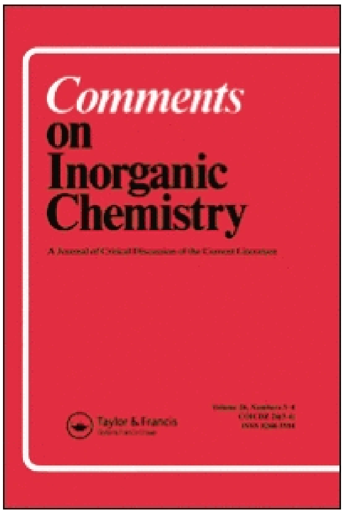

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Investigation of Metastable Niobium Oxides by Transmission Electron Microscopy[1]

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Investigation of Metastable Niobium Oxides by Transmission Electron Microscopy[1]

Refined preparative investigations made it possible to prepare not only the 15 already known oxidation products of NbO_x phases but also five additional ones that were formed at reduced partial pressures of oxygen. All oxidation products are metastable, and because of their composition they can be regarded as Nb_2O_5 modifications. High-resolution transmission electron microscopy proved to be an effective complement to the preparative methods. This made it possible to investigate heavily disordered structures. As the example of the oxidation products of $Nb_{12}O_{29}$ shows, six characteristic, distinctly different block structures occur that can be depicted by averaged structure models.

INTRODUCTION

As was realized, in particular by Wadsley,[2] Transmission Electron Microscopy at sufficiently high resolution is capable of contributing to the elucidation of crystal structures of suitable substances, especially if other methods of structure analysis (e.g., x-ray structure analysis) do not lead to more detailed results.[3,4] Prerequisite for a structure analysis with x rays is the existence of sufficiently large ($\phi \approx 1000$ Å) homogeneously structured crystal areas. However, the nature of deviations from the ideal structure can hardly be detected this way since one obtains a kind of averaged picture. High-Resolution Transmission Electron Microscopy (HRTEM) makes it possible to investigate very small crystal areas. Suitable for examination are the thin edges of fragments of crushed crystals. By this means it is possible to elucidate structures of very small

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single crystals or microdomains with a size of only a few unit cells, as well as of various small confined defects.[3,5,6] The method is especially helpful for investigating crystals that cannot easily be characterized by *one* unit cell because they have such a great number of defects. Structures of this kind were found, in particular, in substances that had been prepared under nonequilibrium conditions.[7-9]

Particularly suitable for HRTEM investigations are crystal structures whose building elements can be projected parallel to an axis onto a plane in such a way that at high magnification and with a high resolution, structural details can be observed and the contrast is as high as possible. Because of the way the samples are prepared for microscopy (producing fragments with thin edges, e.g., by mechanical means) and because of the method of microscopy (exposure to radiation in the EM), certain restrictions as to the kind of substances that can be investigated occur.[3,4] Examples of structures that proved to be suitable for such investigations are binary and ternary oxides, particularly if they have loosely packed structures like the ones of the structural varieties of WO_3 [10] that can be derived from the ReO_3 structure. Similarly appropriate examples are the so-called bronzes[11] and numerous silicates.[12,13] In our research group we thoroughly investigated Nb_2O_5-rich[3-9,15] binary and ternary oxides with "block structures"[14] that also can be derived from the ReO_3 structure. Since the fundamental publications by Wadsley and co-workers,[2,14] these substances turned out to be particularly suitable objects of study because of the dimensions of their unit cells which are large in two directions. Their investigations decisively influenced the subsequent development of HRTEM. Our present paper gives an example where preparative investigations on metastable oxides with block structures were appropriately complemented by the HRTEM method.

PREPARATIVE INVESTIGATIONS

The so-called NbO_x phases ($2.4 < x < 2.5$) of the system NbO_2–Nb_2O_5 are suitable as starting materials for the preparation of metastable Nb_2O_5 modifications.[16] As to the composition (x = O/Nb) and the notation Y for these phases see Table I. At

TABLE I
Metastable oxidation products of NbO_x phases

NbO_x phase Formula	Y	Oxidation product in air	Temp. °C	Oxidation product in rarefied oxygen atmosphere	Temp. °C
$Nb_{12}O_{29}$(mono)	BI	BI → Nb_2O_5(Ox1BI)	200	BI → Nb_2O_5(Ox1BI)	200
		BI → Nb_2O_5(Ox2BI)	400	BI → Nb_2O_5(OxgBI)	550
$Nb_{12}O_{29}$(orth)	BII	BII → Nb_2O_5(Ox1BII)	200	BII → Nb_2O_5(Ox1BII)	200
		BII → Nb_2O_5(Ox2BII)	510	BII → Nb_2O_5(OxgBII)	550
$Nb_{22}O_{54}$	C	C → Nb_2O_5(Ox1C)	200	C → Nb_2O_5(Ox1C)	200
		C → Nb_2O_5(Ox2C)	300	C → Nb_2O_5(Ox2C)	350
		C → Nb_2O_5(Ox3C)	450	C → Nb_2O_5(OxgC)	550
		C → Nb_2O_5(Ox4C)	700	C → Nb_2O_5(OxmC)[a]	850
$Nb_{47}O_{116}$	D	D → Nb_2O_5(OxfD)[b]	200	D → Nb_2O_5(OxgD)	200
		D → Nb_2O_5(Ox1D)	200	D → Nb_2O_5(Ox2D)	>400
		D → Nb_2O_5(Ox2D)	410	D → Nb_2O_5(Ox3D)	>600
		D → Nb_2O_5(Ox3D)	620		
$Nb_{25}O_{62}$	E	E → Nb_2O_5(Ox1E)	200	E → Nb_2O_5(Ox1E)	200
		E → Nb_2O_5(Ox2E)	450	E → Nb_2O_5(Ox2E)	450
$Nb_{53}O_{132}$	F	F → Nb_2O_5(OxF)	200	F → Nb_2O_5(OxF)	200

[a] This oxidation product prepared in rarefied O_2 was denominated Nb_2O_5(OxmC) because of the similarity to M–Nb_2O_5 samples.[17,18]

[b] If one oxidizes very finely comminuted samples at $T < 350°C$ Nb_2O_5(OxfD) is formed.

low temperatures (>200°C) the blue-black NbO_x phases can be oxidized completely to colorless to pale-yellow metastable Nb_2O_5 modifications. From *one* starting compound one can gain up to six different Nb_2O_5 modifications[9] by varying the experimental conditions (temperature, partial pressure of oxygen). Therefore, it is possible to prepare 15 modifications by oxidation in air at different temperatures and five additional ones by lowering the partial pressure of oxygen during the oxidation (Table I). The new modifications that were prepared in air have been characterized by the notation Nb_2O_5(OxnY). Ox refers to the preparation by the method of complete oxidation of one of the NbO_x phases Y listed in Table I and n indicates the stage of oxidation that is reached depending on the temperature chosen during the experiment or on the subsequent thermal transformation[19] of a stage obtained at a lower temperature.

Stages that can only be reached by slow oxidation at lowered partial pressures of oxygen are denominated Nb_2O_5 (OxgY). The letter g in this notation stands for the German word "gering" (≙ low). All metastable Nb_2O_5 modifications, prepared as described above, convert into thermodynamically stable H–Nb_2O_5 [14] at sufficiently high temperature (e.g., 1000°C).

PRINCIPLE OF STRUCTURE

An investigation with x rays, using the guinier powder method, shows that the oxidation products of an NbO_x phase Y yield very closely related patterns which are also still very similar to the diagrams of the starting material. As indicated by the relationship of the guinier diagrams, all the oxidation products mentioned here, the NbO_x phases and H–Nb_2O_5 have a common building principle (block structures) that can be correlated to sections (blocks) of the ReO_3 structure.[14] This can be done by limiting the ReO_3 lattice (corner-sharing octahedra) in two directions by planes of edge-sharing octahedra, thus generating adjacent blocks (differing line thickness in drawing of Figure 1) that are displaced by one-half of an octahedra diagonal with regard to the third direction, the direction of crystal growth (the short crystallographic axis). Moreover,

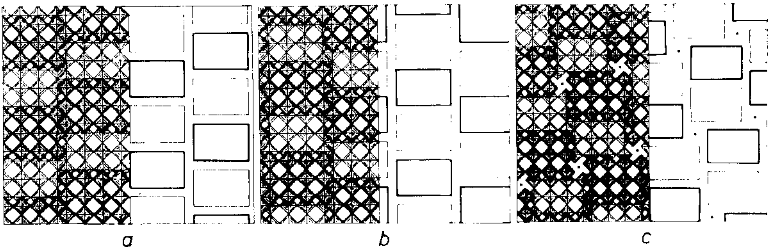

FIGURE 1 Ideal structures of NbO_x phases as examples of block structures.[3] (a) Monoclinic $Nb_{12}O_{29} \triangleq$ BI. (b) Orthorhombic $Nb_{12}O_{29} \triangleq$ BII. (c) $Nb_{25}O_{62}$. The left-hand side of the figures shows the idealized octahedra, which can be regarded as square-base bipyramids. The outlines of the blocks are shown more clearly on the right. The niobium atoms in the tetrahedral positions [cf. (c)] between the blocks are indicated by dots.

shifted blocks at the same height can be connected by edges. Along the third direction the octahedra are continually sharing apexes. This building principle which is also present in ternary oxides and oxide fluorides opens up the possibility of varying the structural anion/cation ratio (A/C) *stepwise* within a wide range. The ratio A/C and O/Nb, respectively, is determined by the size of the blocks and the way they are connected.[14] The main possibilities of connection in NbO_x structures are

(i) blocks at the same height share edges;
(ii) connection by tetrahedral sites.

An example showing only connections as in (i) is $Nb_{12}O_{29}$ (Figure 1a, b). The blocks, having a size of (3 × 4) octahedra, can be arranged in a monoclinic or an orthorhombic way. Therefore, a monoclinic (BI) and an orthorhombic (BII) modification exist.

A combination of connections (i) and (ii) is realized in the other NbO_x phases, e.g., in $Nb_{25}O_{62}$ (E) whose structure is also made up by (3 × 4) blocks (Figure 1c). According to observations[20,21] made up to now, a decisive factor for the process of oxidation is whether the initial structure of the particular NbO_x phase already contains tetrahedral sites. By the example of $Nb_{12}O_{29}$ (mono) the oxidation of an initial structure *without* tetrahedral sites is demonstrated. The reactions of $Nb_{25}O_{62}$ serve as an example for the oxidation of an initial structure *with* tetrahedral sites.

REAL STRUCTURES OF THE OXIDATION PRODUCTS OF $Nb_{12}O_{29}$ (MONO)

According to the electron-optical investigation (Figure 2), the crystal structure of the monoclinic *starting material* $Nb_{12}O_{29}$ (≙ BI) agrees with the ideal structure as shown in Figure 1a. The concentration of observed defects is extremely small.[7] Occasionally rows of blocks with an orthorhombic arrangement (Figure 1b) can be recognized.

1st Stage

The complete oxidation of BI in air or rarefied O_2 atmosphere at 200–400°C is relatively slow and in each case (Table I) ends in Nb_2O_5(Ox1BI). An electron-optical investigation is difficult, because Nb_2O_5(Ox1BI) loses the absorbed oxygen while irradiated with electrons and becomes deoxidized back to $Nb_{12}O_{29}$(mono). This leads to the conclusion that during a first stage of oxidation the oxygen is bound rather loosely. In favorable cases we managed to take pictures of the largely undamaged structure of Nb_2O_5(Ox1BI) (Figure 3) which show that the arrangement of the (3 × 4) blocks of the starting compound remains unchanged by the oxidation.

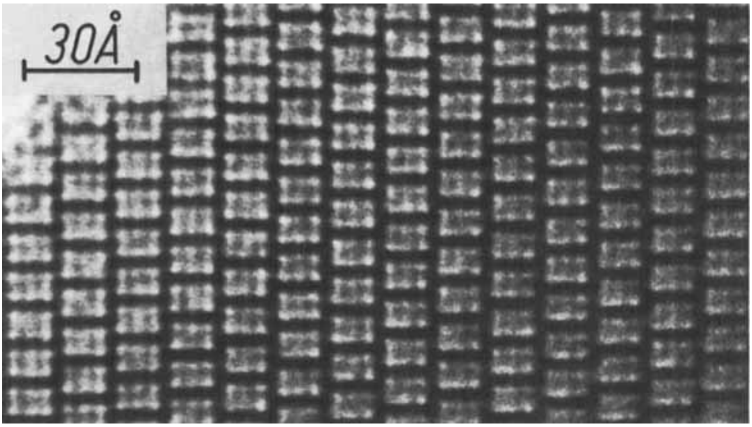

FIGURE 2 Transmission electron micrograph of a crystal region of $Nb_{12}O_{29}$(mono) ≙ BI.

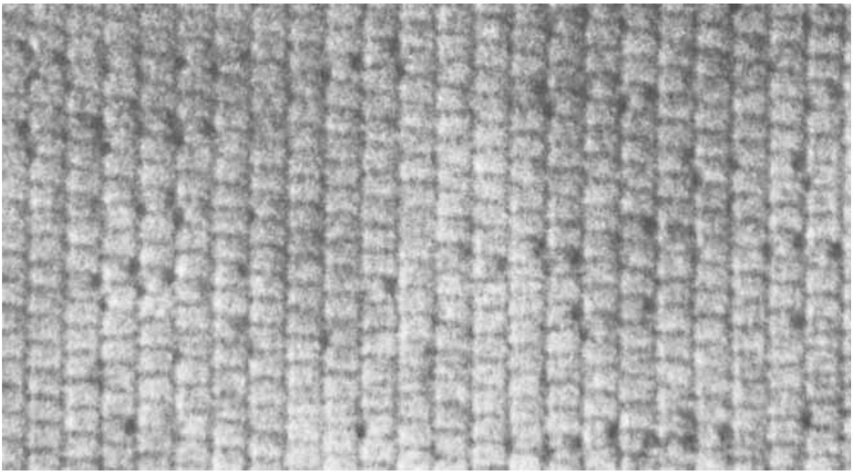

FIGURE 3 Transmission electron micrograph of the largely undamaged structure of Nb_2O_5(Ox1BI).

However, some of the blocks have black spots that form a periodical array. At higher resolution they are found to be pairs of spots. But because of the heavy irradiation load only few of the black spots still remain under these conditions.

A comparable pattern of dark contrasts occurred on pictures of (3 × 4) blocks that were observed by Iijima *et al.*[22,23] Although the atomic arrangement could not be resolved, the authors interpreted these black contrasts by a point defect model assuming tetrahedrally coordinated niobium. Since we observe comparable contrasts, the model which describes the absorption of two O atoms and the resulting increase in O/Nb in a plausible way seemed to be usable for us as a basis for explaining the oxidation of $Nb_{12}O_{29}$ (Figure 4a). Starting from this assumption, a structural model for Nb_2O_5(Ox1BI) was developed that corresponds with the periodicity of the array of point defects in the *a–c* plane, with the superstructures recognizable on diffraction patterns,[7,19,20,24] and also with the composition O/Nb = 2.500. The latter applies if the occupation of the point defect positions (squares in Figure 4b) takes place in such a way that at one-half of all of these positions (hatched squares in Figure 4b) point defects *alternate* with undisturbed (3 × 4) blocks along the *b* direction (the short axis). At the other half of the posi-

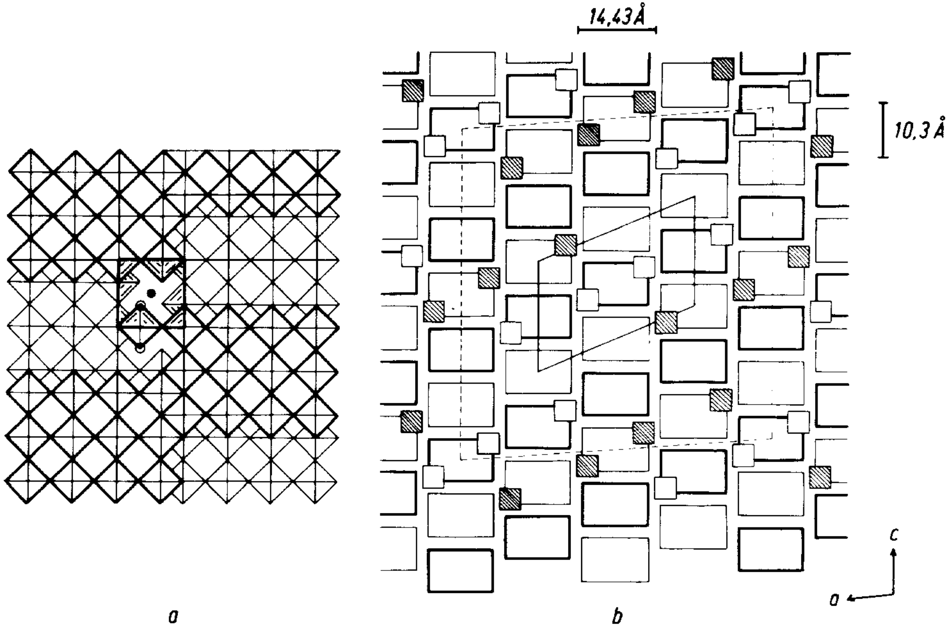

FIGURE 4 Interpretation of the picture of Figure 3. (a) Arrangement of atoms according to the point defect model of Iijima.[22,23] (b) Structure model for Nb_2O_5(Ox1BI). The squares correspond to point defects with an arrangement of atoms as depicted in (a). Hatched squares indicate positions where along the *b*-direction point defects alternate with undisturbed (3 × 4) blocks. Empty squares indicate positions where point defects exist in every layer of octahedra. The resulting unit cell is outlined by a broken line. The unit cell of the matrix structure (BI) is drawn with a continuous line.

tions (empty squares in Figure 4b) there are point defects in *each* layer of octahedra (cf. Ref. 7).

2nd Stage

The oxidation of BI in air proceeds quickly above 400°C ending in Nb_2O_5(Ox2BI). The electron-optical investigation shows that during the transformation into the second stage the arrangement of (3×4) blocks is changed in a characteristic way. The linkage of blocks by tetrahedral sites comes as an additional principle to the initial way of connecting blocks only by edges (cf. structure of $Nb_{12}O_{29}$). The arrangement of blocks is heavily disordered. Nevertheless, rows of $(2 \times n)$ blocks $(3 \leq n \leq 6)$ linked by tetrahedral positions stand out as characteristic features of the structure. The rows of $(2 \times n)$ blocks alternate almost periodically with an average of five rows of $(3 \times n)$ blocks $(3 \leq n \leq 5)$, see Figure 5a. The evaluation of the frequency distribution of occurring block sizes and block arrangements[7] leads to an averaged structure model (Figure 6a) for crystalline Nb_2O_5(Ox2BI).

If this averaged model is looked upon as a "fully occupied" structure[3,5,25] with 16/4 Nb in tetrahedrally coordinated positions, the resulting composition is $Nb_{16/4}Nb_{68}O_{179}$ with O/Nb = 2.486. Comparable values were gained from the evaluation of pictures showing larger areas of crystals[7] In order to interpret the deviation

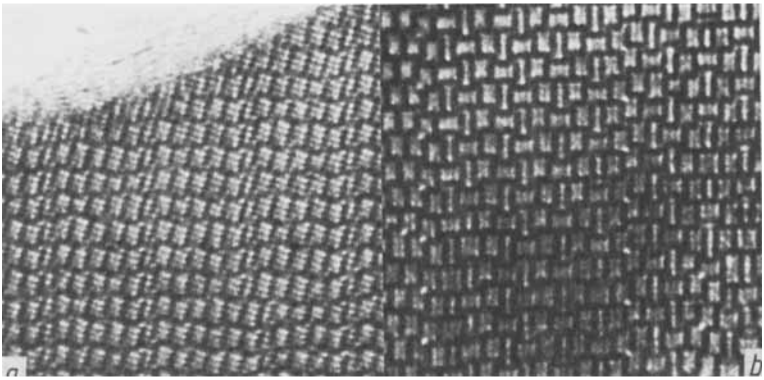

FIGURE 5 Transmission electron micrograph. (a) Nb_2O_5(Ox2BI). (b) Nb_2O_5-(Ox2BII).

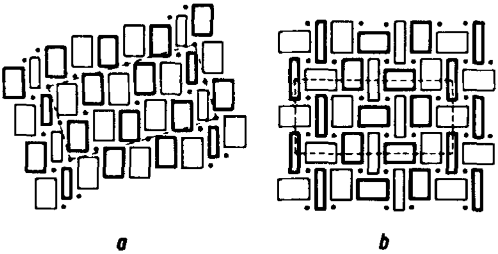

FIGURE 6 Interpretation of the pictures of Figure 5. (a) Averaged structure model of Nb_2O_5(Ox2BI). (b) Averaged structure model of Nb_2O_5(Ox2BII).

by 0.014 O/Nb from a fully occupied structure, we go back to thoughts of Wadsley and Anderson,[14] who consider tetrahedral sites that are not fully occupied. With a slightly lower occupancy (occupancy factor 0.9) than in Ref. 14, the model (Figure 6a) assumes the composition $Nb_{14.4/4}Nb_{68}O_{179} \triangleq NbO_{2.500}$ which corresponds to complete oxidation of the samples.

Product of Slow Oxidation

The complete oxidation of BI at *reduced* partial pressures of oxygen ($\approx 10^{-3}$ vol.%) and at temperatures above 500°C results in the additional oxidation product Nb_2O_5(OxgBI) that cannot be obtained by fast oxidation in air.[9] Also, during slow oxidation the initial arrangement of blocks (as in BI) changes as shown in Figure 7. Although the real structure of Nb_2O_5(OxgBI) is heavily disordered, one can recognize features that are characteristic for this structure, in particular blocks linked in pairs by an R-type tunnel (Figure 8a). The pairs of blocks are connected with each other by tetrahedral positions. The interpretation [as in the case of Nb_2O_5(Ox2BI)] leads to a characteristic averaged model (Figure 8b) which in the case of a fully occupied structure has the composition $Nb_{4/4}Nb_{46}O_{116}$ with O/Nb = 2.468. However, the samples are completely oxidized to Nb_2O_5. Like the second stage, the deviation from the composition O/Nb = 2.500 can be compensated by leaving some of the tetrahedral sites vacant. Corresponding to the greater deviation which amounts to 0.032 = O/Nb, the required composition $Nb_{1.6/4}Nb_{46}O_{116}$ (O/Nb = 2.500) can only be reached with the occupancy factor 0.4.

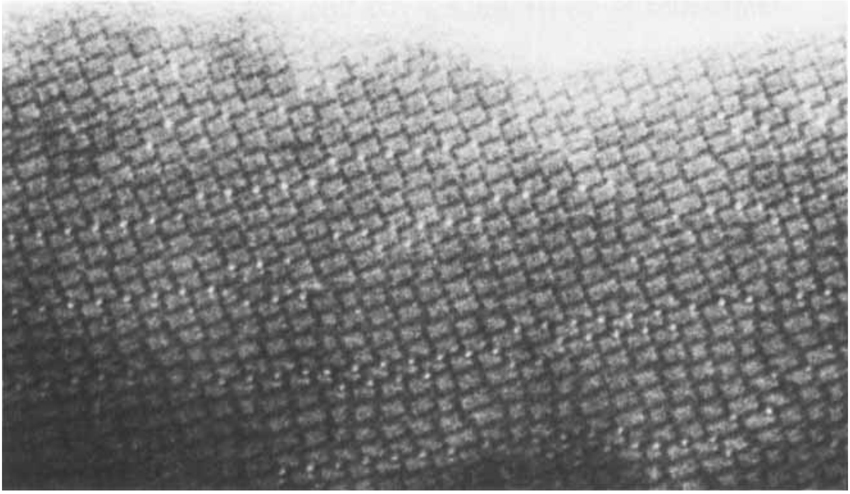

FIGURE 7 Transmission electron micrograph of Nb_2O_5(OxgBI), the product of the slow oxidation of BI.

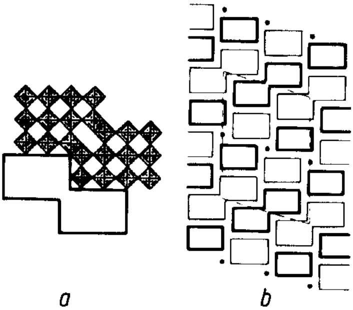

FIGURE 8 Interpretation of the picture of Figure 7. (a) (3 × 4) blocks linked in pairs by a rectangular R-type tunnel. (b) Characteristic average structure model of Nb_2O_5(OxgBI).

COMPARISON WITH $Nb_{12}O_{29}$ (ORTH)

As with monoclinic $Nb_{12}O_{29}$(BI) the oxidation of orthorhombic $Nb_{12}O_{29}$(BII) results in three additional Nb_2O_5 modifications which are also metastable (Table I). The electron microscopic examination of corresponding oxidation products of BI and BII that were made under comparable conditions (Figure 5) shows that they are composed of comparable building elements which differ from those of the initial compounds.[7,8] With regard to the size and the sequence of blocks (Figure 6) they are related to the initial structures of BI and BII. As a result, e.g., in case of a reduction,[26] one can recognize some sort of memory of that $Nb_{12}O_{29}$ modification from which they originate.

OXIDATION OF NbO_x PHASES HAVING TETRAHEDRAL POSITIONS

The observed small differences between guinier diagrams of NbO_x phases with tetrahedral positions (Y = C–F) and diagrams of their oxidation products lead to the supposition[14] that for these substances the process of oxidation differs from the one for $Nb_{12}O_{29}$. In case of an oxidation the modifications of the guinier diagrams[9,19] and the amount of absorbed oxygen are greater for B than for Y = C–F. Our own electron-microscopic investigations on the oxidation products of E (Figure 9b) and F[21] as well as results of Ref. 20 concerning C show that these products have the same structures as the initial NbO_x phases (Figure 9a). The positions of the additional oxygen that entered the structure during oxidation were not detectable. If one drops the model of a fully occupied structure one can come from the observed to the required composition O/Nb = 2.50 by assuming, as proposed Ref. 14, that not all tetrahedral sites (tunnels) are occupied by Nb atoms.[27]

If Nb migrates from these positions to the surface of the crystal and together with the oxygen adds to this surface in such a way as to continue the structure of the initial NbO_x phase, then the process of oxidation merely results in a slight enlargement of volume of the crystal. Therefore, differences in the arrangements of blocks of

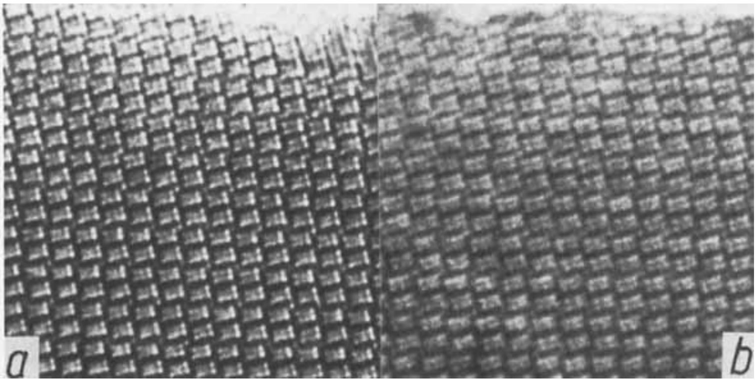

FIGURE 9 Transmission electron micrograph. (a) $Nb_{25}O_{62}$(≙E). (b) Nb_2O_5-(Ox2E), one of the oxidation products of $Nb_{25}O_{62}$ (cf. Table I).

the NbO_x phases and the oxidation products should be undetectable by electron microscopy. This is in agreement with observations.

It is remarkable that up to now it has not been possible to determine from the electron-microscopic investigations of the oxidation products of Y = C–E[20,21] why the guinier patterns of the various stages (Table I) are clearly different from one another. According to these facts, differences in structure ought to be expected. This still needs to be investigated thoroughly.

COMPARISON OF OXIDATION CONDITIONS

The variation of experimental conditions (temperature, partial pressure of O_2) for the oxidation of NbO_x phases leads to distinct metastable Nb_2O_5 modifications (Table I).[9,19] Since oxidation was carried out under defined preparative conditions *outside* the electron microscope, explanations referring to the process of oxidation can only be given if they are based on a comparison of the structures of the initial phase and the oxidation products and with regard to the conditions of preparation. We therefore look at the variation of occupancy of O and Nb positions within comparatively large portions of structure (Table II) of our models (Figure 10). We

TABLE II

$Nb_{12}O_{29}$(orth) ≙ BII and oxidation products: densities and volume of (unit) cells

Compound	Density x-ray g/cm^3	Volume of cell Å^3
BII	4.58	2290.0
Nb_2O_5(Ox1BII)	4.66	2272.4
Nb_2O_5(Ox2BII)	4.59	2280.7
Nb_2O_5(OxgBII)	4.51	2266.1

refer to the oxidation of BII as an example which also can be looked upon as being representative for the reactions of BI.

I. During the oxidation of BII to Nb_2O_5(Ox1BII) the occupancy of Nb positions remains constant while additional oxygen atoms are absorbed into the basic structure of BII. This interpretation is also supported by the increase in density, whereas the volume of the (unit) cell of the averaged model slightly decreases (Table II). In the temperature region characteristic for this step of the oxidation ($T < 500°C$) the reaction rate is low and cannot be substantially influenced by varying the O_2 pressure (20–10^{-3} vol.%). Obviously, it is controlled by the slow heterogeneous reaction. Since at these low temperatures a low rate of diffusion must be expected, it can be seen why the arrangement of blocks for BII is not changed substantially during oxidation to Nb_2O_5(Ox1BII).

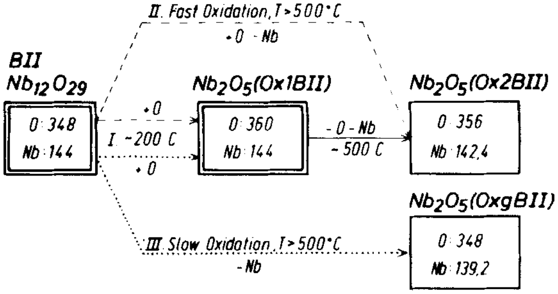

FIGURE 10 Proposed different ways for the oxidation of $Nb_{12}O_{29}$(BII). Broken line: oxidation at low partial pressure of oxygen. Continuous line: thermal transformation. The occupancy of O and Nb positions of equally large sections of a structure is written within boxes. Doubly bordered box: fully occupied structure. Simple box: structure model with incompletely occupied tetrahedral positions ≙O/Nb = 2.500.

II. At higher temperatures of about 500–700°C the type of the reaction product depends on the O_2 pressure. Nb_2O_5(Ox2BII) which is formed by fast oxidation in air has an arrangement of blocks that has largely changed compared with BII and Nb_2O_5 (Ox1BII), respectively. For this the higher mobility of the Nb atoms, as results at $T > 500°C$, is necessary. This transformation involves an increase in occupancy of the oxygen positions and a corresponding decrease with regard to niobium. Accordingly, the density increases only slightly. This can be attributed mainly to a decrease in volume of the (unit) cell (Table II). Apparently, at 500°C the accelerated heterogeneous reaction makes it possible that by absorption of O_2 the Nb(IV) particles are transformed to Nb(V) more easily. The reaction seems to proceed in such a way that, as in condition I, a certain portion of oxygen diffuses into the initial structure. Then, by rearrangement of the blocks, tetrahedral sites are generated which make it possible for the Nb atoms to migrate to the surface of the crystal where a larger amount of oxygen is present.

III. Compared with condition II the oxidation of BII at low oxygen pressures and at $T > 500°C$ proceeds very slowly. Apparently, the rate of oxidation is determined by the limited supply of oxygen. At the required higher temperature Nb should be sufficiently mobile and easily oxidizable (cf. II). Therefore, Nb that migrates to the crystal surface during the rearrangement of the block structure catches the approaching oxygen before it diffuses into the crystal. This corresponds to the model (Figure 10) for the transformation of BII to Nb_2O_5(OxgBII). In this case Nb migrates out of a certain crystal region while the number of O atoms remains constant.

INFLUENCE OF INITIAL STRUCTURE ON THE OXIDATION PROCESS

According to present results, the basic structure of the starting phases C–F does not change during oxidation. The composition $O/Nb = 2.500$ is reached by the incomplete occupation of tetrahedral sites. This also can happen at temperatures $T > 500°C$ without rearrangements inside the blocks, and indicates that tetrahedrally coordinated niobium migrates to the surface and is oxidized there faster than a rearrangement of the block structure can take place.

In the cases of BI and BII the tetrahedral sites with mobile Nb have to be generated by oxidation first, and thereby generate the rearrangement of the block structure. Thus, the ratio O/Nb, as compared with BI and BII, is strongly increased. In this case the value O/Nb = 2.500 corresponding to complete oxidation can only be reached with an incomplete occupancy of tetrahedral positions.

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