

# Ageing of ZnO–NiO ceramics

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Investigation of electrical, mechanical and microstructural properties of ZnO–NiO two-phase ceramics with respect to the ageing process of the material were performed. Two constituent phases, ZnO<sub>ss</sub> and NiO<sub>ss</sub> were identified in those ZnO–NiO ceramics which exhibit a positive temperature coefficient of electrical resistivity (PTCR anomaly). The origin of the PTCR anomaly was explained as a consequence of the different linear thermal expansion of the ZnO<sub>ss</sub> and NiO<sub>ss</sub> constituent phases. The ageing observed in the material is exhibited as an increase in resistivity of the samples and a smaller PTCR anomaly after heating the samples up to the temperature of the resistivity maximum, and cooling them again to room temperature. According to this study, the different linear thermal expansion of ZnO<sub>ss</sub> and NiO<sub>ss</sub> could also cause ageing of the material. © 1998 Kluwer Academic Publishers

## 1. Introduction

Thermistors with a positive temperature coefficient of electrical resistivity (PTCR) are commonly employed in a wide range of applications such as temperature sensors, temperature regulators, fluid-flow sensors and regulators, TV degaussers, for temperature compensation, overheat and overcurrent protection. Donor-doped BaTiO<sub>3</sub> ceramics and composite materials are used for PTCR thermistor applications.

Percolation models [1] have been used to explain the electrical properties of composites constituted from an electrically conductive and a non-conductive phase. At a critical concentration, the conductive phase forms a conductive network in the non-conductive phase and the composite becomes conductive. When the composite is heated, the non-conductive phase expands more than a conductive one and destroys the conductive network and the resistivity of the composite increases [2–6].

A positive temperature coefficient of electrical resistivity (PTCR) was observed in ZnO–NiO two-phase ceramics. The origin of the PTCR anomaly has been explained as a consequence of the different resistivity and linear expansion of the two, ZnO<sub>ss</sub> and NiO<sub>ss</sub>, constituent phases (thermal mismatch) [7, 8]. The microstructural changes which take place during heating and cooling are not reversible in every composite system, hence in some composite systems (see [3–6]), as well as in ZnO–NiO, non-reproducibility of the resistivity versus temperature behaviour and PTCR anomaly with thermal cycling, i.e. ageing of the material, was observed. The ageing of the material reduces the potential possible application of the material as a PTCR thermistor. The aim of this work was to reveal the origin of the ageing process observed in ZnO–NiO two-phase ceramics.

## 2. Experimental procedure

ZnO<sub>ss</sub> and NiO<sub>ss</sub> constituent phases with compositions (Zn<sub>0.97</sub>Ni<sub>0.03</sub>)O and (Ni<sub>0.6</sub>Zn<sub>0.4</sub>)O were pre-

pared by mixing ZnO (Pharma A) and NiO (Inco) with ethanol for 2 h in plastic containers. After drying at 80 °C the powders were fired at 1050 °C (ZnO<sub>ss</sub>) or 1300 °C (NiO<sub>ss</sub>), three times for 2 h in air. The calcinates were milled after each firing for 1 h in SiO<sub>2</sub> medium using ethanol, and dried at 80 °C. Samples with different ZnO<sub>ss</sub> and NiO<sub>ss</sub> contents were prepared by mixing ZnO<sub>ss</sub> and NiO<sub>ss</sub> powders in ethanol for 0.5 h in plastic containers and dried at 80 °C. The powder mixtures were pressed at 70 MPa and sintered at 1420 °C for 2 h in air. An In–Ga electrode was created by rubbing In–Ga alloy on the flat surfaces of the samples.

D.c. electrical resistivity in the temperature range 20–500 °C, at a heating rate 3 °C min<sup>-1</sup> was measured by a Hewlett Packard 3457A Multimeter. Dilatometric measurements at a heating rate 3 °C min<sup>-1</sup> were accomplished by a Bähr 802S Dilatometer. Impedance measurements, in the frequency range 5 Hz–13 MHz, were performed with a Hewlett Packard 4192A LF Impedance Analyser.

The phase composition of the samples was determined by energy dispersive X-ray spectroscopy microanalysis (EDS) using a Jeol JXA 840A scanning electron microscope (SEM). Densities of the sintered samples determined by Archimedes' method with mercury as the immersion medium were 81–75% of the theoretical value. The density decreased with the increasing weight percent of ZnO<sub>ss</sub>. For the transmission electron microscope (TEM) study, samples were prepared by mechanical thinning, dimpling and ion milling with 3.8 keV argon ions. Samples were examined by a Jeol 2000 FX transmission electron microscope (TEM), operated at 200 kV. The chemical composition of the phases was determined using a Link AN-10000 EDS system with an Ultra Thin Window Si(Li) detector, connected to the TEM.

Mechanical strength measurements were obtained with an Instron 1362 at an operating rate of 1 mm min<sup>-1</sup>. The tensile strength of the differentially thermally

cycled samples with 40 and 80 wt% ZnO<sub>ss</sub> was examined by a diametral compression test, which is used for the determination of the tensile fracture stress of brittle materials. Basically, this test involves subjecting a simple plane-faced cylindrical disc sample to two diametrically opposed loads uniformly distributed along the generators of the disc. The maximum tensile stress,  $\sigma_{tf}$ , which acts across a loaded diameter, is uniform and proportional to the applied load, and is given by the generally accepted expression [9]

$$\sigma_{tf} = \frac{2P}{\pi DT} \quad (1)$$

where  $P$  is applied load,  $D$  the diameter and  $T$  the thickness of the compacted discs.

For each measurement, five pellets of each composition were used. The diameters of the pellets with 40 and 80 wt% ZnO<sub>ss</sub> were  $7.31 \pm 0.03$  and  $7.04 \pm 0.04$  mm, respectively. The heights of the pellets were  $5.1 \pm 0.2$  and  $5.5 \pm 0.1$  mm for samples with 40 and 80 wt% ZnO<sub>ss</sub> respectively.

### 3. Results and discussion

#### 3.1. Characterization of ZnO–NiO two-phase ceramics

ZnO–NiO two-phase ceramics are composed of a ZnO<sub>ss</sub> and a NiO<sub>ss</sub> phase. The microstructures of two-phase ceramics with 40 and 80 wt% ZnO<sub>ss</sub> with 80% and 75% relative density, are shown in Fig. 1. In fact, ZnO–NiO two-phase ceramics could be treated as a composite material, which is composed of the high ohmic NiO<sub>ss</sub> phase with a room-temperature resistivity of the order of magnitude of 1 G $\Omega$ cm, and of the low ohmic ZnO<sub>ss</sub> phase with a room-temperature resistivity of about 100  $\Omega$ cm. The resistivity of the studied ceramics is strongly dependent on the amount of ZnO<sub>ss</sub> [10]. When a critical concentration of ZnO<sub>ss</sub> (20 wt%) is reached, a low ohmic network is formed from ZnO<sub>ss</sub> particles. The electrical properties of the ceramics with 20 wt% ZnO<sub>ss</sub> or more, are similar to the electrical properties of ZnO<sub>ss</sub> monophase ceramics. In ceramics with less than 20 wt% ZnO<sub>ss</sub> the influence of NiO<sub>ss</sub> on their electrical properties becomes much greater.

It should be noted that porosity cannot be neglected when comparing the resistivity of different compositions. It is known that the resistivity of porous ceramics is higher with respect to the 100% dense ceramics. In the case of the ZnO–NiO ceramics, the resistivity decreases with the increasing weight percent of ZnO<sub>ss</sub> and at the same time density slightly decreases (from 81% to 75% for the compositions from 10–80 wt% ZnO<sub>ss</sub>). Therefore, the resistivity of the 100% dense ceramics should also decrease with the weight percent of ZnO<sub>ss</sub> and the trend could only be more significant than in the case of the porous ceramics.

In Fig. 2 the resistivity versus temperature characteristics of ZnO–NiO two-phase ceramics with different ZnO<sub>ss</sub> contents is shown. A small negative temperature coefficient of resistivity (NTCR) is observed at temperatures lower than 170 °C. The PTCR anomaly observed above 170 °C has a maximum at

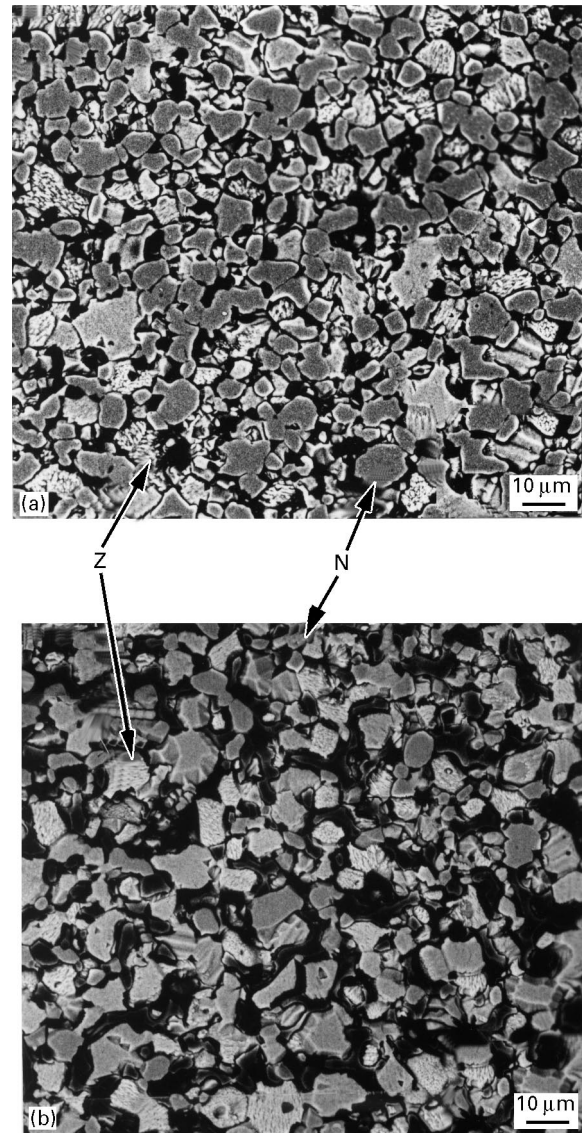


Figure 1 Scanning electron micrograph of a chemically etched ZnO–NiO two-phase ceramic containing: (a) 40 wt% and (b) 80 wt% ZnO<sub>ss</sub>. The dark grains (N) are NiO<sub>ss</sub> and the light ones (Z) are ZnO<sub>ss</sub>.

approximately 420 °C and this is followed by a rapid decrease of resistivity. The origin of the PTCR anomaly in the ceramics studied can be explained as a consequence of the thermal mismatch of the ZnO<sub>ss</sub> and NiO<sub>ss</sub> constituent phases [7, 8].

In Fig. 3, dilatometric curves for the ZnO<sub>ss</sub> and NiO<sub>ss</sub> monophase ceramics are shown. NiO<sub>ss</sub> high-ohmic ceramics exhibited a linear thermal expansion approximately twice as large as ZnO<sub>ss</sub> low-ohmic ceramics in the temperature range of the PTCR behaviour of the two-phase ceramics. In the temperature range 100–500 °C the average linear thermal expansion coefficient of monophase NiO<sub>ss</sub> ceramics is approximately twice than that of ZnO<sub>ss</sub> ceramics, i.e.  $11.5 \times 10^{-6}$  and  $6.5 \times 10^{-6} \text{K}^{-1}$ , respectively. The larger linear thermal expansion of the NiO<sub>ss</sub> phase induces disconnection between low-ohmic ZnO<sub>ss</sub> particles and causes the increase in resistivity above 170 °C (see Fig. 2). The room-temperature resistivity and the PTCR anomaly are strongly dependent on

phase composition. The most significant PTCR anomaly is observed for the samples with 20–60 wt%  $\text{ZnO}_{\text{ss}}$ , with a maximum for the sample with 40 wt%  $\text{ZnO}_{\text{ss}}$  phase (Fig. 2). One can conclude that besides a certain amount of  $\text{ZnO}_{\text{ss}}$  (needed for low-ohmic network formation), a certain amount of  $\text{NiO}_{\text{ss}}$  is also needed for a significant PTCR anomaly to occur. The maximum PTCR anomaly due to thermal mismatch of the constituent phases cannot be achieved if the amount of the  $\text{NiO}_{\text{ss}}$  is too low (lower than 40 wt%).

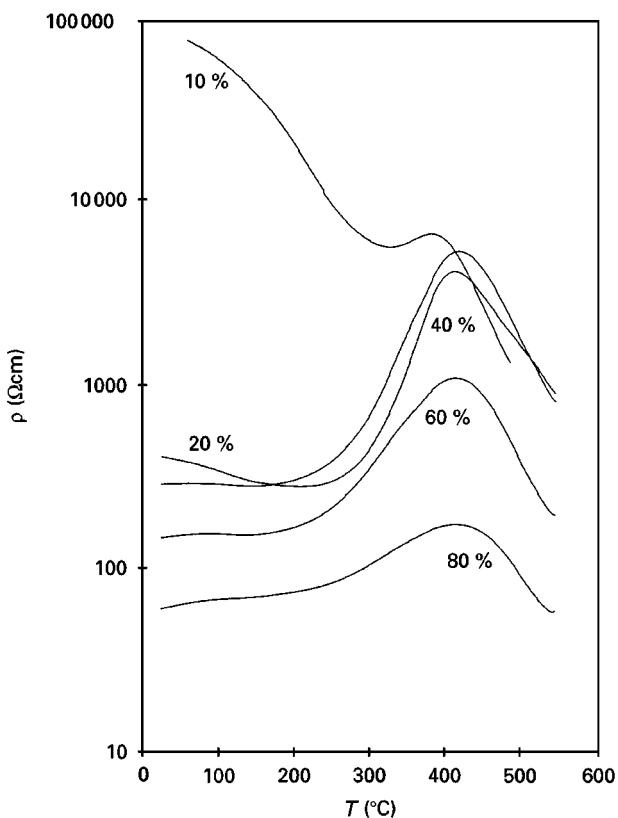


Figure 2 PTCR anomaly of ZnO–NiO two-phase ceramics. Numbers in % indicate the weight percent of the  $\text{ZnO}_{\text{ss}}$  phase.

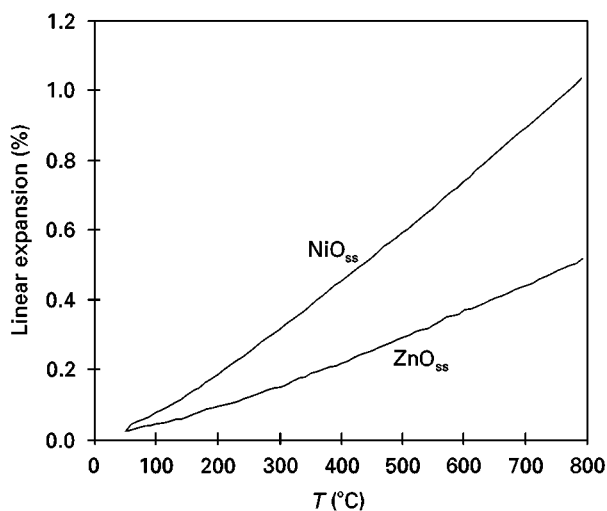


Figure 3 Linear thermal expansion of the two constituent phases  $\text{ZnO}_{\text{ss}}$  and  $\text{NiO}_{\text{ss}}$ .

### 3.2. Ageing process

Ageing of ZnO–NiO two-phase ceramics was observed. The samples were thermally cycled several times and their resistivity versus temperature characteristics were measured after consecutive cycles. One cycle is limited to heating the sample above the resistivity maximum to approximately 500 °C and cooling it to room temperature. Since the ceramics with 40 wt%  $\text{ZnO}_{\text{ss}}$  exhibited the greatest PTCR anomaly (Fig. 2), samples with such composition were used for more detailed investigations of the ageing process. In Fig. 4 the consequences of ageing of ZnO–NiO two-phase ceramics with 40 wt%  $\text{ZnO}_{\text{ss}}$  are shown. The room-temperature resistivity increases with the number of cycles, while the PTCR anomaly decreases. The reason for the increase in the room-temperature resistivity might lie in the poorer electrical contacts between the low ohmic  $\text{ZnO}_{\text{ss}}$  particles after each cycle. The greatest changes occur during the first cycle and are subsequently smaller with every cycle.

In fact, the electrical properties of the material once heated above the temperature of the PTCR anomaly are never the same as before heating. In Table I, the difference in room-temperature resistance before and after the resistivity versus temperature measurement of two-phase samples with different  $\text{ZnO}_{\text{ss}}$  contents, are summarized. The room-temperature resistance of all samples increased, indicating that irreversible processes occur in the material during thermal treatment.

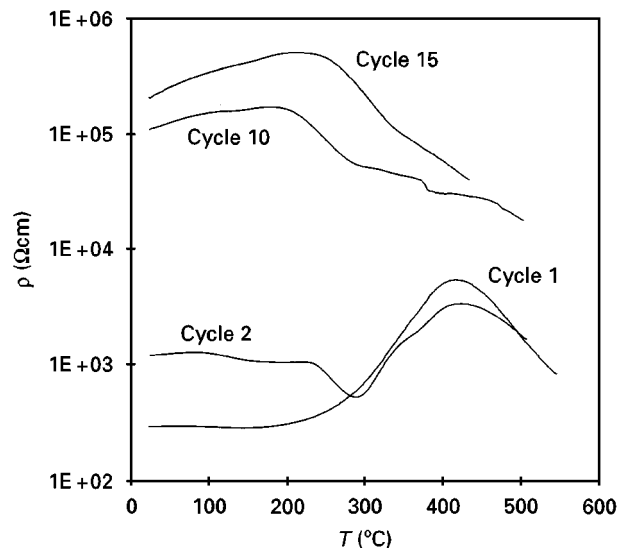


Figure 4 PTCR anomaly of the two-phase ceramic with 40wt%  $\text{ZnO}_{\text{ss}}$  measured after a different number of thermal cycles.

TABLE I. Room-temperature resistance of as-fired samples,  $R_{\text{as-fired}}$ , and room-temperature resistance of samples heated to 500 °C,  $R_{\text{after}}$  as a function of the amount of  $\text{ZnO}_{\text{ss}}$  phase

wt% of $\text{ZnO}_{\text{ss}}$	$R_{\text{as-fired}}$ (Ω)	$R_{\text{after}}$ (Ω)
10	$88\,000 \pm 8\,000$	$630\,000 \pm 50\,000$
20	$430 \pm 30$	$2100 \pm 200$
40	$320 \pm 30$	$2070 \pm 150$
60	$180 \pm 20$	$900 \pm 100$
80	$75 \pm 8$	$180 \pm 30$

One could assume that the microstructural changes resulting from the thermal mismatch of the constituent phases are not reversible.

The increase in room-temperature resistivity indicates poorer electrical contacts between low-ohmic  $\text{ZnO}_{\text{ss}}$  grains in samples thermally cycled once than in the as-fired samples. It could be possible that after the low-ohmic network is disconnected during heating the ceramics to  $500^\circ\text{C}$ , the low-ohmic network cannot be reformed to its previous extent during cooling the ceramics to room temperature. This possibility will be discussed in further sections.

### 3.3. Microcracking

As already mentioned above, the thermal mismatch of the two constituent phases  $\text{ZnO}_{\text{ss}}$  and  $\text{NiO}_{\text{ss}}$  is the origin of the PTCR anomaly in two-phase  $\text{ZnO-NiO}$  ceramics. The same difference could also result in the irreversible resistivity versus temperature behavior. Fig. 5 is a TEM micrograph showing the stress fields at a  $\text{ZnO}_{\text{ss}}-\text{NiO}_{\text{ss}}$  grain boundary in an as-fired sample with 40 wt%  $\text{ZnO}_{\text{ss}}$ . The thermal expansion difference between the constituent phases causes mechanical stresses at the heterophase grain boundaries during cooling of the samples.

These mechanical stresses are relaxed during thermal treatment, i.e. cycling, by the formation of microcracks [11–13]. In Fig. 6, a transmission electron micrograph of 20 nm thick microcrack formed during the first thermal cycle on the  $\text{ZnO}_{\text{ss}}-\text{NiO}_{\text{ss}}$  grain boundary in a sample with 40 wt%  $\text{ZnO}_{\text{ss}}$  is shown. Fig. 7 shows a transmission electron micrograph of a microcrack on the homophase  $\text{ZnO}_{\text{ss}}-\text{ZnO}_{\text{ss}}$  grain boundary formed during the first thermal cycle of the sample with 40 wt%  $\text{ZnO}_{\text{ss}}$ . Uncompensated stresses

originating at the heterophase grain boundaries of the  $\text{ZnO-NiO}$  ceramics are compensated during thermal treatment by the formation of microcracks at hetero- and homophase grain boundaries.

We believe that the induced microcracks are responsible for the ageing of the materials because no changes in the composition of the samples due to the thermal cycling were observed. The low-ohmic network from  $\text{ZnO}_{\text{ss}}$  grains, once disconnected during

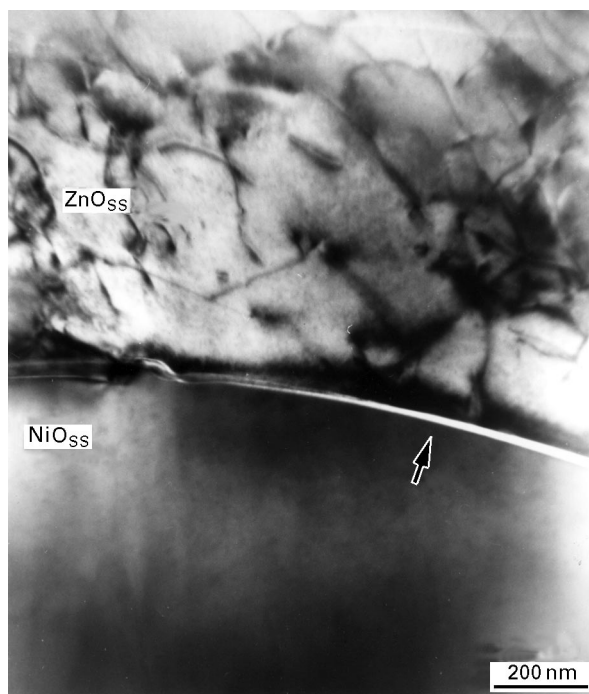


Figure 6 Transmission electron micrograph of a microcrack at the  $\text{ZnO}_{\text{ss}}-\text{NiO}_{\text{ss}}$  boundary in the sample cycled once with 40 wt%  $\text{ZnO}_{\text{ss}}$ .

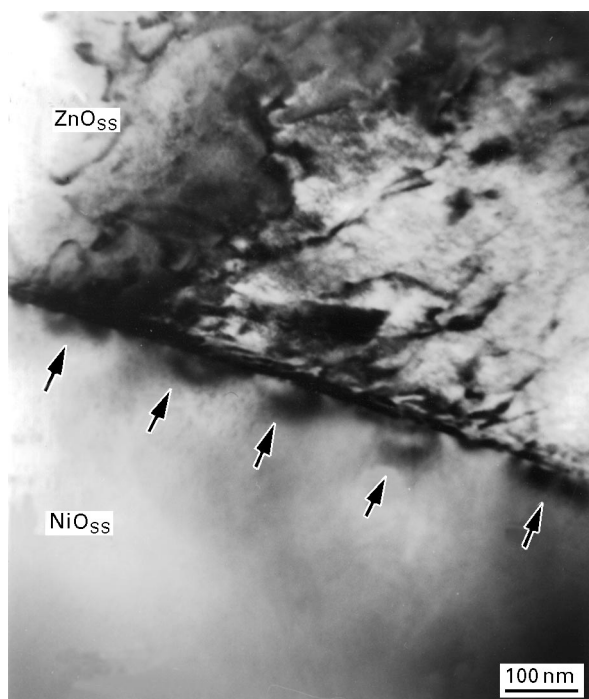


Figure 5 Transmission electron micrograph of stress fields at the  $\text{ZnO}_{\text{ss}}-\text{NiO}_{\text{ss}}$  boundary in the as-fired sample with 40 wt%  $\text{ZnO}_{\text{ss}}$ .

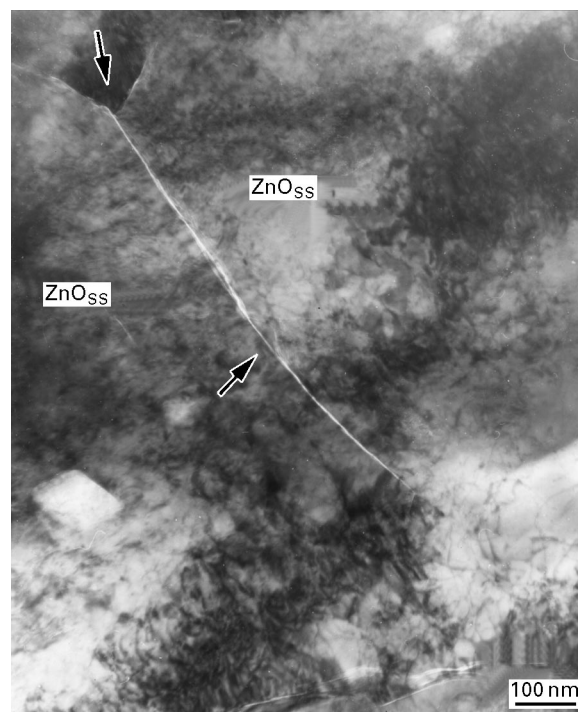


Figure 7 Transmission electron micrograph of a branching microcrack at the  $\text{ZnO}_{\text{ss}}-\text{ZnO}_{\text{ss}}$  boundary in the sample cycled once with 40 wt%  $\text{ZnO}_{\text{ss}}$ .

heating to 500 °C (above the temperature of the resistivity maximum), cannot be reformed to its previous extent during cooling and the room-temperature resistivity of the samples increases. During each thermal cycle, i.e. heating to 500 °C and cooling to room temperature, new stresses on the grain boundaries occur and some of them are relaxed as microcracks, which can also propagate and link into larger ones with each cycle.

### 3.4. Mechanical behaviour

In addition to TEM studies, the influence of microcrack formation on the mechanical behaviour of ZnO–NiO ceramic using a diametral compression test was investigated. The diametral compression test [9] is an experimentally simple, fast and reliable test for relative tensile strength measurements of small research samples which fail in a brittle manner. However, one has to be careful when comparing the values obtained by the diametral compression test and the values obtained by other tests. In our case, this is not of great importance because the values obtained are used only for comparison between differently thermally treated samples of a certain composition. In Table II the maximum tensile strengths,  $\sigma_{\text{tr}}$ , of the as-fired and differently thermally treated samples, of two different compositions, are given.

Because the strength of the ceramics is influenced by their density, the thermal mismatch (or anisotropy of) the thermal expansion coefficients, grain size and also volume fraction of the phases present, we can only compare the values of maximum tensile stress for differently thermally cycled samples of the same composition (see Fig. 1). However, similar behaviour is observed for both compositions, meaning that an increase of maximum tensile strength after the first thermal cycle is followed by a decrease with further thermal cycling.

The mechanical measurements confirmed our assumptions. The microcracks formed during thermal cycling initially increased the strength of the material because the maximum tensile stress of the samples, of both compositions, increased after the first cycle (Table II). The presence of microcracks influences the mechanical properties of brittle materials such as ceramics [11–14]. One would expect poorer mechanical properties of a material in which microcracks were formed as compared to the material without microcracks which, however, is not the case for ZnO–NiO two-phase ceramics after the first thermal cycle. In the as-fired samples the grains are still subjected to residual thermal stresses because during cooling from the

sintering temperature, these stresses were not relaxed by the formation of microcracks. When an external load is applied, many new cracks are formed leading to a reduction in strength compared to unstressed material [13]. During the first thermal cycle, new microcracks are formed. These microcracks tend to branch (see an arrow indicating the branching microcrack in Fig. 7). A consequence of crack branching is the higher energy needed for propagation of the critical and other cracks [11, 14]. This could be a reason for the observed higher strength in ZnO–NiO two-phase ceramics thermally cycled once, in comparison to the as-fired samples.

However, when microcracking becomes too severe, macrocrack growth becomes possible by linking of microcracks, thus reducing the energy needed for critical crack propagation [11, 13, 14]. A decrease in the maximum tensile stress observed for additionally thermally cycled samples could therefore be explained by the increasing number, size and linking of microcracks with thermal cycling. At the same time, the possibility for a critical crack to occur and its propagation is also increasing. Therefore, one could expect that the mechanical strength would decrease after additional thermal treatment.

### 3.4. A.c. impedance measurements

In Fig. 8, a.c. impedance spectra of two-phase samples with 40 wt% ZnO<sub>ss</sub> cycled several times are shown. One can see that the maximum values for the real and imaginary parts of the a.c. spectra increase with cycling. The changes in the a.c. impedance spectra for differently thermally treated samples could be attributed to the irreversibility of the microstructural changes taking place in the samples during cycling. As already discussed above, the evidence for the irreversibility of the microstructural changes lies in the microcracks formed during cooling of the samples to room temperature (Figs 6, 7). Formation of microcracks can modify the a.c. impedance spectra of the samples [15] due to the change in sample geometry as (1) the main crack propagates leading to a proportional resistance increase over the whole spectra, and (2) microcracks form at grain boundaries leading to an apparent increase in grain-boundary resistance.

In the first case, the main crack propagates across the grain boundaries and through the grains. Conducting pathways in the sample are therefore disconnected across the grain boundaries and across the grains leading to an increase of both grain boundary and bulk resistance.

In Fig. 8 an increase of overall resistance (real part of the impedance spectra) with increasing number of thermal cycles is observed, indicating microcracks could form at the grain boundaries and in the grains. The evidence for grain-boundary microcracking is shown in Figs 6 and 7. No cracks in grains were observed by TEM in the as-fired and once thermally cycled ceramics. However, according to the observed reduction in tensile strength of the ceramics after ten and more thermal cycles (see Table II), it could be also possible that some cracks might also extend into grains.

TABLE II. Maximum tensile stress, ( $\sigma_{\text{tr}}$ ) of two-phase samples with 40 and 80 wt% ZnO<sub>ss</sub>, thermally cycled several times

	Number of cycles			
	0	1	10	15
$\sigma_{\text{tr}}$ (40%) (MPa)	20.5 ± 0.8	25.8 ± 0.9	21.2 ± 2.1	13.6 ± 2.8
$\sigma_{\text{tr}}$ (80%) (MPa)	9.0 ± 1.7	19.5 ± 1.3		8.0 ± 1.8

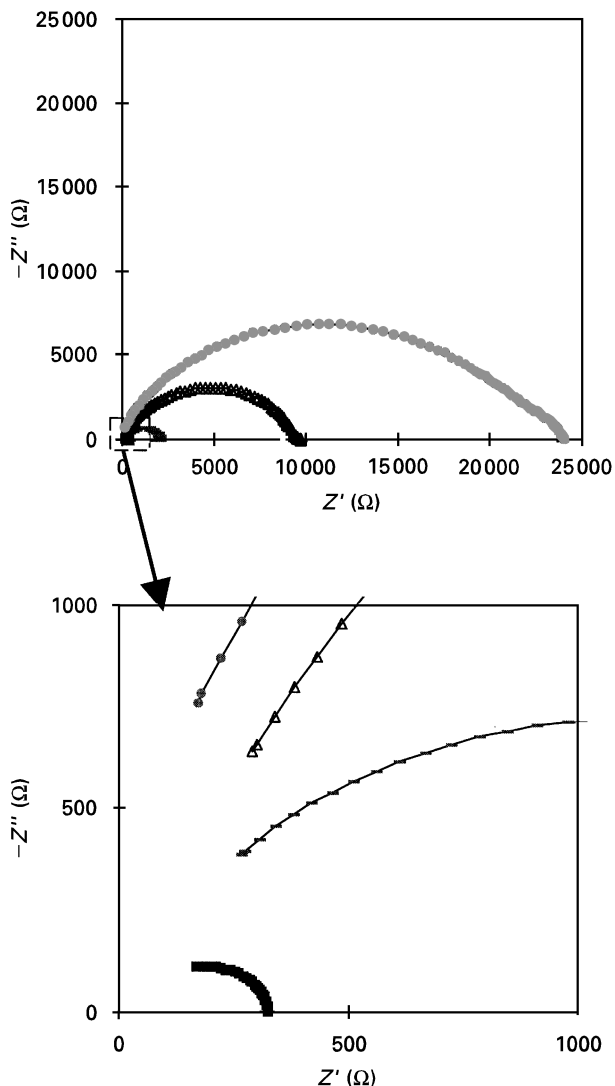


Figure 8 (a) A.c. impedance spectra of differently thermally cycled ceramics with 40 wt% ZnO<sub>ss</sub>, with (b) detail of the high-frequency region indicated in (a). Cycle (■) 0, (□) 1, (△) 10, (●) 15.

#### 4. Conclusion

The difference in linear thermal expansion of the constituent phases is the origin of changes in their PTCR behaviour and in the a.c. impedance spectra for differently thermally treated samples. The thermal

mismatch is big enough to induce stresses first at the hetero- and then also at the homophase grain boundaries, which can be relaxed as microcracks during thermal cycling. This was confirmed by TEM studies as well as by mechanical strength investigations.

Although the difference in linear thermal expansion of the constituent ZnO<sub>ss</sub> and NiO<sub>ss</sub> phases is the origin of the PTCR anomaly in two-phase ZnO–NiO ceramics, it is also the origin of the ageing of the material which reduces the possibility of the application of ZnO–NiO two-phase ceramics as PTCR thermistors.

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