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The Impedance of Ceramics with Highly Resistive Grain Boundaries: Validity and Limits of the Brick Layer Model

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Abstract

Impedance spectroscopy is an important tool to investigate the electrical properties of grain boundaries. For the analysis of the impedance spectra cubic grains, laterally homogeneous grain boundaries and identical properties of all grain boundaries are usually assumed (brick layer model). However, in real ceramics these assumptions are generally violated. Using the finite element method we calculated the impedance of several polycrystals exhibiting highly resistive grain boundaries with microstructures and grain boundary properties deviating from the simple brick layer model. Detours around highly resistive regions (e.g. due to high grain boundary density or enhanced grain boundary resistivity) can play an important role and lead to grain-boundary semicircles depending on bulk properties and even to additional semicircles. Conditions are discussed within which the brick layer model allows for a reasonable evaluation of the spectra. © 1999 Elsevier Science Limited. All rights reserved

Keywords: brick layer model, grain boundaries, microstructure, impedance, electrical properties.

1 Introduction

Grain boundaries and particularly high-resistive grain boundaries as occurring in many semiconducting[1,2] and ionically conducting materials[3–6] can distinctly influence the electrical properties of electroceramics. An important technique to investigate such high-resistive grain boundaries is impedance spectroscopy. However, impedance spectra are usually obtained by a macroscopic measurement and the results average over numerous grain boundaries. (Spatially resolved investigations are rare and mostly restricted to dc-measurements on ZnO.[7–9]) Hence, models are required to analyze the averaged data in order to evaluate local properties as grain boundary resistivity and thickness. In many impedance studies on polycrystalline materials the so-called brick layer model is used to interpret the spectra (Fig. 1): however, the assumptions of cubic grains and laterally homogeneous grain boundaries taken in the model are violated in real polycrystalline material and one may ask how far a brick layer analysis reveals the true grain boundary properties.

In this contribution finite element calculations on the impedance of electroceramics are presented which demonstrate the impact of three important realistic deviations from the brick layer model, namely (i) deviations from the cubic grain shape, (ii) imperfect contacts between the grains, and (iii) distributions of different grain boundaries in space. Moreover, some limits are given within which the brick layer model is a useful tool to estimate electrical grain boundary properties.

2 Results and Discussion

2.1 The influence of different grain boundary patterns

Two-dimensional finite element calculations on different grain boundary patterns reveal that the brick layer model seems to be a reasonable model to estimate grain boundary properties of samples in which the following conditions are fulfilled: homogeneous distribution of grain sizes and grain shapes, isotropic conductivities, relatively narrow grain size distribution and identical grain boundary properties. According to our experience, the differences between the brick layer model and the 'true' impedance scarcely exceed a factor of two. A detailed discussion is given in Ref. 10.

However, serious problems should arise if we met

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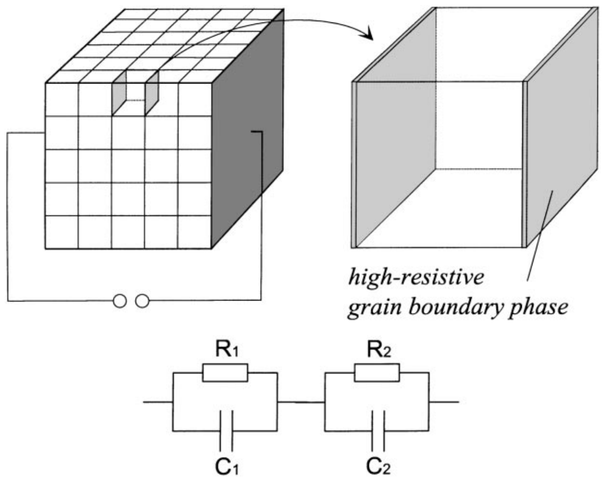

Fig. 1. Brick layer model and the resulting equivalent circuit.

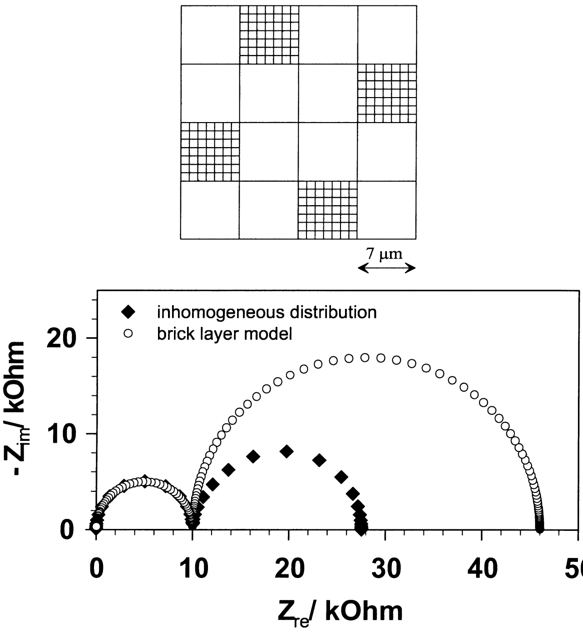

Fig. 2. Artificial microstructure representing the case of an inhomogeneous grain size distribution (top) and resulting impedances spectrum as calculated by the finite element method and by assuming a brick layer model of a mean grain size of 1·9 μm. The (two-dimensional) grain boundary properties are: $\sigma_{gb} = 10^{-7}\,1/\Omega$, grain boundary thickness $= 2\,$nm, bulk conductivity $\sigma_{bulk} = 10^{-4}\,1/\Omega$. (Please note that the unit of a 2D-conductivity is $1/\Omega$.)

i. a very broad grain size distribution with large as well as very small grains: the current can make detours through large grains in order to avoid the small ones;
ii. inhomogeneous grain size distributions (e.g. agglomeration of grains of one grain size): again detours around regions with large grain boundary densities are of importance;
iii. inhomogeneous grain shape distributions: not only quantitative deviations from the brick layer model exist but also the shape of the spectra can distinctly change.[10]

An example of an inhomogeneous grain size distribution is given in Fig. 2. The true grain boundary impedance is distinctly smaller than the impedance of the corresponding brick layer model based on the mean grain size. This is caused by an inhomogeneous dc-potential distribution $\varphi(x, y)$ (Fig. 3) enabling current detours around the small grains. The high-frequency potential distribution (valid for the entire first semicircle), however, is homogeneous (Fig. 3). As a consequence, the current detours only contribute to the low-frequency semicircle and the 'grain boundary resistance' is influenced by the bulk conductivity while the entire first semicircle is not affected by such detours. Hence, an exact determination of bulk parameters from the first semicircle is still possible as long as the volume fraction of the grain boundaries is negligible and highly conducting grain boundary paths do not play any role.[11]

2.2 The influence of laterally inhomogeneous grain boundaries

Partially wetting grain boundary phases or imperfect (porous) contacts between two grains lead to laterally inhomogeneous grain boundary properties, i.e. a change of totally insulating and ideally conducting grain boundary regions. Finite element calculations showed that a second semicircle emerges in the complex impedance plane as already predicted by semi-quantitative models.[3,6,12,13] This low-frequency arc is due to current constriction effects in the grain bulk close to the established contact and can be understood in terms of a transition of the bulk resistance from the dc-value (constriction case) to the ideal ac-value (unconstricted case) due to the dielectrical 'opening' of the insulating grain boundary phase capacitor.

Figure 4 presents the impedance spectra for three different contact diameter. It turns out[14] that the 'grain boundary resistance' R_2 is, in a first approximation, inversely proportional to $\sqrt{n \cdot \alpha_{contact}}$, with n being the number of grain-to-grain contacts per grain and $\alpha_{contact}$ the fraction of contacted area. Hence R_2 is determined by two independent parameters $(\alpha_{contact}, n)$ and an evaluation of the contacted area (fraction of 'blocked' current) solely from the impedance spectrum is not possible. The grain boundary capacitance, on the other hand. allows an estimate of the thickness of the insulating grain boundary phase.

An interpolation formula for R_2 as given in Refs. 14 and 15 can help to estimate the magnitude of the grain boundary semicircle: in many cases we expect the grain boundary resistance due to current constriction to be of the order of magnitude of the ideal bulk resistance or even smaller. However, in porous material (e.g. freshly pressed samples) or if there are only very few holes in a highly-resistive

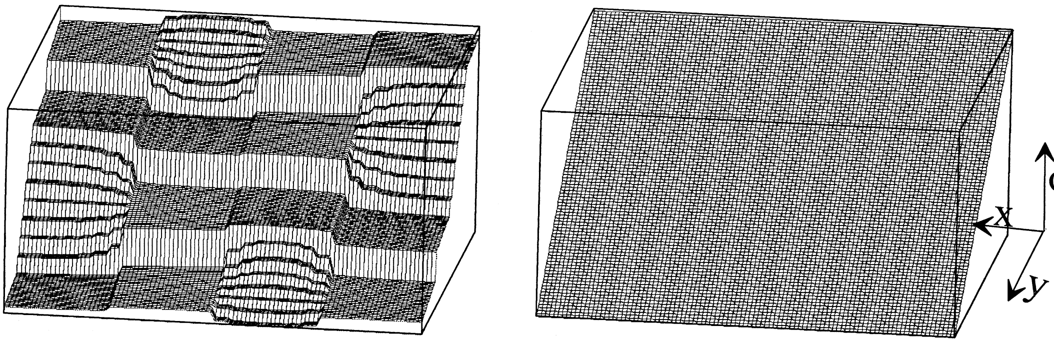

Fig. 3. dc (left) and high-frequency (right) potential distribution within the two dimensional polycrystal of Fig. 2.

grain boundary phase current constriction effects can be considerably larger. A more detailed treatment on current constriction effects including temperature, partial pressure and grain size dependencies of the second semicircle is given in Refs 14 and 16.

2.3 The influence of the spatial distribution of grain boundary properties

In realistic polycrystals different grain boundaries may exhibit different properties. In order to get a first insight, we performed two-dimensional finite element calculations within a polycrystal consisting of 10×10 grains. Each grain boundary is laterally homogeneous and can be described by a grain boundary conductivity σ_{gb} (Fig. 5). The grain boundary conductivities are randomly distributed within the square microstructure according to a given frequency distribution. For a Gaussian grain boundary conductivity distribution it turns out that an analysis using the brick layer model still allows an estimate of the mean grain boundary resistivity (times grain boundary thickness).[15]

Here we present a polycrystal with a 'bimodal' grain boundary distribution: 80% of the boundaries exhibit a conductivity σ_{gb1}, while 20% have a larger or smaller grain boundary conductivity σ_{gb2} (Fig. 5). The values are chosen such that for $\sigma_{gb1} = \sigma_{gb2}$ both grain boundary and bulk semicircle are of the same magnitude. Depending on σ_{gb2} the second arc (Fig. 6) can slightly decrease ($\sigma_{gb1} < \sigma_{gb2}$) or considerably increase ($\sigma_{gb1} > \sigma_{gb2}$). If we decreased σ_{gb2} down to zero for 20% of the boundaries, we typically observe that the grain boundary resistance is more than twice as large as for $\sigma_{gb1} = \sigma_{gb2}$. Whenever the two grain boundary conductivities are strongly different the current distributions turn out to be markedly inhomogeneous and current detours around strongly blocking grain boundaries occurred. As a consequence the

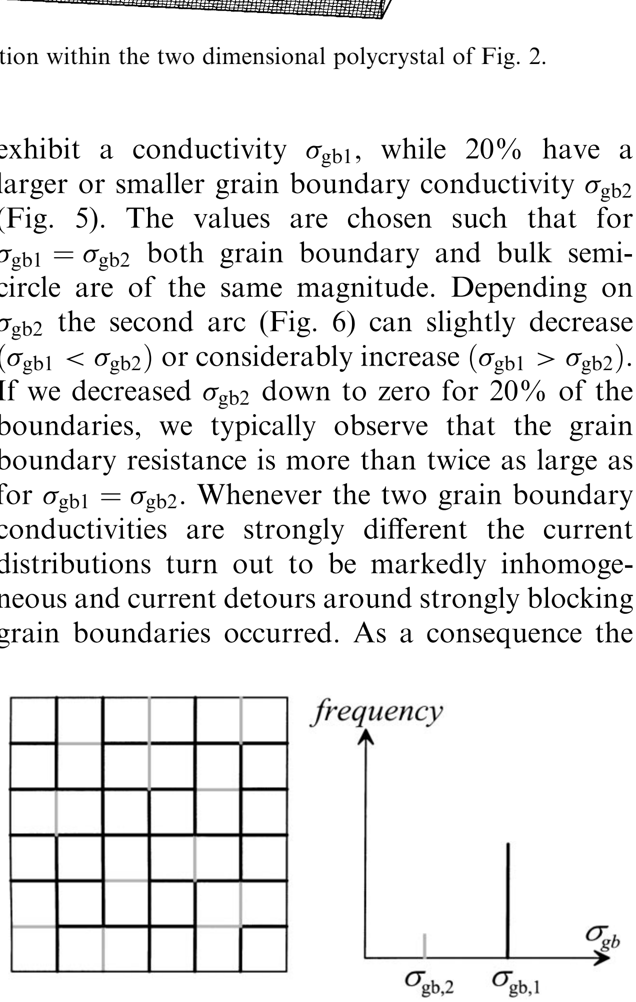

Fig. 5. Two-dimensional grain boundary pattern (left) with two kinds of grain boundaries (grey, black) according to the sketched frequency distribution (right).

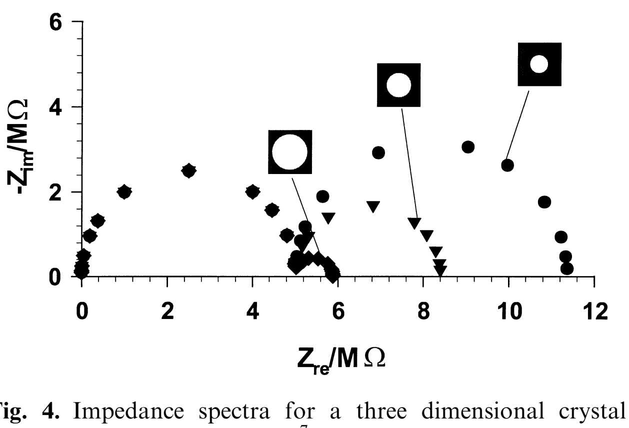

Fig. 4. Impedance spectra for a three dimensional crystal (bulk conductivity $\sigma_{bulk} = 10^{-7} 1/\Omega cm$) with an electrode area of 1 cm^2 and a thickness of 5 mm. All grain boundaries within one sample are identical (thickness of the insulating phase = 2 nm) and exhibit circular perfectly conducting spots with different diameter. The insets sketch cross sections of the grain boundaries with contacted (white) and absolutely blocking (black) regions.

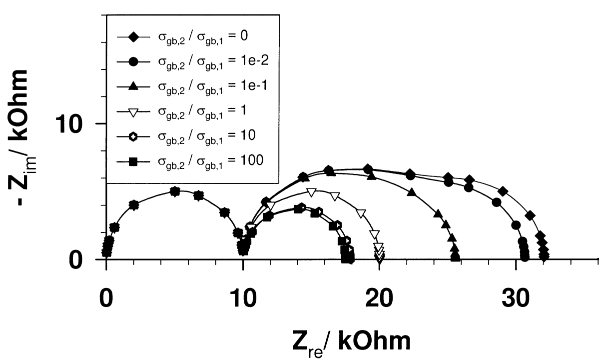

Fig. 6. Impedance spectra of a polycrystal (10×10 grains) similar to Fig. 5 for different ratios of grain boundary conductivities. Parameters: two-dimensional bulk conductivity $= 10^{-4}\ 1/\Omega$, $\sigma_{gb1}, = 10^{-7} 1/\Omega$, grain size = 2 μm, grain boundary thickness = 2 nm.

size as well as the shape of the low-frequency impedance arc do not only depend on the grain boundary properties but also on the bulk conductivity. Hence, the effective activation energy of the 'grain boundary resistance' can differ from the true activation energy of the grain boundary conductivity.

These detour effects are also reflected in the strong distortion of the arc and can even lead to an additional semicircle. However, it has to be emphasized that the additional semicircle cannot be understood in terms of three serial regions with three different conductivities but as a consequence of the frequency-dependent multidimensional current distribution.[14,15] In such a situation only few information can be extracted from the low-frequency semicircle and the brick layer model fails. Further details on these calculations will be discussed in a forthcoming paper.[17]

3 Conclusions

In certain limits the brick layer model is an appropriate model at least to estimate grain boundary properties of polycrystalline material. It is applicable for relatively narrow, homogeneous grain size and grain shapes. In case of spatially distributed different grain boundaries the low-frequency semicircle can still be used as to estimate the mean grain boundary properties if the frequency-distribution of the properties is Gaussian. However, very broad or bimodal distributions yield distinct deviations: Size and shape of the second semicircle are influenced by bulk properties which leads to apparent activation energies differing from the grain boundary activation energy. Further problems occur if imperfect contacts (lateral inhomogeneities) between grains are involved. Current constriction effects dominate the grain boundary semicircle which is proportional to the bulk resistivity. Since the grain boundary resistance depends on the fraction of contacted area as well as on the number of contact points a quantitative analysis is rather involved.

Acknowledgements

The potential distributions were calculated by using the finite element software FLUXEXPERT from Simulog, 1, rue James Joule, 78280 Guyancourt Cedex, France.

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