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Giant permittivity phenomena in layered $BaTiO_3$–Ni composites

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Abstract

Layered $BaTiO_3$–Ni cermet composites with a constant composition but diversified microstructures were produced by a rolling-and-folding processing method. These composites differ from conventional laminates in that their interface has a tendency to be wavy, with a globular or elongated second phase within a continuous matrix phase. Based on an analysis of the (di)electric properties and Monte Carlo simulations we confirmed the critical influence of the composite's microstructural characteristics on the percolation threshold. We found that the dielectric properties of the composite, when it is in the insulation regime, were controlled by the insulating $BaTiO_3$ phase. A giant effective permittivity of around 200 000, with modest losses of $\tan \delta < 0.04$, was measured when the percolation threshold approached the composition of the cermet. Partial decomposition and deformation of the layered structure resulted in the creation of conducting paths, whereas further homogenization again shifted the percolation threshold above the actual composition of the cermet.

Keywords: Suspensions; Composites; Dielectric properties; $BaTiO_3$–Ni; Percolation

1. Introduction

Recently, a new type of layered ceramic-matrix composites with ribbon-like microstructures has been reported.[1] These composites differ from conventional laminates in that their interfaces have a strong tendency to be wavy, with a globular or elongated second phase within a continuous matrix phase.[2] The processing technique builds on the destabilization of the interface that separates two ceramic green tapes with different plasticities under large strain deformation.[3] This can be achieved by repeated folding and rolling or pressing of the starting bi-material laminates. A paraffin-based process that allows repeated deformation processing and shape retention at room temperature was recently suggested. Due to a large layer waviness that reduces the long-range sintering stresses, these bi-materials with ribbon-like microstructures show an improved sinterability.[4] This is also reflected in the superior properties[5] when compared to conventionally formed laminated composites.

In the present study, the rolling-and-folding process was applied to produce $BaTiO_3$–Ni cermet composites in order to study the influence of texture on the electrical properties of such an anisotropic heterogeneous system. It is known that the electrical properties of a system composed of an electrical conductor and an insulator phase are governed by the position of the percolation threshold. Of particular interest are compositions near the percolation threshold, where theory predicts a non-linear or so-called critical behavior.[6,7] Small variations in the composition result in a large variation in the electrical properties. From the point of view of the permittivity a significant increase near the percolation threshold was predicted by theory as well as being confirmed by experiments.[8,9] Interestingly, this behavior of the permittivity, known as a giant permittivity phenomenon, is not simultaneously followed by an increase in the dielectric losses. This suggests that it might be possible to prepare, in a narrow compositional window, a material that would combine high permittivity and modest dielectric losses. Several such systems, which are of great interest to the capacitor industry, have already been reported, this include copper–titanate,[10] Li- and Ti-doped NiO,[11] $BaTiO_3$–Ni cermets,[12] etc. The main problem when it comes to applying these materials in capac-

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itor technology is the bad reproducibility and, therefore, the large variations in of the final electrical performance. It is critical for these systems that the position of the percolation threshold is known and controlled. However, in reality, this is extremely difficult because at a constant composition the exact position of the percolation threshold also depends on the microstructural characteristics of such a heterogeneous system[13] and precise control over the microstructure is difficult to achieve. Furthermore, the corresponding correlations with the electrical properties are still a matter of empirical studies.

The purpose of our study is to apply the rolling-and-folding technique to produce a highly anisotropic microstructure of $BaTiO_3$–Ni cermet composite in order to investigate the correlations between the microstructural characteristics, the percolation behavior and the electrical performance. The rolling-and-folding technique makes it possible to vary the microstructural characteristics, such as the degree of anisotropy, and the cluster size and distribution, within a single system with a constant overall composition. The variations influence the position of the percolation threshold and, consequently, also the functional properties. To understand the variation in the percolation threshold its position was numerically determined with a Monte Carlo simulation for a particular microstructural type.

2. Experimental

The starting powders used in this investigation were high-purity $BaTiO_3$ (Code 219-9, Lot 950094, Transelco, Pen Yan, NY, USA) and nickel (1 μm, Lot 031292305, Ventron, Germany). The nickel powder was first milled in an acetone solution of stearic acid (1 wt.% of stearic acid with respect to the powder) to condition the surfaces to become hydrophobic. The powder was then dried at 120 °C for 4 h. A suspension of $BaTiO_3$ powder and a suspension of a powder mixture containing 50 vol.% $BaTiO_3$ and 50 vol.% nickel powder (Ni/$BaTiO_3$) were prepared using paraffin oil (Kemika, Croatia). In Table 1 are the compositions of the suspensions. The initial suspensions were homogenized at 80 °C using a (water-heated) three-roller mill. The $BaTiO_3$ and Ni/$BaTiO_3$ suspensions were separately rolled on a twin-roller mill at room temperature to form sheets with a thickness of 1 mm. These sheets were stacked to form two-layer composites and then repeatedly rolled to a thickness

Table 1
Composition of the prepared suspensions

Suspension	$BaTiO_3$ (vol.%)	Nickel powder (vol.%)	Paraffin oil (vol.%)	Stearic acid (vol.%)
$BaTiO_3$	57.6	–	39.9	2.4
Ni/$BaTiO_3$	28.5	28.5	39.4	3.6

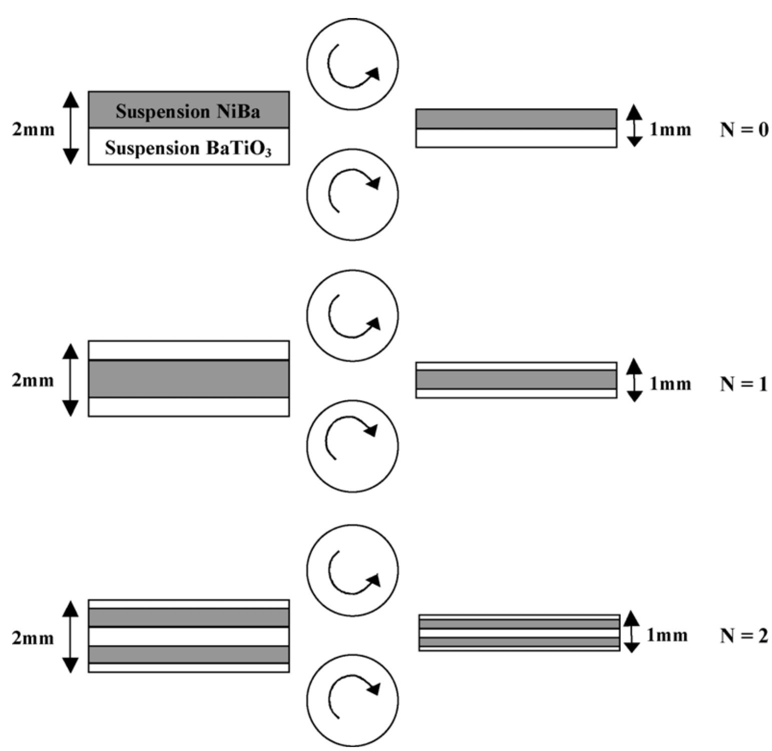

Fig. 1. Schematic representation of the stacking sequence of the $BaTiO_3$ and Ni/$BaTiO_3$ layers and the rolling-and-folding procedure used for the preparation of the composites.

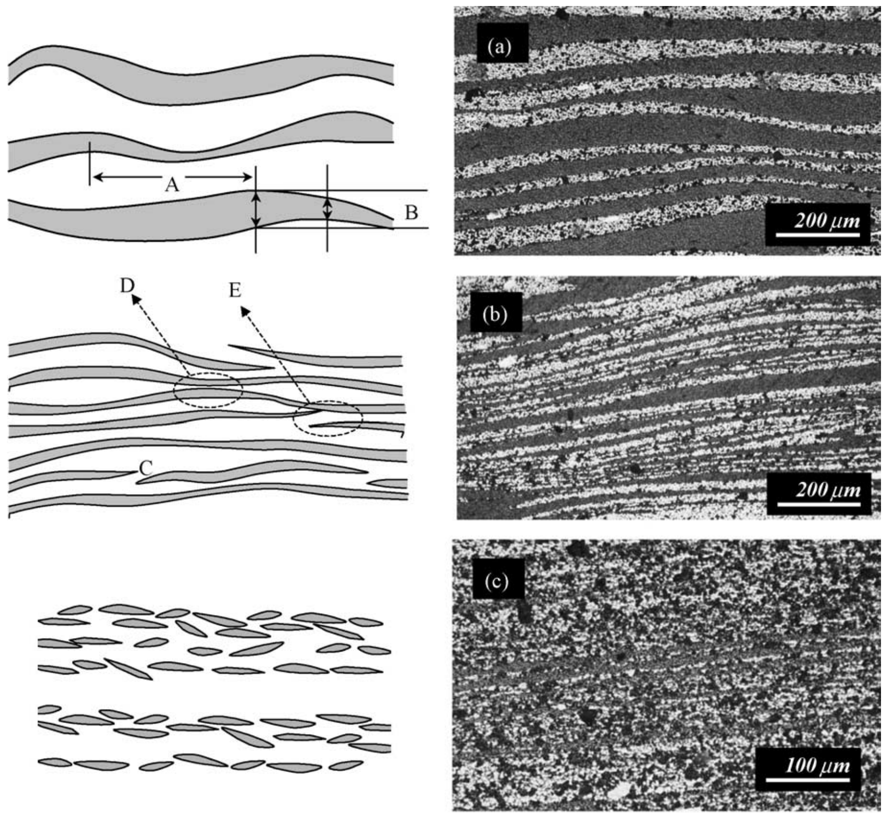

Fig. 2. Microstructural development during the rolling-and-folding process: (a) after 5 cycles, wavy; (b) after 7 cycles, ribbon-like; and (c) after 10 cycles, particulate microstructure. Letters A–D denote the characteristics of the layered composite described in the text.

of 1 mm and folded again (Fig. 1). Samples were taken for microstructural investigations and measurements of the electrical properties after each rolling step. The samples were debinded in an alumina powder bed (0.5 °C/min up to 200 °C, 2 h hold). To avoid any oxidation of the nickel the samples were sintered in a nitrogen atmosphere. The sintering was carried out at 1300 °C for 10 h. The density of the sintered samples was non-uniform. While the Ni-containing layers were almost completely dense, some porosity remained in the $BaTiO_3$ layers (see Fig. 2). Based on a visual inspection of the optical micrographs (Olympus BX60), the average relative density was estimated to be >90%.

For the electrical and dielectric measurements the samples were plated with In–Ga electrodes. The In–Ga electrode was selected to avoid any additional thermal treatment that might cause an undesired interaction of the cermet with the electrode. The AC conductivity was determined with four-point measurements using an LCR meter (Agilent 4284A). Due to the giant permittivity effects the serial resonance of the system was decreased to frequencies of around 1 MHz, so the dielectric measurements were made at frequencies from 1 to 100 kHz. The temperature dependence of the permittivity was measured from −100 to 280 °C by placing the samples in an environmental chamber (Delta Design, Delta 9023) and monitoring the temperature with a copper–constantan (T-type) thermocouple.

3. Results

3.1. Microstructural development

With repeated rolling-and-folding processing steps profound changes in the texturing of the cermet composite are obtained. Initially, a layered structure with alternating conductive and insulating layers is obtained. Typically, such a texture is maintained up to the fourth or fifth rolling-and-folding step. Within this texture type the layers undergo four major modes of deformation: the layers undulate with a wavelength of 1–2 mm and an amplitude of ∼200 µm; the undulated layers shift in terms of phase (Fig. 2A); the thickness of the layers becomes non-uniform (B) and decreases after every rolling-and-folding step. No contacts between two conductive layers are formed. As a result of further thinning of the layers a second texture type develops. Thin layers start to split (C), the phase shifts increase; this generates areas where the conductive layers are in close proximity (D) and some contacts between the conductive layers occur (E). Typically, after 10 rolling-and-folding steps the splitting of the layers is

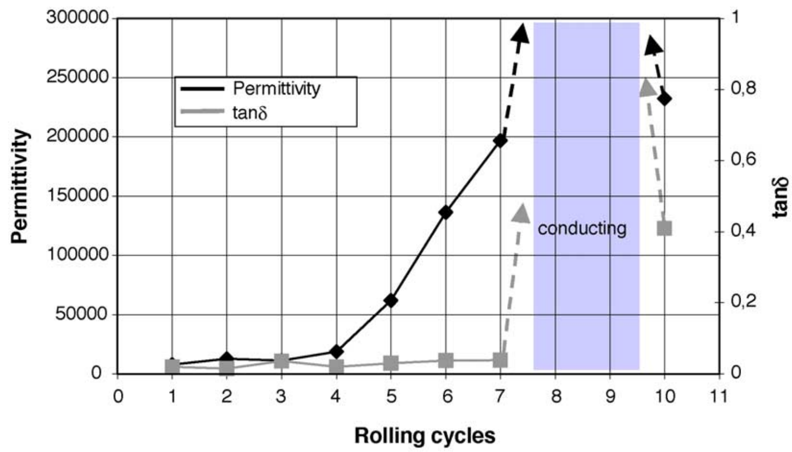

Fig. 3. Permittivity and dielectric losses as a function of the number of rolling cycles, measured at 1 kHz.

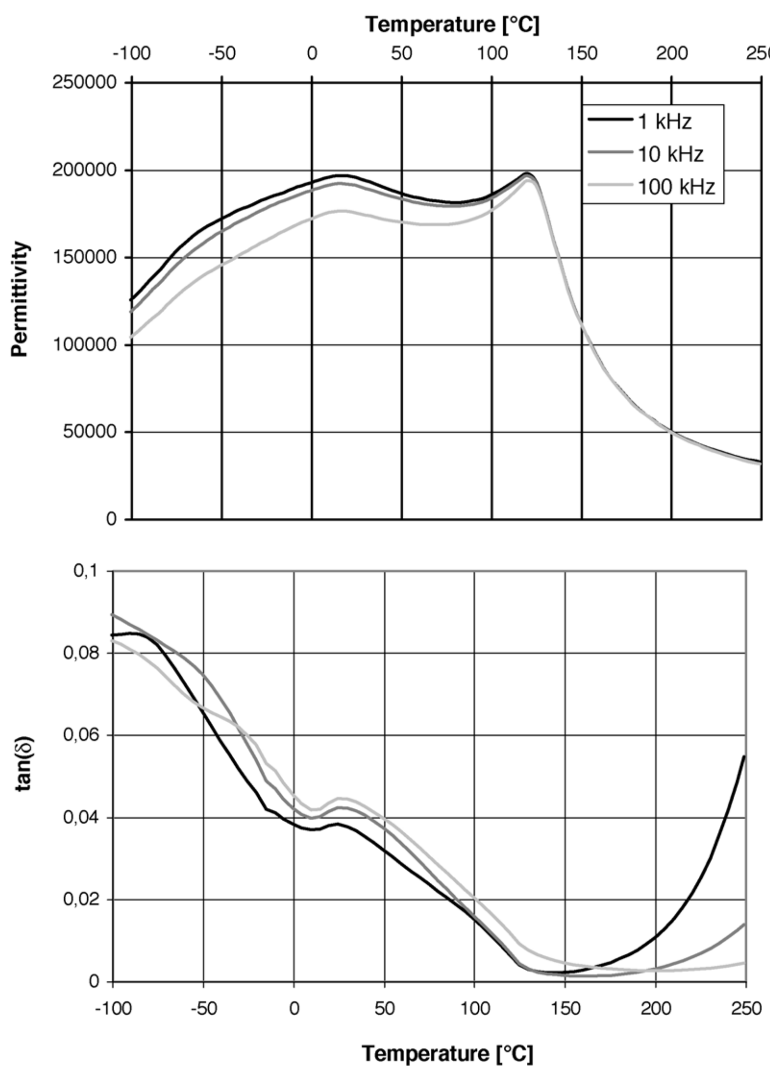

Fig. 4. Temperature dependence of the permittivity and dielectric losses of the sample after seven rolling cycles, measured at 1 kHz.

so extensive that the layers can be considered to have disintegrated. The microstructure consists of conductive clusters that are elongated and preferentially oriented in the direction of the rolling.

3.2. Dielectric properties

The behavior of the permittivity and the dielectric losses was analyzed as a function of the number of rolling-and-folding cycles, frequency and temperature. The dielectric properties were analyzed perpendicular to the rolling plane. All the samples were conducting along the rolling direction with the exception of the sample that underwent 10 rolling-and-folding cycles. The AC resistivity of this sample increased to 100 Ω m.

The room-temperature permittivity is crucially dependent on the number of rolling-and-folding cycles (Fig. 3). During the initial cycles the permittivity remains around 13 000 at 1 kHz. With the fifth cycle the permittivity starts to increase enormously, reaching a value of 200 000 after the seventh cycle. The samples that were rolled-and-folded eight and nine times were also conducting in the direction perpendicular to the rolling plane. Interestingly, after the tenth cycle the conductivity decreased and, again, the permittivities were determined to be >200 000. The room-temperature dielectric losses are also initially low ($\tan\delta \approx 0.02$). Importantly, the dielectric losses do not follow the increase in the permittivity after the fifth cycle and remain so low even after the seventh cycle. As a result, the sample that was rolled-and-folded seven times combines an extraordinarily high permittivity (200 000) with modest dielectric losses ($\tan\delta < 0.04$), which is from the technical point of view important.

Fig. 4 shows a typical temperature dependence of the permittivity and the dielectric losses for these layered cermets. It is obvious that the temperature dependence of the permittivity is controlled by the ferroelectric $BaTiO_3$ phase. Both permittivity maximums closely correspond to the transition temperatures for $BaTiO_3$ ceramics; however, due to internal stresses, which were developed during the sintering processes as reported in Ref. [12], the dielectric anomalies at the transition temperatures were significantly suppressed.[14] Below the ferroelectric transition the permittivity is frequency dispersive, whereas above the ferroelectric transition it becomes frequency independent. Even at 1 kHz and a temperature of 250 °C no significant increase in the permittivity, which would result from the increase in the conductivity of the insulating phase, can be observed. However, the increase of the dielectric losses at high temperature and low frequency indicates on an onset of the space charge polarization probably due to an increase in a concentration of free charge carriers in the insulating $BaTiO_3$ phase. In the low-temperature range, the dielectric losses decrease with the increase in temperature and reach a minimum above the ferroelectric transition.

4. Discussion

The dielectric measurements showed that a material of given composition can exhibit a wide range of permittivities, from 10 000 to as high as 200 000, with modest dielectric losses across the entire range. The dependence of the room-temperature permittivity on the number of rolling-and-folding steps results from the changes in the microstructure of such a layered cermet. Because the microstructure is highly textured the properties are anisotropic.

The conductivity along the rolling direction is governed by the conductive properties of the Ni/$BaTiO_3$ composite layer. It contains 50 vol.% of Ni and 50 vol.% of $BaTiO_3$ phase and both phases are homogeneously distributed. The Ni/$BaTiO_3$ composite layer itself is above the percolation threshold and, therefore, conducting. The percolation threshold for such a type of a composite was modeled by the Monte Carlo simulation to be around 35%. Because of the wavy and ribbon-like types of the entire cermet microstructure (see Fig. 2) the conducting channels of Ni/$BaTiO_3$ layer exist along the rolling direction; the samples conduct electrons in that direction. After the tenth rolling-and-folding step, when the Ni/$BaTiO_3$ layers disintegrate to form clusters with a small aspect ratio, the resistivity also increases in the rolling direction.

In the direction normal to the rolling plane the conductivity, the permittivity, and the dielectric losses are initially determined by the insulating $BaTiO_3$ layers. However, after the fourth rolling-and-folding step the permittivity starts to deviate from that characteristic of $BaTiO_3$ due to the changes in the composite microstructure. After the fourth rolling-and-folding cycle the layers become thin and, locally, they come into very close proximity (see Fig. 1D). It means, there are volumes in the microstructure where conductive clusters are separated by thin insulation layers. Such volumes contribute an extremely large capacitance, which macroscopically results in a giant increase in the effective permittivity. With further rolling-and-folding the increase in the effective permittivity is larger because more such volumes are created. The observed phenomenon is analogous to the critical behavior of the complex dielectric constant near the percolation threshold, and the analogy also explains why the dielectric losses do not follow the increase in the permittivity.[6,7]

After the eighth rolling-and-folding step the layered texture is still present; however, the disintegration of the layers becomes extensive. The conducting layers are frequently in contact with each other, which results in the creation of the conductive channels in the direction normal to the rolling plane. Eventually, the conducting channels extend all across the sample. Such samples are conducting in all directions.

After the tenth rolling-and-folding step the layers disintegrate and the microstructure cannot be treated as layered anymore. The system is closer to a particulate composite with Ni/$BaTiO_3$ clusters of a much smaller aspect ratio than for other two types of microstructure. The conductivity in all directions is significantly decreased, while the permittivity still shows the critical behavior that is typical when being close to the percolation threshold.

To confirm this explanation the behavior of the percolation threshold, corresponding to this particular microstructural development, was modeled and studied by a Monte Carlo simulation. The model consists of an insulating matrix phase ($BaTiO_3$ layers) in which conducting plates (Ni/$BaTiO_3$ composite layers) with different aspect ratios (a.r.) are distributed within the particular degree of orientation (Θ_L spherical polar angle defining the orientation of a cluster long axis). In the model, the rolling-and-folding steps are represented as a gradual decrease in the a.r. values. Details of this study are reported elsewhere.[15] The study shows that for a wide range of investigated Θ_L and a.r. values the percolation volume does not approach the actual volume ratio of the conductive Ni/$BaTiO_3$ composite layers in the studied cermet (50%) but stays much below. The calculated percolation volumes were always smaller than 35%. So, by considering the clusters of disintegrated Ni/$BaTiO_3$ layer to be intact with respect to the composition we would not be able to explain the decrease in the conductivity after the tenth rolling-and-folding. It is more likely that the disintegration of the conductive layers is associated with the change in their composition. As a result of the homogenization process, the clusters get richer in $BaTiO_3$ phase and by themselves fall below the percolation threshold. If this process is still at an early stage the entire composite again shows the critical behavior in terms of dielectric properties that is typical when we consider the proximity of the percolation threshold. Eventually, if the homogenization proceeds the composition of all the clusters drops much below the percolation threshold and the composite behaves similarly like it did after initial three rolling-and-folding cycles.

5. Conclusions

The rolling-and-folding processing method was applied to introduce changes to the texture of $BaTiO_3$–Ni layered composites. Our experiments showed a critical dependence of the (di)electric properties on the microstructural characteristics of this cermet composite. Although the composition of the composite remained constant its electrical properties changed from insulating to conducting and back to insulating in accordance with the shifts in the percolation threshold that were induced by the variations in the microstructural characteristics. The dependence of the percolation threshold on the microstructure of the composite was also reflected in the dielectric properties. For the wavy type of microstructures the dielectric properties are governed by the insulating $BaTiO_3$ layers, while the gradual deformation and decomposition of the layers induced critical behavior of the permittivity near the percolation threshold. Giant effective permittivities of around 200 000, with modest losses of $\tan\delta < 0.04$, were measured for these samples. With further rolling-and-folding the composite became conductive and after extended homogenization of the phases the percolation threshold again shifted above the actual composition of the cermet.

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