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Aging of NTC ceramics in the system Mn–Ni–Fe–O

W.A. Groen [a,]*, C. Metzmacher [a], V. Zaspalis [a], P. Huppertz [a], S. Schuurman [b]

[a] *Philips Research Laboratories, Weisshausstrasse 2, D-52066 Aachen, Germany*
[b] *BC Components n.v./s.a., Avenue Franz Guillaume 70, B-1140 Brussels, Belgium*

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Abstract

The aging behaviour of negative temperature coefficient ceramics in the system Mn–Ni–Fe–O has been investigated by electrical resistivity measurements and magnetic measurements. Comparison is made between samples cooled in air and in a controlled atmosphere in which no oxidation can occur. The results show that the aging is dependent on composition and the oxidation which occurs during the cooling down after sintering. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Negative temperature coefficient (NTC) ceramics or thermistors, based on mixed oxides of Mn, Ni, Fe, Co and Cu which crystallize in a spinel structure, are widely used for temperature sensing and compensation. The main problem with these materials is aging. This is a drift in resistivity with time which occurs during use of the thermistor at elevated temperatures, i.e. 150°C. The specific electrical resistivity is given by: $\rho = \rho_0$.exp ($E_a/K.T$), in which ρ is the specific resistivity, E_a is the activation energy for conduction, k is Boltzmann's constant and T is the absolute temperature. In the field of NTC ceramics the activation energy is replaced by the thermal constant, B in K, which is related to: $B = E_a/k$. Furthermore, the specific resistivity at 25°C is normally used: R_{25}.

In the spinel structure, described by AB_2O_4 there are two sites available for the cations: the tetrahedral site, A-site, and an octahedral site, B-site. The distribution of the ions over the sites: Mn^{3+} will occupy predominantly the B-site while Mn^{2+} will be on the A-site and almost all Ni^{2+} will go to the B-site.[1] At high temperatures, during sintering, there is a tendency for disordering due to entropy. Upon cooling, reordering of the cations to the A- and B-sites occurs. This process should be strongly dependent on the cooling rate. Mossbauer experiments on $Mn_{3-x}Fe_xO_4$ and $Mn_{2.4-x}Ni_{0.6}Fe_xO_4$ show a valency of Fe is 3+.[2,3] Up to Fe = 0.6 the iron occupies equally A- and B-sites. For higher Fe contents approximately 0.3 Fe goes to the A-site while the rest of the Fe goes to the B-site.[2,3]

The NTC ceramics are sintered typically at temperatures between 1000 and 1300°C depending on the composition. Normally, the sintering and also the cooling atmosphere is air and as a result the ceramics will oxidize during cooling down. To prevent oxidation during cooling down it is possible to use a controlled atmosphere, the so called stoichiometric cooling. In this case the amount of oxygen is controlled in a way that no oxidation (or reduction) can occur, in other words the compound remains stoichiometric with respect to oxygen content.[4]

The oxidation reaction can be described by the following reaction:

$$1/2O_2 \rightarrow \quad O_o^* + 1/4V_A'' \; + \; 1/2V_B'' + \; 2p^{\cdot}$$

The formed vacancies are distributed over the A- and B-sites. The formal valency for the A-site is 2 and for the B-site is 3. It can be argued that at high temperatures these will be distributed randomly over the lattice as discussed above, but at low temperatures these cationic vacancies show a preference for the B-sites.

A number of models have been reported to explain the aging phenonema. Zurbruchen and Case[5] conclude

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* Corresponding author. Tel.: +49-241-6003-256; fax: +49-241-6003-483.

E-mail address: wilhelm-albert.groen@philips.com (W.A. Groen).

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that besides contact degradation the degree of inversion, the distribution of the cations between tetrahedral and octahedral sites in the spinel, change upon aging. This is observed from changes in the crystal structure. Feltz[6] reports two models for aging of NTC ceramics: the first is an oxygen uptake or release, the second one is also a redistribution of the cations over the sublattices. Investigations on $Mn_{3-x}Fe_xO_4$ ($x=0.58$ and 1.05) by means of Mössbauer spectroscopy before and after aging has shown that a migration occurs of Fe^{3+} from the A-site to the B-site.[7]

2. Experimental

Samples have been prepared from mixtures of Mn_2O_3, NiO and Fe_2O_3 in the appropriate ratios. These powders have been ball-milled on a roll-bank and calcined at 800°C for 2 h. The calcined powders have been milled again and thereafter been granulated. From the granulated powders rings or pellets have been pressed. From these rings and pellets a first series has been sintered in air for 6 h. at 1250°C and consequently cooled down in air with 300°C/h. The second series of samples is sintered in air and cooled down using a controlled atmosphere (O_2/N_2) to prevent oxidation of the ceramics. The set-up used for these experiments has been described in.[8]

3. Results and discussion

In the first series of experiments the Fe quantity (x) in the spinel $Mn_{2.46-x}$ $Ni_{0.54}$ Fe_xO_4 was varied from 0 to 1.2 with a constant nickel content of Ni = 0.54. Fig. 1 shows R_{25}, the specific resistivity at 25°C, and calculated $B_{25/85}$ values ($B_{25/85} = 1779.7.\ln(R_{25}/R_{85})$, in which R is the specific resistivity at 85°C) as a function of x, the Fe content. After the measurements, the samples have been placed in an oven at 150°C in air for the aging test. They have been measured again after different times of aging (up to 1000 h.). In Fig. 2 the change in resistivity, $\Delta R/R$ and $\Delta B/B$ after 1000 h at 150°C is shown as a function of the Fe content.

As discussed in the introduction, cooling down in air after sintering is expected to result in oxidation of the ceramics. To investigate the effect of this oxidation a series of experiments has been performed with $Mn_{2.46-x}$ $Ni_{0.54}$ Fe_xO_4 in which the ceramics were cooled stoichiometrically with respect to oxygen content after sintering. The measured specific resistivities and $B_{25/85}$ values for these ceramics are slightly higher than those as for the air cooled samples. After the measurements, the samples were tested for aging in an oven at 150°C in air. After 1000 h. the samples were measured again and the resulting shift in R_{25} and $B_{25/85}$ has been calculated. The shift in R_{25} as a function of the iron content, x, in the samples is also presented in Fig. 2. It is shown that the stoichiometrically cooled samples show a much smaller aging than the air cooled samples. These results demonstrate clearly that the oxidation which occurs during cooling down in air has a large impact on the aging behavior of the ceramics. To investigate this in detail magnetic permeability measurements have been performed on $Mn_{1.71}Ni_{0.54}Fe_{0.75}O_4$. In Fig. 3 the magnetic permeability is presented as a function of temperature for the air- and the stoichiometrically cooled samples. On two samples of each batch the magnetic measurements are performed with a satisfactory reproducibility. The magnetic permeability at room temperature is the same for the air- and stoichiometric cooled samples indicating that the bulk magnetic properties did not change upon cooling. A small increase in the Curie point is observed for the air cooled samples. In the shape of the $\mu - T$ curve there are quite large differences dependent on the cooling of the samples, indicating a grain boundary effect. The stresses or defects at the grain boundaries which are formed during cooling in air are cationic vacancies as discussed before.

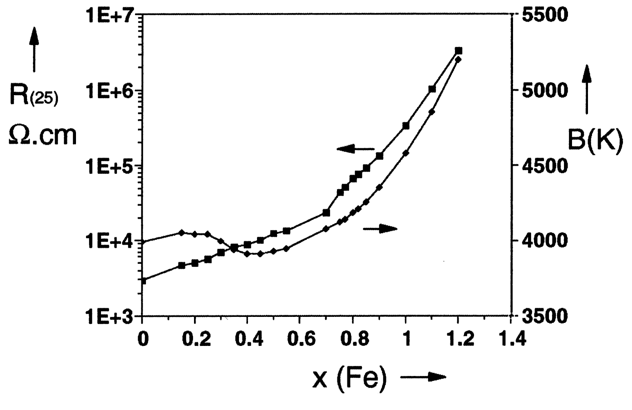

Fig. 1. Specific resistivity at 25°C and B value for the system $Mn_{2.46-x}$ $Ni_{0.54}$ Fe_xO_4 as a function of the iron content, x.

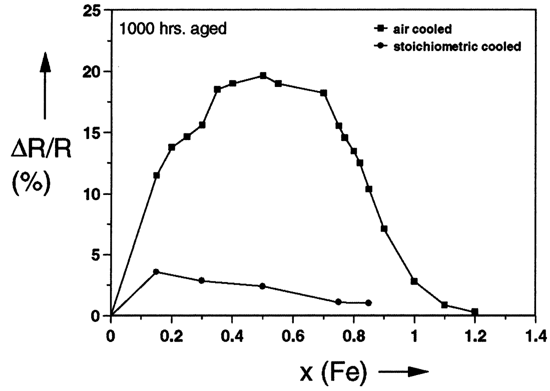

Fig. 2. Relative change in specific resistivity at 25°C and B-value after 1000 h aging at 150°C as a function of the Fe content, x, for air-cooled samples and stoichiometrically cooled samples.

The results of the magnetic permeability measurements after aging of the air cooled samples for 1000 h at 150°C are also presented in Fig. 3. The $\mu - T$ behaviour of the aged samples are nearly the same as observed for the stoichiometric cooled samples. This indicates that upon aging the stressed grain boundaries which are formed during cooling in air, disappear after aging.

The results of the magnetic measurements described above show that the oxidation of the ceramics which occur during cooling down in air results in an oxidation which starts at the grain boundaries. This results in the formation of cationic vacancies. At high enough temperatures these vacancies will diffuse to the grain interior but at lower temperatures these vacancies will remain at the grain boundaries. During the aging tests at 150°C the vacancies which are at the grain boundaries will diffuse slowly to the inside of the grains. In case of stoichiometrically cooled (or quenched samples) there will be no oxidation during cooling down. As a result, the cationic vacancy concentration will be low.

In the introduction it has been discussed that the cation distribution over the sites in the spinel is strongly dependent on the cooling rate after the sintering. Furthermore, it is reported that during aging at elevated temperatures the cation distribution changes. The results described above show that aging is also strongly dependant on the atmosphere during cooling down after sintering. From these observations the following model for aging of NTC ceramics can be postulated:

1. During aging a cationic vacancy migration occurs from grain boundary to bulk.
2. A cation vacancy assisted migration of cations and cationic vacancies occur to thermodynamically more stable sites.

As a result of these processes, there is an increase of metal vacancies on the B-sites in the spinel inside the grains which results in an increase of the resistivity since the hole conduction is over the B-sites in these spinels. Therefore, always an increase of the resistivity is expected during aging which is in agreement with the experiments.

Support for this description of the aging mechanism in NTC ceramics crystallizing in the spinel structure is given by a study on the system $NiAl_2O_4$.[9] Here a disorder of the cations is induced by a temperature-jump experiment, and the kinetics of the cation exchange are studied from relaxation. Samples with cationic vacancies show a fast exchange while samples with no cationic vacancies show a very slow relaxation. It is concluded from these experiments that the cation exchange mechanism is of vacancy controlled type.

The effect of various heat treatments on aging of NTC ceramics using the model described above can be summarized in Fig. 4. In case of stoichiometrically cooled or quenched samples there will be no oxidation during cooling down. As a result, the cationic vacancy concentration will be low. Therefore, it is expected that the stability for the stoichiometrically samples will be good as has been observed. However, for quenched samples the stability is questionable since there will be a strong disordering of the cations.

For air cooled samples there will be an oxidation starting from the grain boundaries which results in the formation of cationic vacancies. At sufficient high temperatures these vacancies can diffuse into the grain but at still lower temperatures the vacancies will be trapped at the grain boundary. The result is a NTC ceramic with a high cationic vacancy concentration and a non-ideal distribution of cations and cationic vacancies, thus the ceramics will be unstable with respect to aging. After

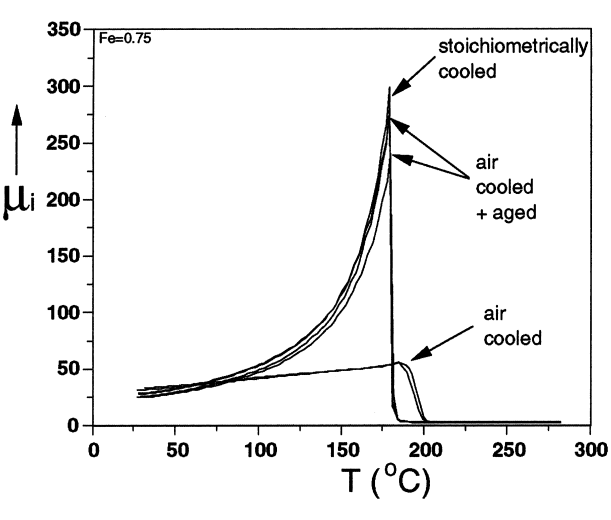

Fig. 3. Magnetic permeability as a function of temperature for air cooled and stoichiometric cooled and air cooled aged samples (1000 h 150°C).

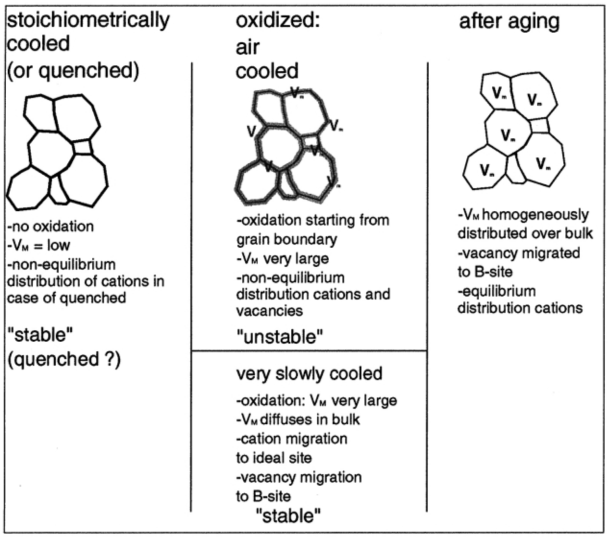

Fig. 4. The impact of various heat treatment on the stability of NTC ceramics.

prolonged aging the cationic vacancies will be distributed homogeneously over the ceramics. Furthermore, the cations and cationic vacancies migrate to their ideal site. Consequently after the aging test, the ceramics reach a state in which they are stable. One problem which arises from too high aging temperatures is a simultaneous oxidation of the ceramics. In this case the ceramics will never be stable because there is a continuous generation of cationic vacancies at the grain boundaries. At last it is of interest to note that is has been reported that ceramics which are extremely slowly cooled in air are stable with respect to aging if the electrical contacts are made by vacuum metallization.[10] For these ceramics there will be severe oxidation and thus formation of cationic vacancies. But since the cooling rate is very slow there will be time for the cationic vacancies to diffuse into the grains and the distribution of cations and vacancies will reach equilibrium. However, when the electrical contact are made by screen printing (and as a consequence are heated for a short time at 850°C for curing) the stability with respect to aging is low.[10] This can be explained because during the short heating cycle a disordering of cations and cationic vacancies will occur.

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