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Electrical properties of NbO_2 and Nb_2O_5 at elevated temperature in air and flowing argon

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NbO_2, heated in air, shows sharply decreasing electrical resistance until oxidation occurs at about 486 °C and forms L-Nb_2O_5. This oxidation is accompanied by a first-order increase in electrical resistance. Further heating causes only a slight decrease in resistance until the occurrence of a minimum resistance anomaly, centered at about 800 °C, and showing for the most part a second-order character of the singularity type. The magnitude of this effect is considerably larger in the cooling direction, and the recovered product gives the x-ray pattern of L-Nb_2O_5 rather than the high-temperature H phase of Nb_2O_5. Heating the sample under flowing argon postponed the reaction to Nb_2O_5 to about 750 °C; however, in the cooling direction, the reversal of the anomaly near 800 °C is clearly observed. The minimum resistance anomaly is interpreted to arise from an intermediate stage of a phase transformation centered about reduction and reoxidation phenomena. Heating β-Nb_2O_5 in flowing argon causes a reversible first-order decrease in resistance beginning at about 450 °C associated with the $\beta \rightarrow \delta$ phase transformation followed by a minimum in resistance at 700–1000 °C interpreted as above. In the cooling direction the minimum in resistance occurs between 900 and 700 °C, and the recovered product gives the x-ray pattern of Nb_2O_5 (105*M*) which is a structure very similar to the H phase.

Niobium dioxide is a grey-black nonconductor of the deformed rutile structure. At room conditions NbO_2 is monoclinic with lattice parameters given as $a_0 = 12.03$ Å, $b_0 = 14.37$ Å, $c_0 = 10.36$ Å, and $\beta = 121° 10'$.[1] At elevated temperature in vacuum a transition occurs in the neighborhood of 800 °C and is associated with an increase in conductivity of about one order of magnitude in the range 700–800 °C.[2] Heating NbO_2 in air as well as in flowing argon results in the formation of white powdery L-Nb_2O_5 (also referred to as $Nb_2O_5[56\underline{0}]$) which has the room-temperature unit-cell dimensions (rhombic) $a_0 = 6.168$ Å, $b_0 = 29.312$ Å, $c_0 = 3.936$ Å, $Z = 8$, and density = 4.965.[3] The L phase undergoes a transition to a high-temperature H phase in the vicinity of 850–900 °C.[3] The high-temperature H phase (also called the α phase) is monoclinic[3] and the structure was later refined by the least-squares method to $a_0 = 21.153$ Å, $b_0 = 3.8233$ Å, $c_0 = 19.356$ Å, $\beta = 119.80°$, $Z = 14$, and density 4.548 g/cm^3, space group $P2/m$.[4] Although the literature quoted this high-temperature phase as being irreversible, it does not give the electrical character of the forward transition.

References 5(a) and 5(b) indicate transformations in Nb_2O_5 at 830–1000 and 1100 °C. Reference 5(c) gives x-ray data for the phase transformation at 830 °C calling it β-Nb_2O_5 but in reality identifying the 105*M* phase. (The literature shows considerable inconsistency in nomenclature.)

Very recent work[6] indicates that β-Nb_2O_5 does not undergo transformation to the stable H phase up to 947 °C in oxidizing conditions, and that at or below 747 °C, β-Nb_2O_5 is reduced to NbO_2. The NbO_2 is then reoxidized to block structures $NbO_{2.5-x}$ from which H-Nb_2O_5 is developed from template growth. This work also shows that under buffered oxygen fugacities the reduction and transformation take place simultaneously at and above 877 °C, with the product being a nonequilibrium intergrowth of H-Nb_2O_5.

Studies of thin film and powdered Nb, heated under various conditions, show a progression of reactions and transformations identified by electron diffraction and x-ray diffraction.[7] The forms of the niobium-oxygen system found in this study include Nb-(O) (solid solution), Nb-O (hexagonal), NbO_x (tetragonal), δ-Nb_2O_5, and two high-temperature monoclinic phases of Nb_2O_5. The latter two phases are referred to by the authors as γ-Nb_2O_5 ($a_0 = 7.317$ Å, $b_0 = 15.728$ Å, $c_0 = 10.749$ Å, and $\beta = 120° 30'$) and α-Nb_2O_5 ($a_0 = 21.20$ Å, $b_0 = 3.824$ Å, $c_0 = 19.39$ Å, and $\beta = 120° 10'$).[7] This α phase appears identical to what we refer to as H-Nb_2O_5 in the present paper. The work in Ref. 7 gives 700–800 °C as the $\gamma \rightarrow \alpha$ transition temperature, obtained when heating in air. The $\gamma \rightarrow \alpha$ transition is reported to occur through a unique rearrangement of niobium and oxygen atoms passing two distinct intermediate stages. The intermediate stage shows a set of intense x-ray reflections that do not correspond to either the γ or α phases. Transitions and reactions in the 500–600 °C range all involved the lower oxides such as NbO_x, NbO_z, NbO, and NbO_2.

Data from Ref. 8 indicate that the δ phase of Nb_2O_5 is developed above 440 °C and is a poorly crystallized form of the γ phase. This work[8] reported

830 °C as the transition temperature between γ-Nb_2O_5 (density 5.17 g/cm^3 at 25 °C) and α-Nb_2O_5 (density 4.55 g/cm^3 at 25 °C). The transition was not observed to be reversible and the α phase (H) was indexed as monoclinic ($a_0 = 21.34$ Å, $b_0 = 2.816$ Å, $c_0 = 19.47$ Å, $\beta = 120°20'$, 14 molecules/unit cell, and x-ray density 4.52 g/cm^3). This study also reported 435 °C as the temperature of transition from amorphous Nb_2O_5 to the γ phase. The α phase and the 105M phase were proposed to be identical.

The present experiment heated in air and in flowing argon ten samples of NbO_2, pelleted from single-crystal material, and ten samples of polycrystalline β-Nb_2O_5. The single crystals were prepared by the Czochralski-Kyropoulos method by Professor Paul Raccah of the University of Illinois at Chicago Circle and obtained through his courtesy. The polycrystalline β-Nb_2O_5 was purchased from Alfa Inorganics. Electrical resistance was monitored as a function of temperature through contact with heavy steel anvils and solid cylinders using a simple dc circuit. The sample was pressed into a $\frac{1}{8}$-in.-diameter hole in a mica holder of dimensions varying from a 4 × 4 in.^{2} to $\frac{1}{2}$-in.-diameter disk, and of thickness 0.050 in. In some experiments platinum foil furnished the contact between the sample and the steel cylinders. Heating was accomplished with a Lindberg furnace (model 51441-S).

Figure 1 gives the sample voltage versus temperature data with values of current at specific points for NbO_2 starting material heated in air. In the up-temperature direction the resistance decreases sharply as a function of temperature until reaching a sharp turning point at 486 °C. The resistance subsequently increases to a level higher than the original material. Samples recovered to room conditions from the 600-°C region indicate a white powder yielding the x-ray pattern of L-Nb_2O_5 as given by American Society for Testing Materials powder diffraction fiche No. 27-1003. The oxidation appears to be complete at about 550 °C as implied from the electrical resistance undergoing a second turning point and thereafter falling off gently until an anomaly is encountered in the neighborhood of 840 °C and clearly shown in Fig. 1. At the termination of this anomally the electrical resistance recovers essentially the same value as prior to the anomaly.

In the decreasing temperature direction, the anomaly in the 800–850 °C region is far more pronounced, however, the resistance discontinuity observed upon heating (at the 500 °C region) is not encountered upon cooling. This confirms that the 500 °C discontinuity is due to oxidation of NbO_2 to Nb_2O_5 which is not reversible during the cooling process.

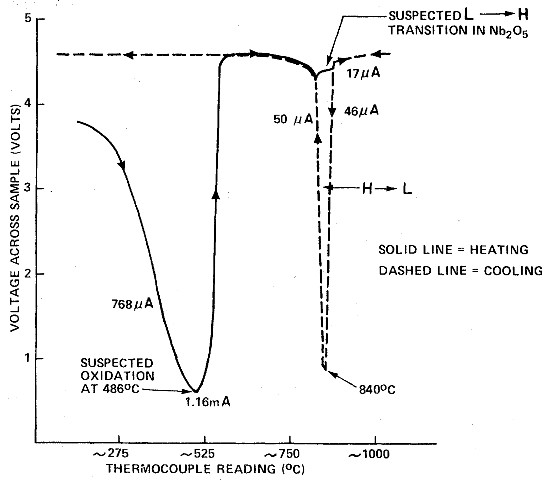

FIG. 1. Raw data from X-Y recorder giving voltage across sample vs temperature for heating and cooling in air environment using NbO_2 single crystal pressed into mica-gasketed pellet. Selected electrical current data points are shown digitally. Down-temperature data are dashed.

The structure of the electrical effect centered at 840 °C gives the appearance of a second-order transition of the singularity type, especially in the cooling direction. However, in the heating direction the fine structure suggests several first-order steps in both the decreasing and increasing aspects of the transition. This step-wise change opens the suggestion of a mixed order transition, or the occurrence of more than one phenomenon during the transition. This interpretation relates to the work of Refs. 6 and 7, indicating that the 800 °C transition in Nb_2O_5 involves two distinct intermediate stages. One intermediate state, or the reduced form, then has a much lower resistance than the final high-temperature phase. This is probably because of the temporary breaking of as much as 20% of the Nb—O chemical bonds and the release of oxygen from the lattice. Excess metal atoms gain an electron and change from Nb^{5+} in Nb_2O_5 to Nb^{4+} forming NbO_2. Any unbonded metal atoms as well as NbO_2 contribute toward lower resistivity. The second state is a reoxidation again producing Nb_2O_5. The difference in the magnitude of the electrical behavior in the up-temperature direction vs the cooling direction suggests different microequilibrium associated with the sequence of a two-process phenomenon. The x-ray analysis at room conditions of the recovered product from the neighborhood of 900 °C yields the pattern for L-Nb_2O_5, a structure very different from that of the H phase. The indication is thus that an insufficient time in the H-phase field, or an unsuitable atmosphere, prevented the H phase to be structurally stabilized for irreversibility. The minimum in resistance could then be associated with the property of an activated or transitory state set up by the reduction to NbO_2, this state having a distinct x-ray pattern.

Figure 2 gives the electrical data for heating NbO_2 in a flowing argon atmosphere (gauge regulator at 15 psi). The electrical effect of oxidation is not evident until about 750 °C. The resistance becomes unstable during this reaction, and it is suspected that the high-temperature transition is masked or hidden in the large discontinuity due to oxidation. Upon cooling, however, a second-order–type anomaly is clearly observed as shown in Fig. 2 (right). The recovered product from the 900 °C region shows a white powder (L-Nb_2O_5) plus a low concentration of grey-black particles (indicating probably residual non-transformed NbO_2).

Thus, notwithstanding the presence of a large amount of flowing argon (one full tank per heating and cooling cycle), the oxidation of NbO_2 still occurs but at a higher temperature and to a slightly lesser extent. The extra oxygen atom per NbO_2 molecule must be derived from oxygen still in the system. It is possible that grain-size effects and ionic effects also influence the conductivity change. However, the important point is that oxidation is associated with increasing electrical resistance based on experimental measurement.

The heating of β-Nb_2O_5 (monoclinic $a_0 = 22.10$ Å, $b_0 = 7.638$ Å, $c_0 = 19.52$ Å, $\beta = 118°15'$) in flowing argon (Figs. 3 and 4) shows a first-order *decrease* in resistance at an average temperature of approximately 452 ± 10 °C, followed by a minimum resistance occurring from about 750 to 1000 °C. The latter effect has again the character of a singularity and parallels the data of Figs. 1 and 2. These data are again in harmony with the interpretation of a two-stage transformation in Nb_2O_5 (in the 700–1000 °C region), the intermediate state showing the minimum electrical resistance (or, as in Fig. 4, two minima turning points upon cooling). The lower temperature electrical phenomenon in Fig. 4 (~450 °C) is a first-order effect causing a decrease in resistance of about four orders of magnitude. This electrical effect at ~450 °C may represent a transition to the δ modification which was reported by x-ray diffraction data[8,9] (at temperatures above 440 °C) to be a poorly crystallized form of the γ phase.[8] In Ref. 7, the δ phase was reported to be developed from NbO_x at 400–550 °C. The decrease in electrical resistance found in the present study is supportive of a reduction to a lower oxide to be associated with the transition to the δ phase.

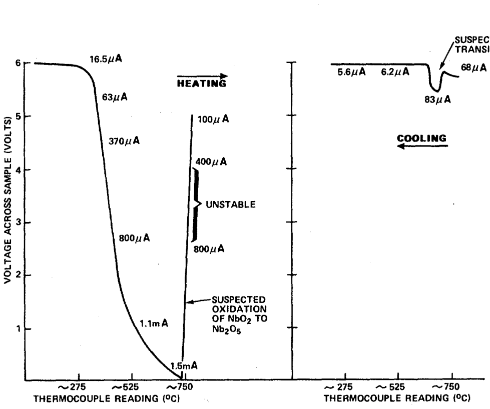

FIG. 2. Raw X-Y data giving voltage (line) and current (digital) for NbO_2 pressed single crystal heated in flowing argon (left) and cooling in argon (right). Both Figs. 1 and 2 suggest that increasing resistance is associated with oxidation.

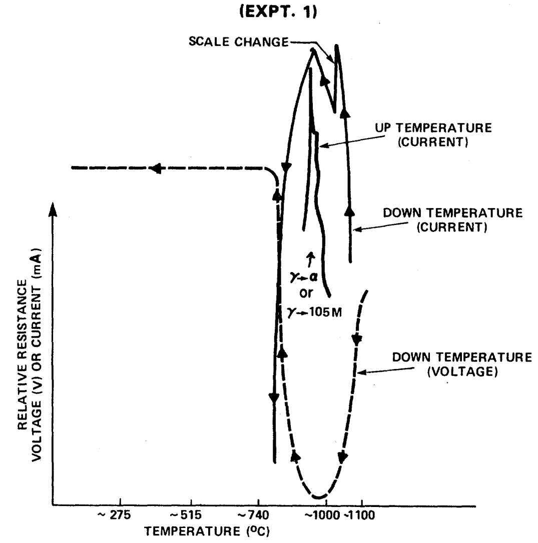

FIG. 3. X-Y recorder data for voltage vs temperature and current vs temperature for heating and cooling using Nb_2O_5 polycrystalline starting material (in argon). Electrical resistance minimum (current maximum) occurs at temperature range similar to that of Fig. 1.

The x-ray data taken at room conditions of the grey-white products recovered from the β-Nb_2O_5 ex-

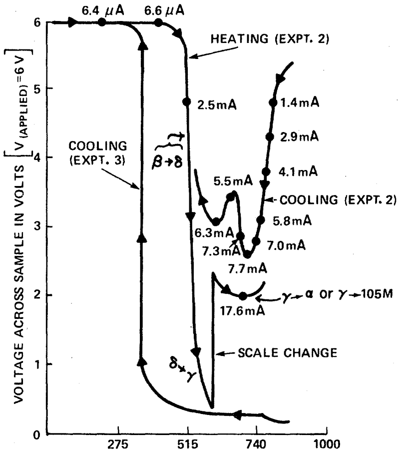

FIG. 4. X-Y recorder data for voltage with digital current at data points vs temperature for heating and cooling polycrystalline Nb_2O_5 in flowing argon. Data show two different starting samples. The high-temperature electrical anomaly recorded upon heating is similar as that given in Fig. 1, and the anomaly recorded upon cooling is similar to what is shown in Fig. 2 during cooling cycle.

periments after high-temperature treatment correspond to Nb_2O_5 (105*M*) which is a monoclinic phase with lattice parameters[5] $a_0 = 20.24$ Å, $b_0 = 3.82$ Å, $c_0 = 20.24$ Å, and with $Z = 15$, $\beta = 120°$, and density 4.84. Thus the 105*M* phase is quite similar to the high-temperature *H* phase, and is less dense than the *L* phase as expected for a high-temperature phase.

The high-temperature electrical effect in Fig. 3 and to some degree that in Fig. 4 shows different electrical behavior depending upon whether heating or cooling. The character and temperature range of these electrical effects reinforce the interpretation that they show similarity to the effects given in Figs. 1 and 2, however, the recovered product from the β-Nb_2O_5 starting material is the 105*M* phase contrasting the *L* phase being recovered from the experiments starting with NbO_2.

It should be pointed out that the structural fluctuations and reported second-order transition at 808 °C in NbO_2 (Refs. 10 and 11) may further complicate the electrical data in Figs. 1–4. If the transition from γ- or *L*-Nb_2O_5 to *H*-Nb_2O_5 does in fact involve a reduction to NbO_2 and a reoxidation to Nb_2O_5 (Refs. 6 and 7), then if the NbO_2 transitory reduced state occurs at a temperature equal to or greater than 808 °C, there should occur electrical effects due to the second-order transition in NbO_2. The observation of some grey-black material in the recovered product, which is probably residual NbO_2 from the experiments that used NbO_2 as a starting material, supports this possibility.

The study that started with Nb_2O_5 shows that the phase that developed at about 450 °C (Fig. 4) is associated with a sharp decrease of electrical resistance over the range 450 to about 550 °C. This effect is interpreted to be due to the $\beta \rightarrow \delta$ transition where the δ phase is believed to be a poorly crystallized version of the γ phase. The development of the δ phase may be associated with a reduction to a lower oxide thereby explaining the decreasing resistance. As temperature and time increase the δ phase probably evolves into the γ phase.

The further but less sharply decreasing electrical resistance from 550 °C to the minimum resistance at 740 (Fig. 4) is believed to be associated with the $\delta \rightarrow \gamma$ evolvement and further reduction, followed by reoxidation as resistance starts to increase. This reduction and reoxidation is interpreted to be related to the $\gamma \rightarrow \alpha$ (or $\gamma \rightarrow H$) phase transition which is reported to occur via two distinct stages. The minimum resistance state is suspected to represent the intermediate reduced stage of the $\gamma \rightarrow \alpha$ phase transformation reported in Ref. 7. The phase recovered from temperatures above the resistance minimum is the 105*M* phase which is very similar to the *H* phase. It may be that at equilibrium in a reducing atmosphere or at higher temperature the *H* phase would have been recovered. Upon decreasing temperature the resistance minimum is consistently reversible, and in one experiment the major resistance effect (Fig. 4) at lower temperature was reversible; however, no indication of the γ, δ, or reduced phases is found from x-ray diffraction. This indicates that electrical effects were associated with reversible reduction and/or oxidation phenomena but not with the reversal of the structural phase transition to the 105*M* phase. The differences between the electrical data in the up- and down-temperature directions is thus suspected to be due to the absence (upon cooling) of the component of the resistance change arising from the difference of the electrical properties of the two phases (thus including only resistance changes due to oxidation and reduction).

Heating NbO_2 in air and in a flowing argon-air mixture (Figs. 1 and 2) results in oxidation to the *L* phase of Nb_2O_5 (the $[56\underline{0}]$ phase). At higher temperature the very sharp resistance minimum (840 °C) is believed to be related to reduction and oxidation. However, because of the absence of a reducing atmosphere and perhaps because of insufficient time at high temperature neither the *H* phase nor the similar 105*M* phase is stabilized, and instead the *L* phase $[56\underline{0}]$ is observed upon recovery to room conditions. The oxidation from the initial NbO_2 to the resulting Nb_2O_5 is on the other hand irreversible from both the electrical and structural data.

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