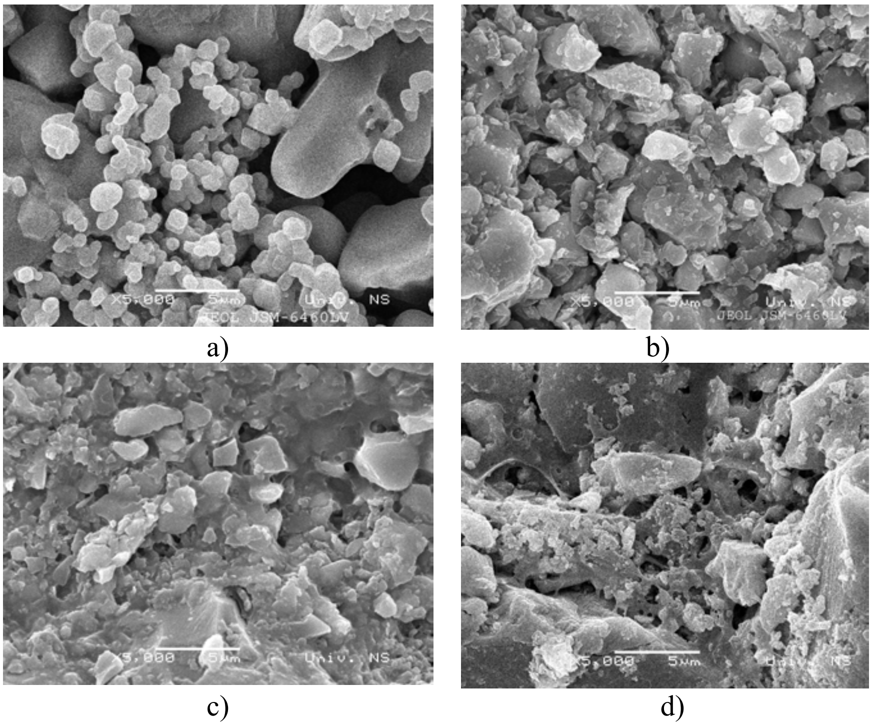


Fig. 3 a)Scanning electron microphotography of samples sintered at (a) 900°C, (b) 1050 °C, (c) 1200°C and (d) 1300°C for 30min (5000 x)

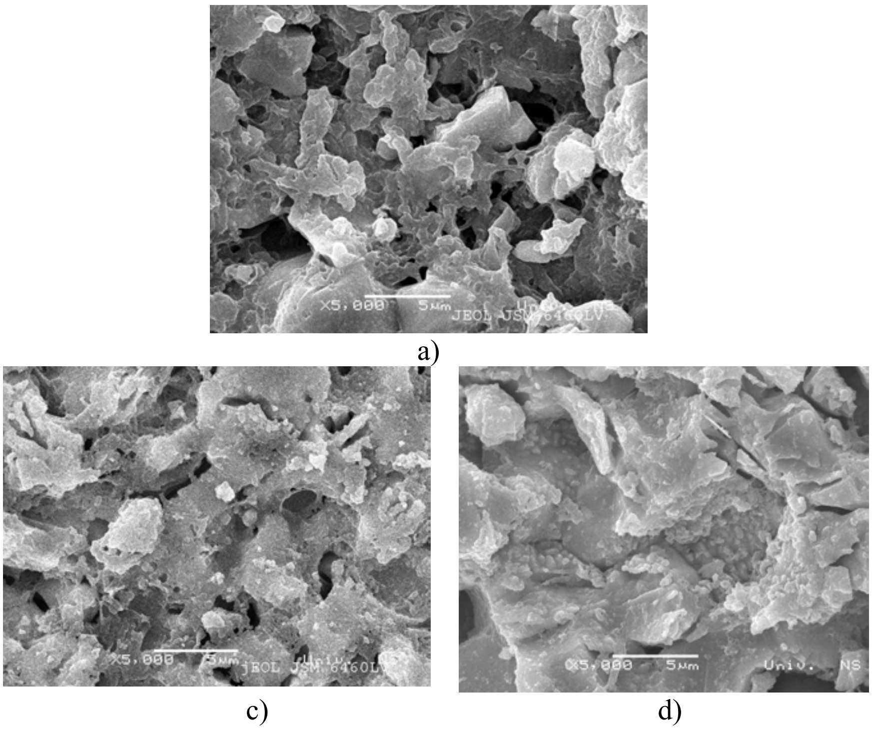
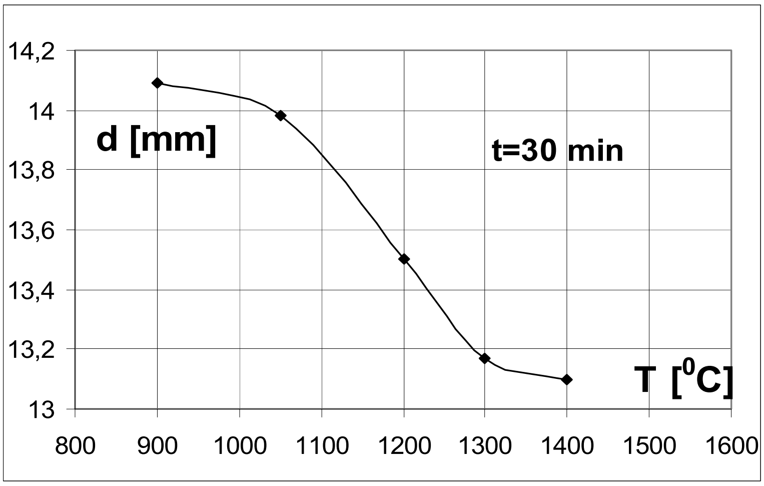


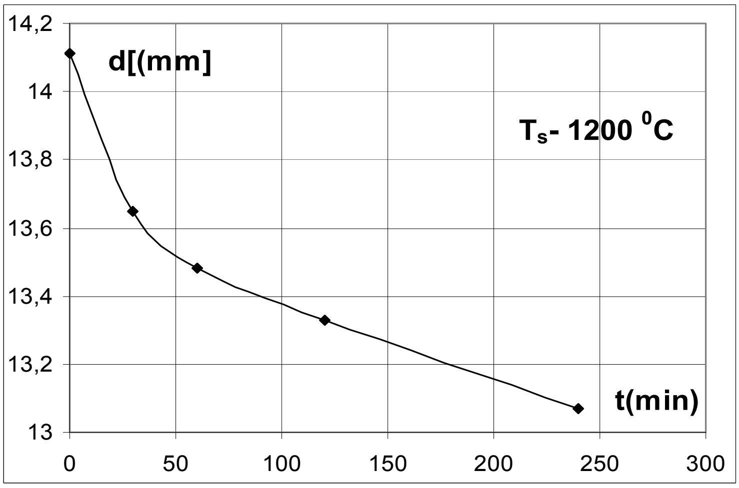
Fig. 4 SEM microphotography of samples sintered at 1200^{o}C (a) 60 min, (b) 120 min and (c) 240 min (5000 x)

Disc shaped pellets of the powder were pressed at a pressure of 2.5 MPa.The green samples were sintered in the temperature range of 900-1400°C during 30-240 min. Then the samples were polished and etched for 15 min in HNO_3 and HCl (1 : 3) acid solution and observed under optical and SEM microscopes. A very thin layer of gold was evaporated onto the surface of etched samples. The average grain size of the thermistor structure was determined from SEM pictures such as the ones given in Figs. 3 and 4 (microstructure development vs. variation of the sintering temperature and vs. sintering time respectively).

After that mechanical and electrical characterization was performed. Variations of mechanical properties for the same thermistor samples were observed vs. the sintering temperature and time.



a)

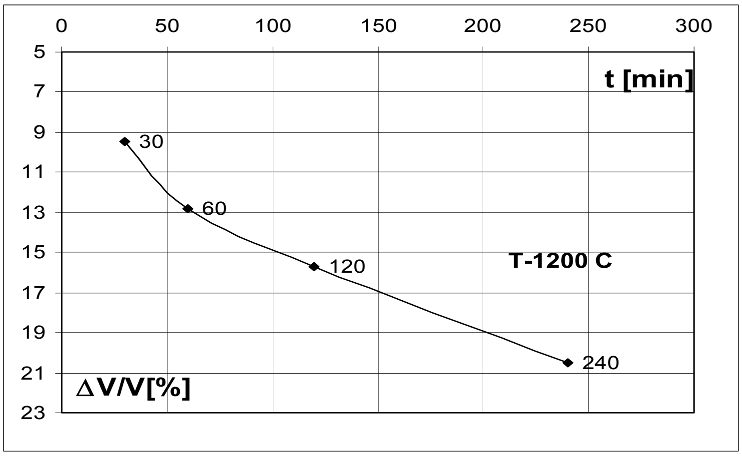


b)

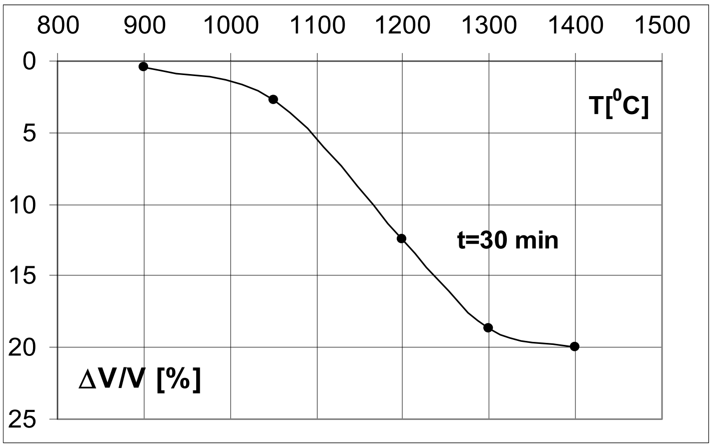
Fig. 5 Change of sample diameter vs. temperature of sintering (a) and time of sintering (b)

In Fig. 5 sample diameter (a) and porosity (b) changes were shown as a function of the sintering temperature, which varied from 900 to 1400 °C (the sintering time was half an hour). In Fig. 6 the same properties for a fixed sintering temperature of T=1200°C were shown as a function of the sintering time.

Specific volume resistivity was measured on the same samples used for SEM at room temperature (20^{o}C). The results obtained are given in Fig. 7, as a function of the sintering temperature.



a)



b)

Fig. 6 Relative volume change vs. temperature (a) and time of sintering (b).

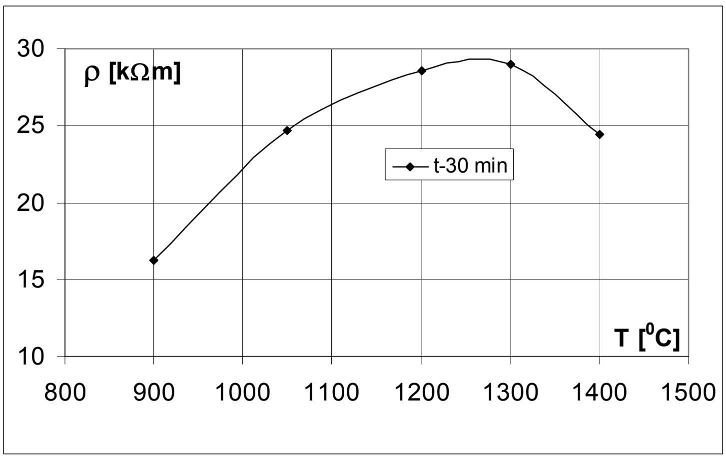
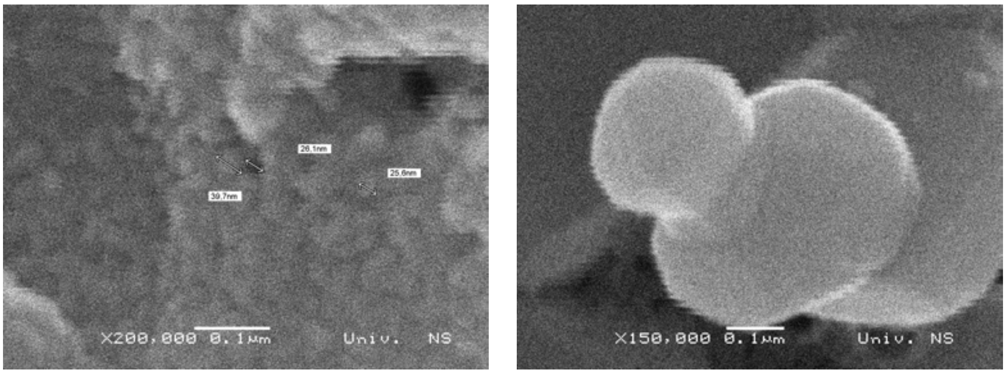


Fig. 7 Specific volume resistivity vs. temperature of sintering



a) b)

Fig. 8 Nanometric structure of grains, melted nanograins (a) and isolated nanograins (b).

Discussion

The microstructure development of thermistor ceramics during sintering was analyzed on SEM pictures recorded with different magnifications (5000 to 150000). The average grain size was determined from SEM pictures of the thermistor microstructure such as the ones given in Figs. 3 a, b, c, d and 4 a, b, c, d (magnification 5 000) where microstructure variation is given vs. the sintering temperature and time. The microstructure evolution observed on SEM photographs of NTC thermistor ceramics could be explained by an inter-particle contact increase vs. a sintering temperature increase.

In fig. 3 at 900°C (a) the grains are clearly separated, and contact formation and the process of conglomeration begin. The presence of open porosity is evident. At 1050°C (b) the open porosity almost disappears, and the number of closed pores is bigger. At 1200°C (c), the process of conglomeration is not over yet. The existence of large captive pores is present at 1300°C (d) – where an almost compact structure besides a small number of smaller pores is obtained marking the final step of sintering.

In fig. 4 the change of microstructure vs. time of sintering is much smaller. It can be seen that the change of sintering temperature has a larger influence on the microstructure, than varying of the sintering time (for instance, the increase of T for 100°C has a larger influence than the increase from one to four hours of sintering.)

Differing from previous research, where characteristics of 3K3 95/2 [3] thermistor NTC paste were optimized, the properties of a new NTC thermistor powder, containing clusters with an average size of 0.9μm are optimized here. The new NTC thermistor powder consisted of nanometer particles with sizes from 25 to 50 nm. On the SEM micrographs we can see polycrystalline grains consisting of nanometer particles (fig. 8 a and b). Conglomeration arises as a consequence of the magnetic effect of Ni and Co in nanometer particles of the powder.

SEM analysis of sintered samples shows a heterogeneous structure with an average grain size of 0.5 μm (over 50%) with a small percentage of particles bigger than 2μm. Practically after sintering a heterogeneous polycrystalline structure is formed, with an average grain size of 1-10μm based on melted clusters, which were formed of magnetically agglomerated nanometric particles (now sub gains).

In accordance with microstructure changes, caused by changes of sintering parameters such as temperature and time of sintering, the change of geometrical properties of samples occurs also (diameter, relative volume change, and specific volume resistivity).

Increasing the temperature of sintering above 1000°C, results in almost linear decreasing of the diameter and cubic relative volume decreasing occurs, that results in a decrease of porosity (figs. 5 and 6). The specific volume resistivity change is correlated to microstructure development change vs. temperature of sintering as given in fig 7. Resistivity increases to a gentle maximum at 1300°C, during the increase of average grain size and decreasing porosity of pills. Addition of SiO_2 or CuO could decrease specific volume resistivity for more than one order of magnitude.

Conclusion

Based on the experimental results shown, forming of NTC paste sintered on 1100-1200°C, very different from 3K3 NTC paste sintered on 850°C, seems quite real. Specific volume resistivity can be a few times lower than the resistivity of 3K3 paste using 0, 3-0, 5% SiO_2 or CuO additive. This new paste can be very suitable for thick sensor applications. Electrodes can be made of Ni paste for the new NTC paste and sintered in a protective atmosphere (N_2) or PdAg paste with large contents of Pd. New NTC paste with a new connective glass for higher temperature (SiO_2) can possibly be applied for higher thermistor heating power, and could have smaller porosity, better stability, and smaller long-term resistivity change than NTC 3K3 paste.

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Садржај: *NTC термисторски прах, синтетисан од смеше оксида Mn, Ni, Fe и Co, калцинисан је 60 минута на* 1050^0C*. Прах је затим млевен у кугличном млину, до просечног пречника четица од 0,9 μm. Мале пилуле облика диска су пресоване под притиском од 2.5 MPa и синтероване у температурном опсегу од 900 до* 1400^0C *у трајању од 30 до 24о минута. Мерена је промена запреминске и специфичне запреминске отпорности у функцији услова синтеровања. Посматран је развој микроструктуре употребом СЕМ-а.На основу добијених резултата извршена је оптимизација параметара синтеровања, у циљу одређивања оптималних електричних својстава за термистор одабраног састава.*
Кључне речи: *$(Mn,Ni,Fe,Co)_3O_4$, НТЦ термистор, запреминска отпорност, микроструктура.*