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THE PROPOSED ENERGY DIAGRAM MODEL OF DISORDERED SYSTEM Al_2O_3+xAl

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In the last few years our attention has been paid to the studies of the electrical properties of sintered specimens of aluminium oxide with metal excess. These systems are significantly different from simple oxides, because they posses some properties typical of the given composite system itself but completely different from pure Al_2O_3 and pure Al properties. At the same time some of its properties are common for many disordered systems. Experimental evidence has been obtained from the measurements of thermoelectric power, dc and ac conductivity as a functions of temperature and metal excess (1). On the basis of the experimental data we have suggested a simple model of the electronic structure of this disordered material.

In our first investigations this composite system was classified as a nonstoichiometric oxide $Al_{2+x}O_3$, but the notation Al_2O_3+xAl will be further used in the text for the following reasons. Namely, during sintering process a small part of excess aluminium is probably incorporated in Al_2O_3 grains as a nonstoichiometric excess, but the second phase Al particles their mean size and dispersivity are the main factors controlling electrical properties of sintered specimens.

The samples were examined in the scanning electron microscope and COMPO (and TOPO) micrographs were obtained (Fig.1).

Due to the rather complex technique of fabrication the microstructure is very complex. The surface under investigation exhibits Al_2O_3 grains (Position 1), the second phase as Al precipitates (Position 2) and subgrain boundaries with finely dispersed Al particles (Position 3). An average composition of Al and O over the line AA' is also shown in Fig.1. From the given micrograph it is obvious that the phenomenon known as discontinuous grain growth occurs during the sintering process (2) and the resulting ceramic has a complex structure of grain boundaries with a nonuniform distribution of the two components. The observed frequency dependences of resistivity and apparent dielectric constant also point to that, because such dependences are characteristic for grainy structures (3).

The previous results of the measurements of ac and dc conductivity as a function of temperature and metal excess (1) show that the activation energy and preexponential factors are functions of metal excess and the temperature dependence of thermoelectric power indicate n-type conductivity. Such compositional dependences are also observed in many composite systems (4). The shape of ac and dc vs. 1/T curves also indicates that specimens Al_2O_3+xAl belong to the class of disordered systems. Therefore the experimental results are interpreted more precisely in the frame of the "bended band model" according to Ryvkin and Shlimak (5,6). At higher temperatures (1200 K - 1500 K) the frequency independent conductivity

$$\sigma_1 = \sigma_{10} \exp\left(-\frac{E_1(x)}{k\,T}\right) \qquad (1)$$

prevails. The preexponential factors σ_{10} are compositionally independent and lie in the range from 10 $ohm^{-1}cm^{-1}$ to 100 $ohm^{-1}cm^{-1}$ indicating that the conduction is by the carriers in delocalized states with the energies above E_1. The observed increase in conductivity with the increase of metal excess is only due to the decrease in activation energy E_1 with x (Fig.2.). It is interesting that experimental ln E_1 vs. x curve is linear and could be very well fitted by the simple relation

$$E_1(x) = 2.6 \exp(-x) \quad \text{eV} \tag{2}$$

At lower temperatures (900 K - 1200 K) the conductivity

$$\sigma_2' = \sigma_{20} \exp(-\frac{E_2}{kT}) \tag{3}$$

has also activated character with E_2 values about 0.9 eV, but the factor σ_{20} increases as the metal excess increases (Fig.3.). The experimental σ_{20} curve could be approximated by the equation

$$\sigma_{20} = K \exp(-\alpha r_o(1-ax)) \tag{4}$$

with $K = 2.5 \times 10^{-2}$ ohm^{-1}cm^{-1}, a = 2 and $\alpha^{-1} = 8 \times 10^{-8}$ cm. The magnitude σ_{20} suggests that σ_2 is the hopping like conductivity through "islands of allowed atates" in the tails of the conductivity band, whose depth is determined by E_1-E_2, as discussed by Kočka, Triska and Štourac (7). The higher the depth E_1-E_2 the smaller are the "islands" and σ_{20}. The proposed model of energy structure of sintered Al_2O_3+xAl specimens is drawn in the top right corner of Fig.2. The density of states at the Fermi level is obtained from ac measurements (300 K - 600 K) and is estimated to be of the order of 10^{19} eV^{-1}cm^{-3} (1).

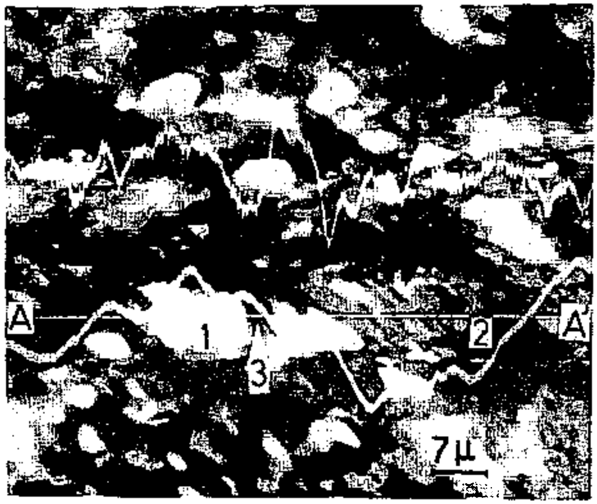

Fig.1. **COMPO Electron micrograph of sintered aluminium oxide surface (2000 X) and the concentration profile for Al (upper curve) and O (lower curve).**

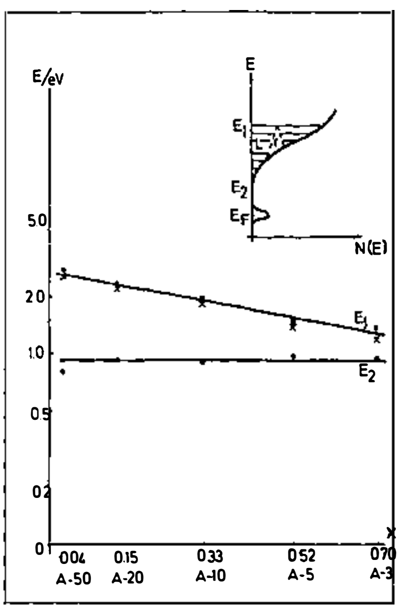

Fig.2. Activation energies E_1 and E_2 as a function of metal excess. Dots and circles are experimental values. The values calculated according to Eq.(2) are represented by crosses. The proposed model of Al_2O_3+ xAl is also shown.

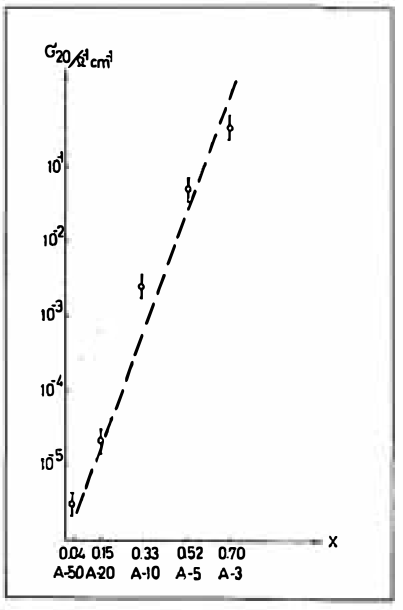

Fig.3. Preexponential factor σ_{20} in Eq.(3) as a function of metal excess (circles - experimental values). Eq.(4) is represented by the dotted line.

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