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The Effect of Annealing on the Concentration of Wadsley Defects in the Nb_2O_5–WO_3 System

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Mixtures of $x\mathrm{Nb_2O_5} \cdot y\mathrm{WO_3}$ with $x{:}y = 9{:}8$, $8{:}5$, and $8{:}1$ have been annealed at high temperatures for prolonged periods before quenching to room temperature. The concentration of Wadsley defects, estimated from lattice image electron micrographs of a few fragments in each sample, is reduced during this treatment. The results indicate that (1) the high temperature equilibrium is attained very slowly, and in stoichiometric samples probably involves the complete removal of Wadsley defects; (2) the high temperature situation is not seriously affected by the quenching treatment; and (3) variations in stoichiometry may be accommodated by means other than the presence of Wadsley defects.

1. Introduction

A closely related family of phases has been identified by single crystal X-ray structure analysis in the binary system Nb_2O_5–WO_3 (*1–4*). The subsequent examination of the same samples (from which the single crystals were taken) by electron optical methods (*5*) has revealed the presence of Wadsley defects—coherent intergrowths of one member of the family in a matrix of another. These intergrowths are frequently only half a unit-cell wide, and therefore they were not detected in the X-ray studies. They alter the stoichiometry of the phases in which they occur, and when present in large numbers, they may form ordered sequences. For example, $W_4Nb_{26}O_{77}$ (*4*) is an ordered intergrowth of $WNb_{12}O_{33}$ and $W_3Nb_{14}O_{44}$, and may be regarded as a distinct phase, whose composition is intermediate between those of its component parts.

These observations have aroused considerable interest and discussion (*6*), and some of the resultant questions are as follows:

(1) In a sample whose composition corresponds exactly to that of one of the members of the family of phases, does the concentration of Wadsley defects depend upon thermal history, and if so, is the equilibrium phase free of these defects, or does it contain a small residual concentration?

(2) The samples were all quenched from about 1620°K to room temperature before examination (*1*). Does the structural information obtained from such samples truly reflect the high temperature situation, or do substantial changes occur during cooling?

(3) Is *all* the nonstoichiometry in these materials accommodated by means of Wadsley defects, or does each phase have a narrow range of homogeneity, independent of Wadsley defects?

This paper describes the results of some experiments which were performed in order to obtain information relevant to these questions. We have annealed samples of $x\mathrm{Nb_2O_5} \cdot y\mathrm{WO_3}$ with the molar ratios $x{:}y = 9{:}8$, $8{:}5$, and $8{:}1$ for varying periods of time, and examined the products in an electron microscope in an attempt to measure the concentration of Wadsley defects.

The 9:8 and 8:5 phases have large unit cells and are therefore relatively easy to examine by the lattice imaging technique. Both phases have incongruent melting points in the vicinity of 1650°K, and have minimum temperatures of stability of about 1538°K (for 9:8) and 1363°K (for 8:5) (7). Hence any changes during cooling should be particularly noticeable in these cases.

The 8:1 sample was chosen because in the phase analyses of the system (1, 7), using X-ray methods, it was indistinguishable from the 6:1 phase whose composition corresponds to that expected from its crystal structure. Thus it appeared that $WNb_{12}O_{33}$ had a small range of homogeneity, and it was postulated (7) that some form of intergrowth might account for this.

2. Experimental

2.1. Sample Preparation

High purity Nb_2O_5 and WO_3 were mechanically mixed in the molar proportions 9:8, 8:5, and 8:1. Each composition was calcined in a large sealed platinum tube for 2 hr at 1620°K and quenched into water. Portions of each of the calcines were then heated in separate smaller sealed platinum tubes at temperatures and for times shown in Tables II and III. In all cases the tubes were finally quenched from the annealing temperature into water.

2.2. Electron Optical Examination

Each sample was ground in an agate mortar and a portion of it was collected on a specimen grid bearing a carbon support film. Thin fragments were sought, and if they could be tilted so that one or both of the intersecting sets of shear planes in the structure lay parallel to the electron beam, lattice images showing these planes were recorded. Because the technique is time consuming and rather tedious, only about 12 images from each sample were recorded. This number is insufficient to provide data for statistical analysis; however the results indicate a distinct trend in spite of this limitation.

3. Results

3.1. 8:5 and 9:8 Compositions

Nature of the Defects. Figure 1 shows two lattice images from the same fragment of a 9:8 sample, after annealing for 4 hrs at 1620°K. It serves to illustrate the most frequent types of defects we have found in both the 8:5 and 9:8 samples. The orientation of the fragment was adjusted so that the two intersecting sets of shear planes in the structure were revealed separately in Figs. 1(a) and 1(b). In the pure phase, $W_8Nb_{18}O_{69}$ (3), the periodicity of the shear planes is 18.6 Å ($=a/\sqrt{2}$), and the majority of the fringes in Fig. 1 have this spacing. The shear planes are separated by blocks or columns of the ReO_3 type structure, which in $W_8Nb_{18}O_{69}$ are five octahedra wide by five long, and extend right through the crystal in the third (*c*) direction. The fringes in Fig. 1 which have spacings of 14.9 Å and 22.7 Å are due to the insertion of slabs of material in which the block size is not 5 × 5, but rather 4 × 5 and 6 × 5 respectively (5). They are Wadsley defects—intergrowths of the compositions $W_5Nb_{16}O_{55}$ (4 × 5 blocks) and $W_{11}Nb_{20}O_{83}$ (6 × 5 blocks) in the matrix of $W_8Nb_{18}O_{69}$. It is evident from Fig. 1 that Wadsley defects can occur parallel to *both* sets of shear planes, and structural models for intersecting defects have been proposed previously (5). The defects may occur as single slabs, half a unit-cell wide, or as microdomains of the neighbouring composition, such as at A in Fig. 1(a). Table I shows the relationship between fringe spacing, block size, and composition for the matrix structures and defects encountered in this study.

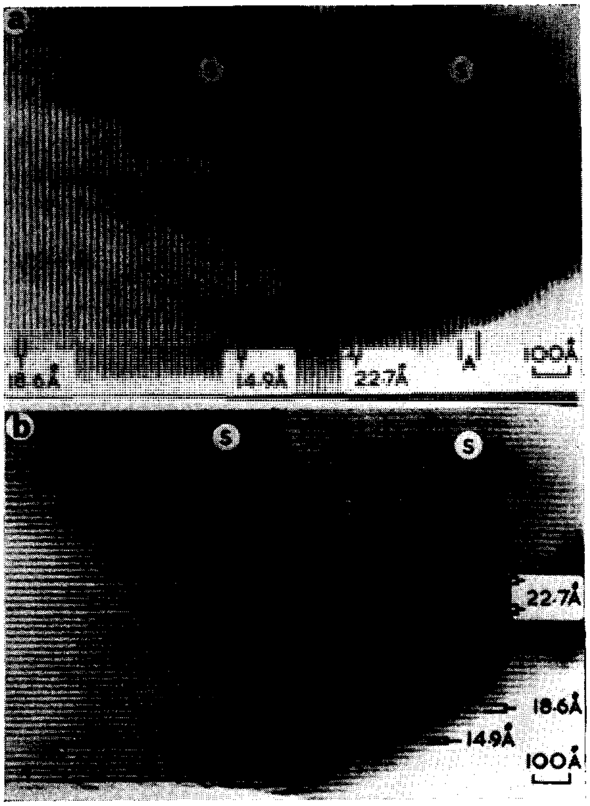

FIG. 1. Lattice images from a fragment of $9Nb_2O_5 \cdot 8WO_3$ after annealing for 4 hr at 1620°K. The two sets of shear planes are imaged separately in (a) and (b). The matrix has the composition $W_8Nb_{18}O_{69}$, and is characterized by fringe spacings of 18.6 Å. Some of the Wadsley defects, having fringe spacings of 14.9 Å and 22.7 Å, are marked. Displacement defects occur in the encircled regions labelled S.

TABLE I

CORRELATIONS OF FRINGE SPACING, BLOCK SIZE, AND COMPOSITION

Nominal composition	Fringe Spacings (Å) matrix	defect	Block size	Composition	Nb_2O_5/WO_3 Ratio
8:5	14.9 18.6	—	4 × 5[a]	$W_5Nb_{16}O_{55}$	1.600
	14.9	18.6	5 × 5	$W_8Nb_{18}O_{69}$	1.125
	18.6	14.9	4 × 4	$W_3Nb_{14}O_{44}$	2.333
	18.6	22.7	4 × 6	$W_7Nb_{18}O_{66}$	1.286
9:8	18.6	—	5 × 5[a]	$W_8Nb_{18}O_{69}$	1.125
	18.6	14.9	5 × 4	$W_5Nb_{16}O_{55}$	1.600
	18.6	22.7	5 × 6	$W_{11}Nb_{20}O_{83}$[b]	0.909

[a] Matrix structure.

[b] Pure phases containing these block sizes are unknown, but slabs of these structures may occur as Wadsley defects (*5*).

More complex defects were observed occasionally in some fragments. Fringe displacements, such as at S in Fig. 1, were comparatively rare in most specimens. These, and several other arrangements of faults have been described previously (*5*). They were not examined in detail in this investigation.

Effect of Annealing. The following information was tabulated after a careful examination of each micrograph:

(1) The number of fringes with spacings of 14.9 Å, 18.6 Å, and 22.7 Å, e.g., 8, 78, and 1 respectively, in Fig. 1(a).

(2) The maximum size of groups of fringes, or microdomains of neighbouring composition, in the matrix, e.g., 3, at A in Fig. 1(a).

(3) The total number of defects—each microdomain was regarded as a single defect, regardless of its extent. There are therefore six defects in Fig. 1(a).

(4) The presence or absence of interesecting defects was noted.

(5) Any appearance of ordered intergrowth between 14.9 Å and 18.6 Å fringes was noted. The composition of such an intergrowth would be $W_{13}Nb_{34}O_{124}$, intermediate between $W_5Nb_{16}O_{55}$ and $W_8Nb_{18}O_{69}$.

The results, derived from micrographs of an average of eight fragments in each sample, were accumulated, and relevant numerical data are recorded in Table II. The data were used to calculate the defect concentration

$$\left(\text{column } 9 = \frac{\text{col. } 8 \times 100}{\text{cols. } 4+5+6+7}\right)$$

and also an estimate of the Nb_2O_5/WO_3 ratio (column 10) for each sample. In order to derive this ratio, it was assumed that all departures from stoichiometry were accommodated by Wadsley defects, and that the composition was simply the sum of the compositions characteristic of individual fringes, given in Table I. The analysis also implies that the slabs of structure in the sample are all of the same cross-sectional area, and may only vary in width according to Table I. This is obviously untrue, because the fragments were of irregular shape and thickness; nevertheless the results should reveal any significant trends in composition.

Apart from the results in Table II, the following general observations were made:

(1) The defect concentration in individual fragments in any one sample usually lay within a factor of two of the mean value quoted in column 9 of Table II. When this mean was below about 1 %, a significant proportion (30–70 %) of fragments were completely free of Wadsley defects.

(2) No 11 Å fringe spacings, characteristic of blocks three octahedra wide, were observed. In principle, it should be possible for Wadsley defects in the 8:5 composition (4 × 5 blocks) to contain 3 × 5 blocks of octahedra.

(3) The number of fringes in any one defect, or the size of a microdomain, varied considerably. After short anneals, the distribution of sizes was very wide, from single fringes up to groups of over 50; but after long anneals, only isolated single fringes or pairs remained. The variety of sizes persisted much longer for the 9:8 composition than for the 8:5. In some cases, individual fragments

TABLE II

ANNEALING OF $8Nb_2O_5 \cdot 5WO_3$ AND $9Nb_2O_5 \cdot 8WO_3$

1	2	3	4	5	6	7	8	9	10
Compn	Anneal time hr at 1620°K	Number of fragments	Total matrix fringes	Total defect fringes			Total Wadsley defects	% Wadsley defects	Nb_2O_5/WO_3 Ratio
				14.9 Å	18.6 Å	22.7 Å			
8:5	2	9	2207	433[a]	25	19	60	2.2	1.665
	4	8	2190	185	44	33	99	4.2	1.614
	15	7	2320	24	57	9	50	2.1	1.585
	65	9	2805	30	20	18	44	1.5	1.597
	168	10	3030	23	8	3[d]	22	0.7	1.601
	336	7	2415	3	2	—	3	0.1	1.600
	768	6	3620	3	3	—	5	0.1	1.600
9:8	2	7	1602	864		53	211	8.4	1.234
	4	8	2812	159		33	80	2.7	1.138
	15	8	2650	212		14	74	2.6	1.146
	65	8	2580	81		4	49	1.8	1.134
	168	8	4610	209		14	80	1.7	1.137
	336	8	2411	303[b]		10	71	2.6	1.159
	768	7	1491	112[c]		2[d]	3	0.2	1.146

[a] Two fragments were mostly $W_3Nb_{14}O_{44}$.

[b] Two fragments were mostly $W_5Nb_{16}O_{55}$.

[c] One fragment was perfect $W_5Nb_{16}O_{55}$.

[d] Only one fragment in the group contained 22.7 Å fringes.

contained a majority of fringes characteristic of a neighbouring structure, lower in WO_3 content than the nominal composition of the sample. Fragments consisting largely of $W_3Nb_{14}O_{44}$ (4 × 4 blocks) were found in the 8:5 sample after 2 hr annealing, and similarly, the 8:5 structure predominated in some fragments of nominal 9:8 composition, even after long annealing. One fragment in the 768 hr sample of 9:8 composition was a perfect crystal of $W_5Nb_{16}O_{55}$.

(4) The tendency for ordered intergrowth of 14.9 Å (4 × 5 blocks) and 18.6 Å (5 × 5 blocks) fringes was small. The largest observed groups of this sequence were four periods (seen once) and three periods (seen twice).

(5) A few crystals of a completely different phase were found in the 9:8 sample, particularly after short anneals. The electron diffraction patterns of this phase corresponded to those expected for the 1:1 composition, WNb_2O_8 (*7*). The structure of this phase differs completely from those of the family containing lesser amounts of WO_3.

(6) Intersecting defects were observed in about 16% of the 8:5 fragments examined, and 50% of the 9:8 fragments. They were most common in samples after short anneals, and disappeared more rapidly in the 8:5 composition than in the 9:8.

3.2. 8:1 Composition

Nature of the Defects. Diffraction patterns from samples of the 8:1 composition were similar to those of the stoichiometric 6:1 compound, $WNb_{12}O_{33}$, but occasionally they showed streaking parallel to the a^* direction in reciprocal space. Lattice images from fragments tilted to reveal the shear planes parallel to a in the $WNb_{12}O_{33}$ structure (which contains 4 × 3 blocks) showed a uniform set of sharp fringes with a spacing of 14.9 Å, traversed at an angle of about 49° by randomly spaced diffuse bands (Fig. 2a). The diffuse bands became wider as they moved away from the edge of the crystal. The reason for this is that the fragment is wedge-shaped, and the defects lie at an angle of a few degrees to the electron beam. The diffuse bands represent a projection of the defects, and this increases in width as the thickness of the fragment increases.

It was anticipated that the 8:1 samples would contain Wadsley defects due to the intergrowth of $WNb_{12}O_{33}$ with high temperature (H-) Nb_2O_5. This composition interval was studied previously (*8*),

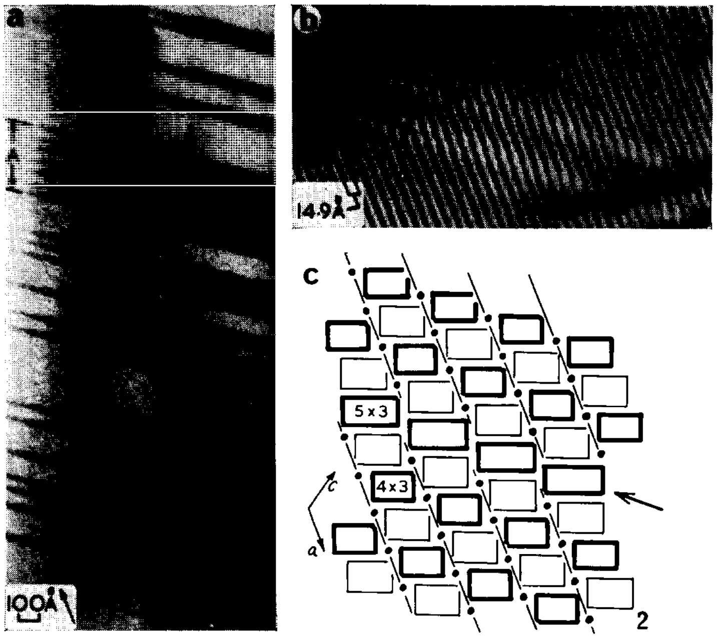

FIG. 2. (a) Lattice image from a fragment of $8Nb_2O_5 \cdot WO_3$ after annealing for 2 hr at 1707°K. The Wadsley defects appear as a set of diffuse black bands. They lie at an angle of 49° to the shear planes, whose direction is marked by an arrow.

(b) High magnification image showing the intersection of two Wadsley defects with a set of shear plane fringes, whose spacing is 14.9 Å. Note the slight deviation of these fringes as they cross the defects.

(c) Idealized model of the structure of $WNb_{12}O_{33}$ (4×3 blocks) containing a defect of the type seen in Fig. 2(a, b), (5×3 blocks, arrowed). The light and dark rectangles represent blocks of octahedra, which lie at two levels half a unit-cell apart in the structure. The black dots represent tungsten atoms in tetrahedral coordination. Shear planes, 14.9 Å apart, are marked.

and several ordered arrangements were found, containing slabs of the 5×3 blocks of octahedra which occur in H-Nb_2O_5, coherently intergrown with 4×3 blocks of $WNb_{12}O_{33}$. The intergrowing slabs lay at an angle to both sets of shear planes, as shown in the model in Fig. 2(c). This model satisfactorily accounts for the orientation of the Wadsley defects in Fig. 2(a), the direction of the observed streaking in the diffraction patterns, and the slight deviation of the 14.9 Å fringes in Fig. 2(b) as they traverse the defects.

In the very early stages of annealing, defects were observed in other directions (Fig. 3a). They can probably be described in terms of the intergrowth of $WNb_{12}O_{33}$ and the N-form of Nb_2O_5 (*9*), which contains 4×4 blocks of octahedra. Similar intergrowths involving this structure have been found in the TiO_2–Nb_2O_5 system (*10*). A likely model, showing the intersection of this defect with another of the type shown in Fig. 2, is drawn in Fig. 3(b).

Effect of Annealing. The observations on the 8:1 samples are summarized in Table III. In this case, each defect fringe was regarded as a single fault, even when they occurred in groups, as at A in Fig. 2(a). The number of observations made is considerably less than for the 9:8 and 8:5 samples, but nevertheless it is clear that for the 8:1 composition, the number of Wadsley defects drops rapidly to zero after annealing for relatively short times.

4. Discussion

The results described in the previous section have been obtained by examining 131 fragments of material at the unit-cell level of resolution. The total mass involved is estimated to be of the order of 5×10^{-12} g, orders of magnitude less than could be handled by any X-ray technique.

Because the proportions of each of the samples which were actually examined are so minute, it is inevitable that the question "are the results truly representative of the whole sample?," must arise. The only way to answer this question is to continue the study using much larger numbers of fragments, and obtain quantitative measures of the defect concentration. It is certainly true that in some cases

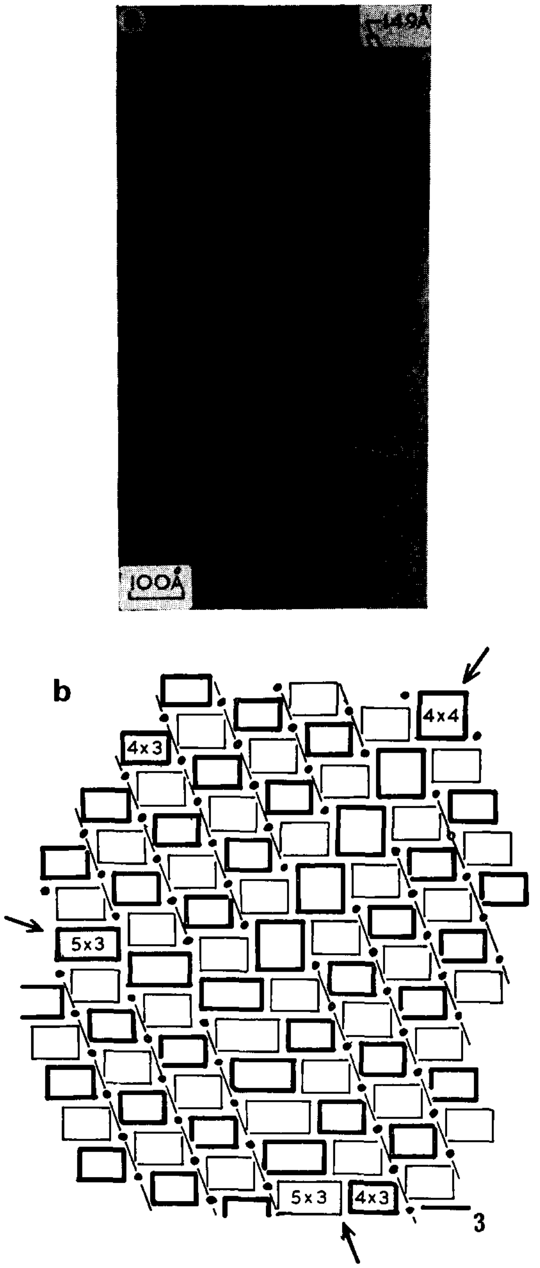

FIG. 3. (a) Lattice image from a fragment of $8Nb_2O_5 \cdot WO_3$ after annealing for 2 hr at 1707°K, showing defects lying in three different directions (arrowed).

(b) Idealized model of the intersection of these defects, circled in Fig. 3(a). The defects are slabs of 5 × 3 blocks and 4 × 4 blocks, which converge to form a third defect running parallel to the shear planes marked by lines.

the defect concentration varied widely between individual fragments in the same sample. However, we believe that the general trends which are evident in Tables II and III are valid, and would be substantiated by more extensive experiments.

A second question which is frequently asked is "do the methods of preparation, particularly the grinding procedures, introduce defects?" It is quite clear from the fact that fragments from some samples contained no defects at all, that a negative answer can be given in the case of these particular materials. Nevertheless, this problem must always be borne in mind, and some oxide samples (e.g. high temperature Ta_2O_5) are severely damaged by grinding, and are therefore difficult to examine in powder form in the electron microscope.

Let us now consider the implications of the results relative to the questions which were referred to in the introduction to this paper.

(1) The results in Table II indicate clearly that the concentration of Wadsley defects in both the 8:5 and 9:8 compositions is reduced by annealing the samples at high temperatures. Although the defects were never entirely removed from any sample, over half the fragments in the 8:5/336 hr, 8:5/768 hr and 9:8/768 hr samples were completely free of defects of any kind observable at the resolution of the microscope (ca. 10 Å). The remaining defects are likely to be due to departures either from true equilibrium, or from the exact stoichiometry required by the crystal structure. In the former case, we would expect to find Wadsley defects which had opposite effects on the composition in the samples, and that annealing would eventually produce homogeneous perfect crystals. Table II shows that even after 768 hr, there are defect fringes corresponding to $W_3Nb_{14}O_{44}$ and $W_8Nb_{18}O_{69}$ in the 8:5 sample, and $W_5Nb_{16}O_{55}$ and $W_{11}Nb_{20}O_{83}$ in the 9:8 sample. This implies that true equilibrium has not been achieved, although it is interesting to note that *individual fragments* in both these samples never contained more than one type of defect fringe spacing, showing that equilibrium is attained on a microscopic scale. It is not surprising that macroscopic equilibrium is difficult to achieve in this system, in view of the likelihood that the differences in free energy of neighbouring phases is very small.

The possibility that nonstoichiometry is the cause of remaining defects seems likely in the case of the 9:8 composition. An inspection of the estimated Nb_2O_5/WO_3 ratios in Table II (column 10) indicates that for the 8:5 composition, fluctuations from the nominal value (=1.600) are random, and become negligible after annealing for 168 hr or more. On the other hand, the ratio in the 9:8 case is always higher than the nominal value (1.125) and varies

TABLE III

ANNEALING OF $8Nb_2O_5 \cdot WO_3$

Anneal time (hr)	Anneal temp. (°K)	No. of fragments	Matrix fringes	Defect fringes	Other defects	Defect conc %
2	1707	7	2535	85	8	3.7
5	1690	5	1425	22	—	1.5
20	1704	6	1840	—	—	0
187	1701	3	1180	—	—	0

randomly about an average of 1.143. This difference may be explained in part by the occasional observation of fragments of WNb_2O_8 in the 9:8 sample, but the reduction of W^{6+} to W^{5+} is probably a more important contributor, particularly after long periods of annealing. The possibility of reduction of WO_3, even when heated in sealed platinum capsules, has been discussed previously (*7*). The consequent change in stoichiometry can be readily accommodated by the formation of small amounts of $W_5^{6+}(W_x^{5+}Nb_{16-x})O_{55}$, having the 8:5 structure. This material has the same Nb/W ratio as $W_8Nb_{18}O_{69}$ for $x = 1.46$, and 5 mole% of it in the sample would be sufficient to explain the discrepancy in overall stoichiometry. This involves the reduction of about 1% of the W^{6+} ions to W^{5+}.

(2) We are confident that the results apply to the materials as they exist at the annealing temperature, and are not seriously affected by the subsequent quenching treatment. If this were not so, we would not expect to observe a systematic trend in defect concentration with annealing time, but rather a probably high density of randomly arranged defects, depending critically on the exact conditions of the quench. The only observation which could be interpreted on the basis of the influence of quenching is that several fragments of the 9:8 composition after long annealing consisted predominantly or entirely of the 8:5 structure. It is known that $W_8Nb_{18}O_{69}$ is unstable below about 1538°K, and if held at 1370°K, it will decompose to WNb_2O_8 and $W_5Nb_{16}O_{55}$ (*7*). However, the likelihood of this occurring during a quench seems small, and if it did occur, we might expect to see highly defective fragments of $W_5Nb_{16}O_{55}$, rather than the observed relatively perfect crystals. It is much more probable that the fragments with the 8:5 structure are a consequence of slight reduction, as discussed earlier.

(3) We have assumed so far that all departures from stoichiometry are accommodated by Wadsley defects. However, the results of annealing samples with the 8:1 composition indicate that this is not true, at least in the case of the $WNb_{12}O_{33}$ structure. We had anticipated that intergrowth of the kind seen in the early stages of annealing (Fig. 2a) would have persisted throughout the heat treatment, leading perhaps to an ordered array of Nb_2O_5 slabs in the $WNb_{12}O_{33}$ matrix. It is easy to show (*8*) that an ordered structure in which rows of 5 × 3 blocks of the type shown in Fig. 2(c) are arranged regularly in the ratio of one to every eight rows of 4 × 3 blocks, has the overall composition $W_7Nb_{112}O_{301}$, i.e. $Nb_2O_5:WO_3 = 8:1$. The separation of the rows of 5 × 3 blocks would be about 77 Å. Figure 2(a) shows the highest density of defects which was observed in any of the 8:1 samples; their average spacing is about 130 Å, indicating that even here there are only about half the number of defects required to explain the departure from stoichiometry.

A second possibility is that high temperature Nb_2O_5 separates out as a second phase after annealing. However, no fragments of Nb_2O_5 were detected by electron diffraction, and a Guinier X-ray powder diffraction pattern of the 187 hr sample showed no lines apart from those of the $WNb_{12}O_{33}$ structure.

We conclude that the annealed 8:1 material is a homogeneous phase, basically similar to $WNb_{12}O_{33}$, but with either an excess of cations or a shortage of anions, expressed by the formulae $8Nb_2O_5 \cdot WO_3 = M_{13.05}O_{33}$ or $M_{13}O_{32.88}$. Two similar anomalies of composition have appeared during recent studies of Nb_2O_5-based oxide structures. The compound $9Nb_2O_5 \cdot GeO_2$ (*11*) appears to be isostructural with a number of other oxides $9Nb_2O_5 \cdot M_2O_5$ (M = P, As, V), containing only pentavalent cations. The structure of these compounds (*12*) is analogous to that of $WNb_{12}O_{33}$, but contains 3 × 3 blocks of octahedra instead of 3 × 4 blocks, the unit-cell contents being $M_{20}O_{50}$. The exact stoichiometry of the germanium compound is not known (*13*), but even if it is actually $9.5Nb_2O_5 \cdot GeO_2 = M_{20.2}O_{50}$ or $M_{20}O_{49.5}$, it is still nonstoichiometric with respect to the ideal unit cell contents. A further example is that of $22Nb_2O_5 \cdot P_2O_5$ (*14*), whose X-ray powder pattern, together with single crystal electron diffraction and lattice images, indicate that its structure is analogous to that of the intergrowth phase $W_4Nb_{26}O_{77}$, but the component blocks are 3 × 3 and 3 × 4, rather than 3 × 4 and 4 × 4. The stoichiometry of this structure is $M_{10}O_{25} + M_{13}O_{33} = M_{23}O_{58}$, in contrast to that of $22Nb_2O_5 \cdot P_2O_5$ which is $M_2O_5 = M_{23.2}O_{58}$ or $M_{23}O_{57.5}$.

In each of these cases, the nonstoichiometry cannot be explained by reduction of one of the cations, because this would *increase* the discrepancy in composition. Nor can we invoke an increase in valence of some of the cations, because they are all in their maximum valency states. At this stage there are at least two possible explanations for these phenomena.

(a) Excess cations might be accommodated at random in the structures, possibly in the channels occupied by cations in tetrahedral coordination. In this connection it is noteworthy that an *hkO* refinement of the $GeO_2 \cdot 9Nb_2O_5$ single crystal X-ray data failed to reduce the conventional *R* value below 15.5% when excess cations were inserted in this position (*15*).

(b) The nonstoichiometry might be accommodated by some type of partially ordered reduction in the coordination number of certain cations. In the case of $9.5Nb_2O_5 \cdot GeO_2$ ($M_{20}O_{49.5}$) and $22Nb_2O_5 \cdot P_2O_5$ ($M_{23}O_{57.5}$) the number of missing anion "available lattice sites" appears to be explainable as the simple fraction one-half, but no simple fraction can account for the 8:1 specimen. Perhaps a combination of cation reduction and unoccupied anion sites may best explain the experimental data. The resolution of this problem requires very careful single crystal X-ray studies of one or more of these phases.

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