SAXS INVESTIGATION OF THE SINTERED NIOBIUM POWDER: METHOD OF STABILIZING POROSITY AND FRACTAL PROPERTIES

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ABSTRACT

Compact structures obtained by vacuum sintering of niobium powder are widely used in electronic engineering as metal plates in oxide-semiconductor electrical capacitors. This communication presents the small-angle X-ray scattering (SAXS) investigations of the method for stabilizing porosity in the structures by using both Nb powder hydrogenation and nitriding of niobium hydride sintered pellets (Part A) and also an experimental study of sintered niobium powder surface fractal dimension (Part B). It should be noted that the fractal geometry of different natural and artificial objects was a subject of active investigations during last years.

Part A

INTRODUCTION

The entire history of the generation of oxide-semiconductor capacitors based on Nb-MDS systems consists of a chain of experiments aimed at producing Nb-metal-dielectric-semiconductor (MDS) system features (first of all, specific capacitance and thermal stability) that are similar to Ta-MDS system based oxide-semiconductor capacitors. Recently, reports on the generation of MDS systems based on NbH (niobium hydride) powders have been published, where dehydrogenation of niobium powders is combined with the sintering of pellets compacted out of NbH powder. However, the experiments conducted showed that such MDS systems with high specific capacitance exposed to external impacts, demonstrated low thermal stability.

To increase thermal stability, sintered Nb pellets were doped by gaseous nitrogen. In 1 presents results of an investigation into niobium based metal oxide bilayer degradation as a function of chemical composition of base metal. Nitrogen dissolved in metal increases thermal stability of chemical composition and increases stability of electrical properties of oxide films grown on the metal surface by anodic oxidation. The objective of the present study is to examine the processes of stabilizing porosity an Nb based structure.

MATERIALS AND MEASUREMENTS

Some NbH powder was compacted in a steel cylinder to a compact density of 4g/cm³ and then sintered at T=1500K for 30 min under 10 mm⁻¹⁻¹ Hg vacuum. The resulting cylindrical specimens were polished to 80 nm thickness, controlled by a IKV-3 optimeter. The sintered NbH was nitrided by bleeding gaseous nitrogen in a vacuum chamber when the specimen cooled after sintering, subsequently keeping the cooled specimen in a nitrogen atmosphere to complete gas absorption (vacuum level restoration).

The powder dispersity was controlled by a Mastersizer laser analyser. The SAXS indicatrixes were registered by a small-angle X-ray diffractometer using slitlike collimation of the primary MoKα X-ray beam. During treatment, the SAXS intensity for each scattering angle was transformed to pointlike collimation according to a technique described in 2,3. The SAXS absolute intensity was measured against a calibrated standard.

For each X-ray measurement the small-angle diffractometer background curve was also calibrated. The reproducibility error of this curve in the range of scattering angles investigated, as well as that of the SAXS experimental indicatrixes, was 1.5 – 2%.

The SAXS indicatrixes were treated according to a special programme which included background curve subtraction using a five point cubic interpolation technique in the vicinity of every experimental point. The permissible error in the above subtraction technique is in accordance with digital simulation data and did not exceed 4-5%. The nature of angular distribution, asymptotes, and integral parameters (invariants) of the SAXS indicatrixes, which were used to determine the morphology of the electron density scattering inhomogeneities, were analysed. As the experimental specimens appeared to contain polydisperse system of those inhomogeneities, the tangent technique was used for the treatment of the SAXS
indicatrices; this technique made it possible to divide the whole set of scattering inhomogeneities into some arbitrary dimensional fractions. The presence of nitrogen in the specimens was checked by a mass spectrometric technique using EMAL-2, a laser energy mass analyser. The microstructure of specimens was studied by scanning electron microscopy.

RESULTS AND DISCUSSION

The SAXS investigations show that Nb powder hydrogenation results in a large increase of Nb scattering ability characterized by the indicatrix invariant curve (Fig.1). This is caused by the intensive formation and growth of new electron density scattering inhomogeneities such as submicrometre pores with differing dispersity. An increase in Nb powder scattering ability is observed in the entire angular range, but the most significant buildup occurs in the superflow scattering angle region and is a result of the predominant formation of the greater ( > 15 nm ) submicrometre pores.

The hydrogenation assists the growth of the sintered powder specific surface via stimulation of gas vacancy pore formation processes. To a certain extent, it promotes the formation of the labyrinth porous structure, which is more resistant to subsequent external effects caused by the predominating volume contribution of large submicrometre pores, which are surface exposed. Evidently, this, along with alternative factors, which aid in improving the NbH based MDS capacitor system properties, is a decisive factor in the production development. However, the porous structure of hydrogenated powders is characterized by the rather high volume of small submicrometre pore low stable fractions.

Nitriding of NbH powders brings about a decrease in the SAXS intensity, primarily in the region of super small angle scatterings. In addition, the nature of angular intensity distribution also changes, the SAXS indicatrix integral width increases, and their asymptotics appreciably change. The correlation peaks caused by the predominance of scattering inhomogeneities of a certain shape, disappear (Fig.2). In the specimens under study, SAXS was mainly a result of scattering on the electron density volumetric inhomogeneities (i.e. submicrometre pores), whose minimum size exceeds the irradiation wavelength (0.7 nm), whereas its maximum size is limited by the largest possible degree of localization of primary X-ray beam and does not exceed 150 nm in the system used. In this connection, the observed SAXS picture may be interpreted as representing variations in submicrometre pore morphology and volumetric concentration in the given dimensional range.
Viewed as a gas – solid kinetics reaction, the transformation of the powder's porous structure during its nitriding (detected by the SAXS technique) is a result of volumetric and structural changes. These changes stem from diffusion, i.e. chemical reactions on pore surfaces, formation of gas vacancy complexes, and their mutual interactions with free surface, inner interfaces, and with structural imperfections.

The analysis of the changes in angular distribution and the SAXS intensity level, as well as the integral parameters, scattering indicatrix asymptotics, and calculations of the submicrometre pore sizes and concentrations suggest the following conclusion, namely that the porous system is noted for nitriding, which differs from the initial system by the greater number of submicrometre pores formed in different dimensional fractions. This redistribution appears as a dramatic decrease of small submicrometre pores (< 15 nm) (Table 1), probably owing to the pores being blocked by the products of interaction of sintered powder particles and the gas phase. The decrease in total submicrometre pore volumetric concentration is not important from the practical viewpoint, since the portion of large (> 15 nm) and mainly open submicrometre pores, which determines the useful porosity, increases considerably (Table 1). The contribution of small submicrometre pores, which are easily blocked while the capacitor system operates, can be ignored for the corresponding analysis of the process. Thus, nitriding assists in generating a porous system and stabilizing it, and facilitates oxide restoration in the surface electrolyte contact areas.

**PART B**

**INTRODUCTION**

The present communication reports an experimental study of the surface fractal dimension D of porous solid niobium obtained by vacuum sintering of niobium powder. Here we present observation of the modified Porod law and also give stipulation of the obtained surface dimension which are based on the employment of the independent method of Hg porosimetry.

**RESULTS AND DISCUSSION**

As is known, for describing X-ray scattering even in the Porod law the well known q law must be modified. The main formula of this theory which is useful for explaining our results is as follows:

\[ I(q) \sim (\text{constant} \times q^{-6}) \] (1)
Here $D$ is the dimension of the object being irradiated (in our case $D$ is a surface dimension) and the only discrepancy between the theory obtained by Wong $^7$ and that by Bale and Schmidt $^8$ is in the prefactor. The scattered intensity/wavevector relationship (Fig.3) shows the fractal behaviour. Indeed, on the graph the angle of the slope of the curve part, which be closely approximated by a line, is of the order of $73^\circ$ which corresponds to the following power law: $I(q) \sim q^{-3.19}$. Comparison of this result with formula (1) gives directly the surface dimension $D_s = 2.81$ (the subscript "s" denotes values obtained by experiments based on the SAXS).

$\text{Figure 3. Logarithmic dependence of SAXS intensity } J_\alpha \text{ vs the wave vector } q \text{ for the porous solid Nb: (+) – experimental data: (-) – approximation linear range.}$

As it was pointed out by Wong $^7$, complete treatment of the data obtained by SAXS, as well as by any method based on reflected radiation, is not unique. Another independent method should be used to support the measurements of the fractal dimension. That is why we made use of Hg porosimetry.

Due to the ability of the device to provide quite a high pressure we could investigate open pores of small radii reaching the region of the SAXS validity. This technique allows the distribution of open pores to be investigated by injecting mercury under pressure. As is clear, a pressure increase allows one to take into account pores of lower radii. If one considers the smallest pore radius to be appropriate yardstick $\varepsilon$ for the surface area measure then a pressure rise means in fact a transition to a smaller scale and has to give as a result the power dependence of the specific surface area $S_p$ on the smallest pore radius $R_p$. The surface dimension $D_p$ (the subscript "p" stands for values obtained by Hg porosimetry) can be determined in this case by relationship:

$$S_p \sim R_p^{(2-D_p)} \sim \varepsilon^{(2-D_p)}$$

well known in fractal theory $^7$.

We have observed the identical behaviour. It is represented in Fig.4 where the dependence of the open pore surface area of the sample is plotted as a function of the lowest pore radius registered by Hg porosimetry. The fact that the surface area dimension is predicted by the SAXS to be greater than 2 means that the cumulative surface area is actually determined by porosity. Hence $S_p$ in Fig.4, can be equated to the total effective surface area. The simple estimate of the angle of the slope approximated by a line yields the surface dimension $D_p$ equal to 2.84 (in accordance with relationship (2)). This result is in full compliance with that obtained by the SAXS method and gives further experimental support to the law formula (1).
CONCLUSIONS
The main results of Part A investigation are:
A1. Niobium powder hydrogenation leads to the formation of porous structures with predominancy of open submicrometre pores;
A2. Nitriding of NbH sintered powders stabilises the porous structure through coarsening, i.e. the volume contribution reductions of small submicrometre pores.

The main results of Part B investigations are:
B1. The surface dimensions are stated to be of the order of 2.8 which is a stipulation of a highly developed porous structure;
B2. Our results provide experimental support to the SAXS theory developed earlier.

Table 1. Volume concentration of submicrometre pores with different sized fractions
( R is pore size )

<table>
<thead>
<tr>
<th>Specimen</th>
<th>R, nm</th>
<th>2 – 5</th>
<th>5 – 6</th>
<th>15 – 17,5</th>
<th>23 – 33</th>
<th>C, %</th>
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<tbody>
<tr>
<td>Un-nitrided NbH</td>
<td>2,5</td>
<td>4,5</td>
<td>8,1</td>
<td>11,9</td>
<td>27</td>
<td></td>
</tr>
<tr>
<td>Nitrided NbH</td>
<td>0,8</td>
<td>1,3</td>
<td>0,7</td>
<td>10,2</td>
<td>13</td>
<td></td>
</tr>
</tbody>
</table>

REFERENCES