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Fractal Approach to ac Impedance Spectroscopy Studies of Ceramic Materials

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Abstract. A novel fractal model for grain boundary regions of ceramic materials was developed. The model considers laterally inhomogeneous distribution of charge carriers in the vicinity of grain boundaries as the main cause of the non-Debye behaviour and distribution of relaxation times in ceramic materials. Considering the equivalent circuit the impedance of the grain boundary region was expressed. It was shown that the impedance of the grain boundary region has the form of the Davidson–Cole equation. The fractal dimension of the inhomogeneous distribution of charge carriers in the region close to the grain boundaries could be calculated based on the relation $d_s = 1 + \beta$, where β is the constant from the Davidson–Cole equation.

Keywords: fractal, model, ceramics, grain boundary, impedance spectroscopy

1. Introduction

Ac impedance spectroscopy (IS) is a well-known technique for investigating the electrical behaviour of electrochemical cells and ionically conducting materials such as polymers, ceramics and glasses. Impedance spectroscopy analysis of ceramic materials enables separation of bulk and boundary components of the conductivity [1, 2]. In an ideal case, the result of IS measurements over a wide range of frequencies can be presented by several semicircles in the complex Z_{Re}–Z_{Im} plane (Nyquist plot) [2, 3]. Each semicircle represents the contribution of a particular process (electrodes and contacts, grain boundaries, grains interior) to the total impedance of the sample. Measured values in the form of Nyquist plots are rarely ideal semicircles. Most of the authors describe them as depressed and/or deformed semicircles, with their centre lying below the x-axis (Fig. 1(a)). This phenomenon, called non-Debye relaxation [4, 5], is attributed to the distribution of Debye relaxations with different time constants [6]. There are several papers in the literature [1, 7–9] treating this phenomenon very systematically. Possible explanations for a non-Debye relaxation behaviour of grain boundaries are [10–12]:

(i) It is the consequence of inhomogeneity and variations among the grain boundaries combined in series/parallel connection, (ii) it is intrinsic to the measured response of each individual grain boundary and (iii) it is a combination of the former two reasons.

Distribution of relaxations with different time constants may be mathematically expressed by the Cole–Cole equation [10]

$$Z = Z_{Re} + j \cdot Z_{Im} = R_G + \frac{R_{GB}}{1 + (j\omega R_{GB} C)^{(1-\alpha)}}, \quad (1)$$

where Z is the overall impedance, Z_{Re} and Z_{Im} are the real and imaginary components of the impedance, R_G is the resistance of the grains interior, R_{GB} is the resistance of the grain boundary region, α is a constant, while C represents the capacitance of the grain boundary region. Parameter α is related to the depression angle shown in Fig. 1. by the equation $\alpha = \theta/(\pi/2)$. The Cole–Cole distribution is symmetrical with respect to a central frequency or relaxation time (Fig. 1(b)).

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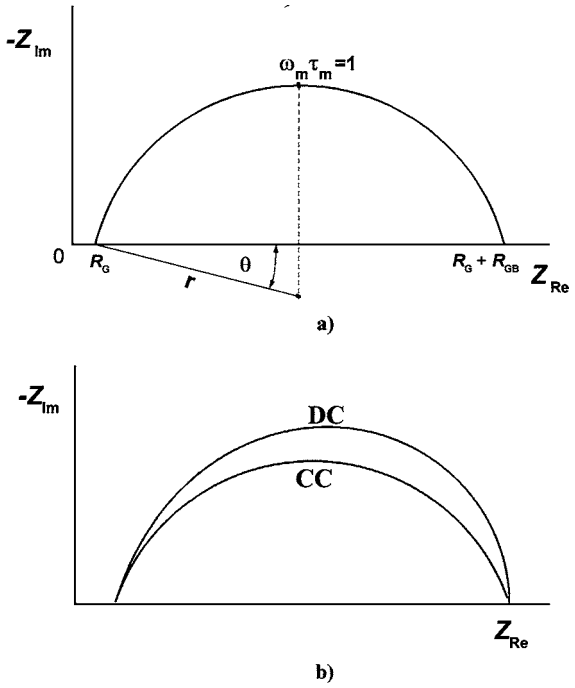

Fig. 1. (a) Impedance plot of depressed semicircle (θ-depression angle), (b) complex impedances associated with the Cole–Cole (CC) and the Davidson–Cole (DC) expressions (for $\beta = 1-\alpha = 0.8$).

Another well-known function is the Davidson–Cole equation [7, 13]:

$$Z = Z_{\mathrm{Re}} + j \cdot Z_{\mathrm{Im}} = R_{\mathrm{G}} + \frac{R_{\mathrm{GB}}}{(1 + j\omega R_{\mathrm{GB}} C)^{\beta}}, \quad (2)$$

in which parameters Z, Z_{Re}, Z_{Im}, R_{G}, R_{GB} and C have the same meaning as it was given for the Cole-Cole equation, and β is constant. The Davidson–Cole equation leads to a skewed arc in the complex plane (Fig. 1(b)). It is a semicircle at low frequency, but asymptotic to $\beta \cdot \pi/2$ at high frequencies [7]. Also, there are some other functions, such as that of Havriliak–Negami, which have a more general form [13]. All these functions are empirical, so the parameters such as α and β do not have physical explanation. Nevertheless these equations are very useful in fitting experimental results.

The starting point in our investigation were the results of M. Seitz et al. [10]. They performed experiments on samples with only two grain boundaries, as well as on multi-junction ZnO varistors and found almost the same depression angle for both kinds of samples. They concluded that the non-Debye relaxation is intrinsic to the response of the individual grain boundary and is the result of a spectrum of relaxation times within each grain boundary.

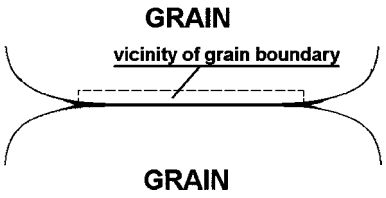

Fig. 2. Region in the vicinity of grain boundaries considered by proposed model.

In our model the problems of non-Debye relaxation processes in ceramics containing highly resistive grain boundaries were treated. It has to be pointed out that this model considers a region inside the grains, close to the grain boundaries, with laterally inhomogeneous distribution of defects and dopants and consequently inhomogeneous distribution of charge carriers (Fig. 2). Inhomogeneous distribution of the charge carriers in the vicinity of grain boundaries results in local fluctuations in the resistance of this region. These effects lead to a non-ideal response of the grain boundary region.

In this work, a model that considers laterally inhomogeneous distribution of charge carriers in the vicinity of the grain boundaries was constructed using fractal theory. The possibility to calculate a fractal dimension of the grain boundary region for ceramic materials using IS measurements is demonstrated. The equation that connects the fractal dimension with the parameter β from the Davidson–Cole equation was derived.

2. Model Discussion

It is assumed that there are locally inhomogeneous distribution of defects and dopants in the vicinity of grain boundaries. These effects result in laterally inhomogeneous distribution of charge carriers and are supposed to be the main reason for the non-Debye behaviour of the grain boundaries. The region in the vicinity of the grain boundary can be presented by the scheme shown in Fig. 3. As can be seen (Fig. 3(a)) the grain boundary is presented as a smooth plane, but there are differences in local distribution of defects in the vicinity of the grain boundary which result in lateral variations of resistances in the region close to the grain boundary. This region could be as thick as 100 nm, or 1 μm or even more, but it is not essential for the model construction. It is only important that base plane (zero plane)

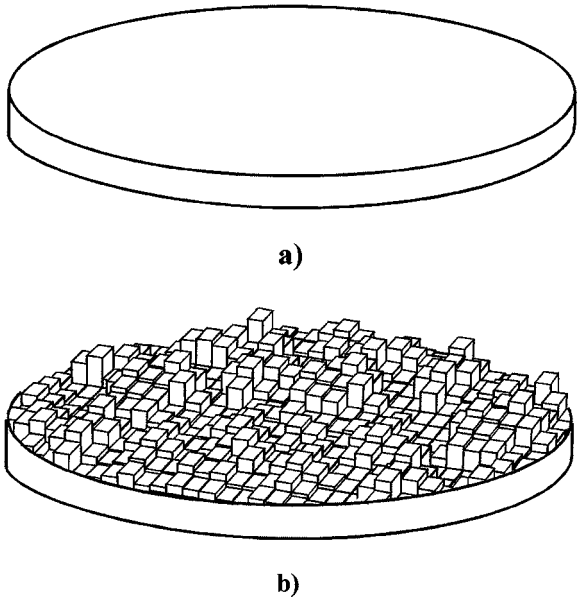

Fig. 3. (a) Grain boundary as a smooth two-dimensional surface, (b) inhomogeneous distribution of defects in the vicinity of the grain boundary resulting in different resistance (parts with different resistance are shown as boxes of different heights).

is constructed, from which, up to the grain boundary, we can recognize inhomogeneities. If the region in the vicinity of the grain boundary is observed with one resolution, it could be represented by boxes with different heights, where the height of the box is proportional to the resistance (Fig. 3(b)). Hence, boxes with larger resistance are higher and vice versa. The associated capacitance is proportional to the area (S) of the surface normal to the electrical field direction and is the grain boundary capacitance. The associated resistance of this interface is proportional to S^{-1} and is named the grain boundary resistance. If the resolution is increased it will be possible to recognise nonuniformity within

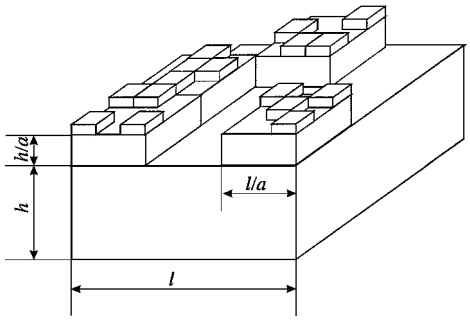

Fig. 4. Self-similar model for the surface of the region in the vicinity of grain boundary.

each box, so that each box could be divided into new boxes with uniform resistance and capacitance, and so on. It was also assumed that the observed region could be treated as a fractal object. A region in the vicinity of the grain boundary, shown in Fig. 3(b), could be divided into M parts (not necessarily of the same shape) with the same surface area and the same concentration of charge carriers. An example of such a part is shown in Fig. 4. Magnification of this picture by factor a (scaling factor) will show that each part has local inhomogeneities, i.e., there are N randomly distributed boxes with a higher resistance within each part. Resistance R_{B} is the resistance of the whole part up to $z = h$. The capacitance of that surface ($z = h$) is C and the interface resistance is R_I. The resistance of each of the N boxes has the value $R_{B1} = a \cdot R_B$, the capacitance has the value $C_1 = C/a^2$, and the interface resistance is $R_{I1} = R_I \cdot a^2$. Further magnification by a reveals a new layer with $R_{B2} = a^2 \cdot R_{B1}$, $C_2 = C/a^4$, and $R_{I2} = R_I \cdot a^4$ etc. The impedance of a whole region in the vicinity of the grain boundary is $Z_{\mathrm{tot}} = Z(\omega)/M$, where $Z(\omega)$ represents the impedance of the part shown in Fig. 4. The equivalent circuit for such a part is given in Fig. 5 and can be described by the following equation:

$$Z(\omega) = R_B + \cfrac{1}{\cfrac{1 + j\omega R_I C}{R_I} + \cfrac{N}{R_B \cdot a + \cfrac{1}{\cfrac{1 + j\omega R_I C}{R_I a^2} + \cfrac{N}{R_B \cdot a^2 + \cfrac{1}{\cfrac{1 + j\omega R_I C}{R_I a^4} + \cfrac{N}{R_B \cdot a^3 + \cfrac{1}{\cfrac{1 + j\omega R_I C}{R_I a^6} + \cdots}}}}}}} \tag{3}$$

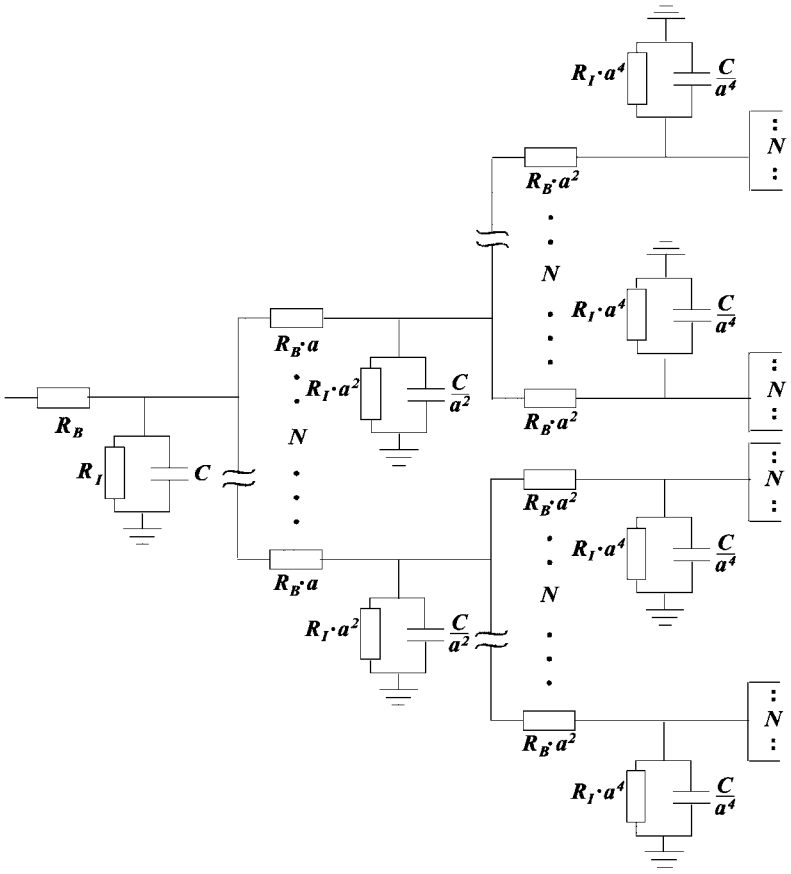

Fig. 5. The equivalent circuit of the model shown in Fig. 4.

In order to simplify this equation we introduced a new function Ω that has the following value:

$$\Omega = \frac{1 + j\omega R_I C}{R_I}. \tag{4}$$

Substitution of Eq. (4) in Eq. (3) gave a simpler equation for the observed impedance:

According to literature data [14–16] the metal-electrolyte interface shows similar non-Debye relaxation as ceramic materials, assuming that the origin of such a behaviour is a roughness of the interface, which has fractal nature. T. Kaplan et al. [14] made the self-affine Cantor block model for the metal-electrolyte interface and developed an equation for the impedance

$$Z(\Omega) = R_B + \cfrac{1}{\Omega + \cfrac{N}{R_B \cdot a + \cfrac{1}{\cfrac{\Omega}{a^2} + \cfrac{N}{R_B \cdot a^2 + \cfrac{1}{\cfrac{\Omega}{a^4} + \cfrac{N}{R_B \cdot a^3 + \cfrac{1}{\cfrac{\Omega}{a^6} + \cdots}}}}}}} \tag{5}$$

of such an interface, which has some similarities with Eq. (5). Following their mathematical procedure the impedance of the equivalent circuit given in Fig. 5 could be derived by the following procedure.

Replacing Ω in Eq. (5) with $\Omega \cdot a$ and multiplying the fraction throughout by a yields

$$Z(\Omega \cdot a) = R_B + \frac{a}{\Omega \cdot a^2 + \dfrac{N}{Z(\Omega)}} \tag{6}$$

Assuming that we observe the case when the grain boundary region is highly resistive in comparison to the grain interior, i.e. $R_I \gg R_B$, and supposing that $Z(\Omega) \to \infty$ and $\Omega \cdot Z(\Omega) \to 0$ when $\Omega \to 0$, Eq. (6) becomes

$$Z(\Omega \cdot a) = \frac{a}{N} Z(\Omega) \tag{7}$$

The solution of this equation has a form

$$Z(\Omega) = K\Omega^{-\beta} = K\left(\frac{1 + j\omega R_I C}{R_I}\right)^{-\beta} \tag{8}$$

where K is constant, and other symbols have the earlier defined meanings. It has to be highlighted that the Eq. (8) has the form of the Davidson–Cole equation.

Substitution of Eq. (8) in Eq. (7) give the following value of parameter β:

$$\beta = \frac{\ln N}{\ln a} - 1, \tag{9}$$

Now it is possible to calculate the fractal dimension of the observed model by ac impedance spectroscopy measurements using the following relations. According to the definition, the fractal dimension (d_s) of the deterministic fractal is given by

$$d_S = \frac{\ln N}{\ln a}. \tag{10}$$

Combination of Eqs. (9) and (10) leads to a final equation which connects the fractal dimension (d_S) with parameter β:

$$\beta = d_S - 1, \tag{11}$$

$$d_S = 1 + \beta. \tag{12}$$

This fractal dimension is related to the inhomogeneous distribution of charge carriers in the vicinity of the grain boundary surface. If there is a laterally homogeneous distribution of charge carriers at all resolutions, then the fractal dimension of this surface will be equal to 2, i.e., ideal semicircle will be found. In our model this corresponds to the case when $N = a^2$. In contrast, an inhomogeneous distribution of charge carriers results in a fractal dimension less than 2, i.e., there is non-Debye response of grain boundaries. In our model this is the case when $N < a^2$, meaning that there are N convexities at the observed surface.

In order to illustrate the application of this model on real ceramics materials derived relations were applied on results of impedance spectroscopy measurements of SnO_2 sample doped with 0.025% Cr_2O_3. Temperature and frequency ranges of the measurements were chosen on way that allows the measurement of the impedance of the grain boundary region. The Nyquist plot of the sample is given in Fig. 6. Experimental results were fitted using the Davidson–Cole equation. As it could be seen from this figure, experimental results showed a great deviation from an ideal semicircle. The obtained value of the parameter β was 0.676. The fractal dimension of the grain boundary region was calculated using Eq. (12) and the obtained value was 1.676. This result suggests a rather strong inhomogeneity of the charge carriers in the vicinity of the grain boundaries as already expected from the shape of the experimental curve.

As it was shown the impedance function of the grain boundary region was derived in the form of the Davidson–Cole equation. On this way the parameter β obtains a physical meaning, because it represents a measure of the inhomogeneity of the distribution of charge carriers in the vicinity of grain boundaries. The derived model enables a calculation of the fractal dimension of the grain boundary region in any ceramic

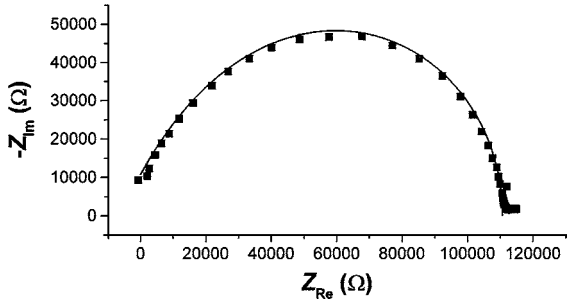

Fig. 6. Nyquist plots of investigated Cr_2O_3 doped SnO_2 samples (measurement temperature was 488°C).

materials that contain highly resistive grain boundaries. So we have a new parameter for the characterization of these materials. Also, application of fractal theory in materials science, as well as the possibility to calculate fractal dimensions using the simple method of impedance spectroscopy, open a new approach of investigation with a more pronounced consideration of the influence of inhomogeneities and defects on materials properties.

Recently, several excellent articles about the impedance of highly resistive grain boundaries in real ceramics were published [17–19]. These authors considered the impact of three important deviations from the commonly used brick-layer model: laterally inhomogeneous grain boundaries, grain boundary properties varying from boundary to boundary and deviations from a cubic grain shape [17, 19]. They simulated all these situations and found that the brick-layer model fails in some of the cases. It is interesting that these authors also obtained distorted, i.e. skewed arcs, when they simulated some deviations from ideal brick-layer model. Nevertheless these authors did not use fractal theory to describe deviations from ideal cases although fractal theory is very convenient for describing disordered systems.

Finally it has to be emphasized that our model could be applied on the investigation of rough surfaces. In such a case the parameter β would represent the roughness. However we believe that the inhomogeneous distribution of charge carriers is a more common disorder than the grain boundaries surfaces roughness in ceramic materials.

3. Conclusions

Based on a simple fractal model it was shown that an inhomogeneous distribution of charge carriers in the vicinity of grain boundaries results in a non-Debye behaviour and distribution of relaxation times in ceramic materials. The impedance function of a grain boundary region was derived in the form of the Davidson–Cole equation. The fractal dimension of the inhomogeneous distribution of charge carriers in the region close to the grain boundaries could be calculated based on the relation $d_s = 1 + \beta$, where β is the parameter from the Davidson–Cole equation. On this way the parameter β obtains physical meaning, because it represents the measure of the inhomogeneity of the charge carriers distribution in the vicinity of grain boundaries. The derived model enables the calculation of fractal dimension of the grain boundary region in any ceramic materials that contain highly resistive grain boundaries, using the simple method of impedance spectroscopy.

It has to be emphasized that our model could also be applied on the investigation of rough surfaces. In such a case the parameter β would represent the roughness.

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