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THE EFFECT OF STRESS ON THE
LOW-TEMPERATURE OXIDATION OF NIOBIUM

by

Lawrence John Weirick

Ph.D. Thesis, May 1969

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THE EFFECT OF STRESS ON THE
LOW-TEMPERATURE OXIDATION OF NIOBIUM

by

Lawrence John Weirick

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THE EFFECT OF STRESS ON THE
LOW-TEMPERATURE OXIDATION OF NIOBIUM*

Lawrence John Weirick

ABSTRACT

A lateral compressive stress of about 94,000 psi was found to exist in a thin film of niobium pentoxide which had formed on niobium oxidized near 425°C in oxygen at atmospheric pressure for up to three hours. This compressive stress agreed very well with a known value of room-temperature compressive strength of niobium pentoxide of 117,000 psi. A compressive stress in an 'effective' thin film of NbO_x was found to be about 125, 150 or 177 thousand psi if the thin film is composed of Nb_6O , Nb_5O , or Nb_4O , respectively, the reported formulae for NbO_x . The resulting tensile stress on the substrate surface due to the oxidation process was found to be small, around 10,000 psi.

It was found that the formation of niobium suboxide needles or plates, NbO_x , formed during the oxidation of niobium in the temperature range of 425°C to 440°C, was a function of initial specimen oxygen concentration, oxidation temperature, and applied tensile stress. It was further found that when the oxygen concentration at the substrate surface had reached an equilibrium level and the suboxide plates had formed, only a small tensile stress (less than 10,000 psi on low oxygen content niobium) was needed to form microcracks in a surface of the metal associated with these suboxide needles. Evidence was given to show that these microcracks upon further oxidation formed niobium pentoxide wedges into the metal which caused premature failure of niobium metal parts.

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INTRODUCTION

The instability of niobium and niobium alloys in an oxygen atmosphere is a major shortcoming and deters their use at higher temperatures. Accurate knowledge of the oxidation characteristics of pure niobium should be of value in developing means to reduce its rate of oxidation. The effect of temperature and oxygen pressure on the oxidation of niobium has been studied quite extensively by a number of investigators. The effects of specimen pretreatment, surface preparation, impurity content and specimen geometry on the oxidation of niobium have been studied less frequently but published data are available. The effect of stress on the oxidation of niobium has been studied briefly and semiquantitatively by Pawel and Campbell. Observation of niobium oxide 'spikes' has been reported by Kolski and Doyle but no explanation of why this phenomenon occurred was presented. This work was undertaken in an attempt to contribute to the overall knowledge of the oxidation of niobium particularly in the area of the effect of stress and the reason for the occurrence of oxide 'spikes'.

PRIOR WORK

Oxygen Solubility in Niobium

The first work published on the solubility limit of oxygen in niobium was done by Seybolt (1) in 1954. Using lattice parameter measurements and microscopic examination, he found the solubility to vary from 0.25 w/o oxygen at 775°C to 1.0 w/o oxygen at 1100°C. Elliot (2) reported the solid solubility of oxygen in niobium to vary from 0.25 w/o oxygen at 500°C to 0.72 w/o oxygen at 1915°C, which data were obtained by microscopic examination in 1959. Bryant (3) in 1962 used vacuum fusion to analyze the oxygen content of prepared samples. He found the solubility to vary from 0.13 w/o oxygen at 700°C to 0.97 w/o oxygen at 1550°C. During this same year Lenel, Regitz, and Hulsizer (4) used lattice parameter measurements and microscopic examination to briefly investigate the solid solubility of oxygen in niobium between 650°C and 1250°C and found their data to correspond closely to those of Elliot.

In 1963 Gebhardt and Rothenbacher (5) employed electrical conductivity, microhardness, and lattice parameter measurements to determine the solubility limit of oxygen in niobium between 500 and 1900°C. They found the solubility increased from 0.19 w/o oxygen at 750°C to 0.97 w/o oxygen at 1540°C closely

matching the findings of Bryant, especially at the higher temperatures. They found considerable deviations from their analytical equation above 1540°C and below 750°C . They believe the deviations above 1540°C are partially caused by degassing of the niobium samples and partially by instability of the highly supersaturated α -solid solution during quenching. The deviations which were found between 750 and 500°C were ascribed to a lack of equilibrium between oxide and α -solution. This conclusion was drawn from data on the precipitation of oxides from homogeneous supersaturated niobium oxygen solid solutions. The simultaneous formation of several oxide phases indicates that equilibrium was not achieved at lower aging temperatures and/or that some of the observed oxides are metastable phases.

In 1965 Lenel and Hulsizer (6), upon doing some further work on the solubility of oxygen in niobium, corrected some earlier data and reversed some previous statements about the solubility limits. They then gave values ranging from 0.27 w/o oxygen at 850°C to 0.70 w/o oxygen at 1300°C . In 1967, Taylor and Doyle (7) used X-ray diffraction, micrographic, and thermal techniques using both a dynamic leak method and a Sieverts apparatus to find the interstitial solid-solubility of oxygen in niobium. They found the solubility increased

from 0.47 w/o oxygen at 1000°C to 1.07 w/o at 1775°C. Above 1775°C in vacuum they found the samples degassed rapidly with increasing temperature.

A summary of the conditions used by the preceding workers (1-7) in determining the solubility limit of oxygen in niobium as a function of temperature is given in Table 1. A summary of the data reported by these investigators is shown in Figure 1.

An important result to be noticed in Figure 1 is that, with the exception of Elliot's data, if the curves are extrapolated to a temperature of 500°C, the value for the oxygen solubility in niobium falls between 900 and 1000 ppm for all the extrapolations.

Niobium Oxides

NbO_x

By heating niobium powder at 350°C Brauer and Müller (8) found that niobium may take up more oxygen than that corresponding to the saturation values. The body-centered cubic niobium lattice is thereby transformed into a closely related body-centered tetragonal lattice, which they designated NbO_x. Brauer, Müller, and Kuhner (9) have estimated the oxygen content to be about 2.5 wt. % which would give the approximate

composition of Nb_6O . In a number of cases, Hurlen et al. (10) found separate and well defined X-ray diffraction peaks adjacent to and at the low angle side of the strong Nb-peaks. Their results show that the interplanar spacing for NbO_x , within experimental errors, always comes out with the same value, independent of the conditions under which it was formed, and independent of the corresponding values for the Nb- spacing. They suggest this indicates that NbO_x really is a separate phase and not just an oxygen saturated part of the niobium phase. Norman et al. (11) have shown that NbO_x has a metallic appearance with optical properties very similar to those of the metal.

NbO_z

Another tetragonal niobium oxide was found by Hurlen et al. (10) on sheets oxidized at medium temperatures ($400\text{--}500^\circ\text{C}$) in oxygen at pressures from 100 torr and below. This oxide was first called NbO_y by Hurlen et al. but later it was designated NbO_z . Attempts to produce this phase by arc melting niobium and Nb_2O_5 have not been successful. NbO_z has a strong tendency to form platelets which penetrate the metal matrix. Doyle (12) found this oxide present next to the metal in the temperature range of 500 to 575°C . He found the number of

NbO_2 needles and the total oxidation rate increased very rapidly with an increase in temperature in this range. Doyle also found that the temperature for formation of NbO_2 needles could be suppressed below 500°C by cold working the niobium before the oxidation studies. Norman et al. found that the (100) plane of an NbO_2 needle was parallel to one of the 100 planes of the Nb metal lattice. Upon oxidizing the surrounding metal substrate as well as the NbO_2 needle, a trail of holes is left by the NbO_2 needle. By roughly analyzing the volume of the holes produced as opposed to oxide in between the holes, an approximate composition of NbO_2 can be taken as Nb_2O . Norman et al. (11) showed this oxide to be gray in appearance and to be optically active.

TaO_2 Van Landuyt and Wayman (13) reported a study by electron microscopy, electron diffraction and optical microscopy concerning the initial stages of the reaction of tantalum with oxygen. In tantalum sheets oxidized for short times (~10 min) at 500°C in oxygen of atmospheric pressure, the TaO_y orthorhombic suboxide phase was detected, which appears in the shape of plates in a layer near the surface highly enriched in oxygen. The orientation relationship between the parent and

product phase was determined from electron diffraction. The plates have a $\{320\}$ habit plane. An internal fine structure in the plates was identified as microtwins with a (101) twinning plane.

Van Landuyt and Wayman detected a surface tilt associated with the plates using a two-beam interference microscope. This result, together with their electron transmission and diffraction observations, and the results of a hot stage optical study strongly suggest that the transformation to TaO_y can be considered martensitic.

Van Landuyt and Wayman obtained evidence that the controversy existing in the literature about the habit plane of the suboxide phases can be explained by the formation of a TaO_z overgrowth on top of the TaO_y plates.

NbO

Brauer (14) found that NbO has a very narrow homogeneity range and a defect sodium chloride structure. Andersson and Magneli (15) have found NbO to be stable up to the melting point and O'Driscoll and Miller (16) found that NbO evaporates without disproportionating at temperatures to 2200°C at low pressures. The above data (15,16) indicate a density of 7.27 g/cm^3 in good agreement with the pycnometrically determined

value (14,15) of 7.30 g/cm^3 . Brauer (14) has shown that NbO is gray with a metallic luster.

NbO₂

NbO₂ also has a very narrow homogeneity range (14). Magneli et al. (17) found that the powder X-ray diffraction pattern of NbO₂ was compatible with a tetragonal unit cell very close to a rutile structure. The density calculated from these data (17) is 5.90 g/cm^3 which is in fair agreement with the pycnometrically determined value (17) of 5.98 g/cm^3 . NbO₂ is gray-green to black and is very optically active.

Nb₂O₅

The homogeneity range for Nb₂O₅ was found by Brauer (14) to be NbO_{2.50}-NbO_{2.40} at 1400°C . He reported three allotropic forms of the pentoxide with the following transformations: T to M at 1000°C and M to H at 1100°C . Holtzberg et al. (18) showed later that the M- form was a poorly crystallized state of the monoclinic H- phase. They found the transformation from T to H to occur irreversibly at 830°C without any measurable heat effect. H. Goldschmidt (19) found that when pure H or α -Nb₂O₅ was heated isothermally for prolonged periods at temperatures within the nominal T or γ -Nb₂O₅ region, under no circumstances could it be broken down. In contrast, when T or

γ -Nb₂O₅ was heated at constant temperatures, even in the " γ " region, it always transformed to " α ", very slowly at 600 and 700°C, and at increasing rates at 800, 900, and 1000°C.

M. Goldschmidt (20) found results similar to these.

Arbuzov and Chuprina (21) gave the structure of γ and α -Nb₂O₅ based on X-ray diffraction data as crystallizing in the rhombic system. Gatehouse (22) assigned the high-temperature form of Nb₂O₅ to the monoclinic system. Holtzberg et al. (18) have also assigned the α -Nb₂O₅ to a monoclinic system and calculated a X-ray density of 4.52 g/cm³ in excellent agreement with his pycnometric density (18) of 4.55 g/cm³. A choice of the monoclinic system for γ -Nb₂O₅ by Frevel and Rinn (23) gave an X-ray density of 4.99 g/cm³ which was in poor agreement with the pycnometric density of 5.17 g/cm³ reported by Holtzberg et al. (18). Therefore, this choice was questionable. It is interesting to note that the density is lower for α -Nb₂O₅ (4.55) than for γ -Nb₂O₅ (5.17). It is still lower for amorphous Nb₂O₅ (4.36) (18).

All allotropic forms of Nb₂O₅ are white when stoichiometric but darken appreciably when the oxygen content decreases slightly.

Oxidation of Niobium

The oxidation of niobium has been studied by a great number of investigators (8-68). Some (69,70) have also reviewed and critically discussed the data available to them.

The methods used by the various authors in studying the oxidation rate of niobium briefly:

- the interference color method

- the electrical resistivity method

- the capacity method

- the volumetric method

- the monometric method

- the intermittent weighing method

- the quartz helix method

- the micro-torsion balance method.

Most of the rate experiments have been performed at constant temperatures. The oxidation process has, moreover, been studied "in situ" by means of X-ray diffraction (19) and electron diffraction (71) techniques.

A number of investigations have also been made on oxidized specimens after cooling to room temperature, and the following techniques have been applied by various authors:

- X-ray diffraction

electron diffraction

electron microscopy

metallographic examination

micro-indentation hardness measurements.

These investigations mostly concern the oxides formed on the metal surface. The micro-indentation hardness measurements (and partly also the X-ray diffraction measurements) give information on the penetration of oxygen into the metal core. The oxidation process and the oxides formed have been studied by Hicks (39) using motion pictures.

The earliest work on the oxidation of niobium was done by McAdam and Geil (57) in 1942. The next work was done by Phelps, Gulbransen, and Hickman (71) in 1946. Gulbransen and Andrew (34) continued doing the first fairly extensive work in 1949-50. In the 1950's many more investigators tried varying techniques and checked different parameters affecting the oxidation of niobium. Inouye (41), Bridges and Fassel (29), Klopp, Sims, and Jaffee (43), Gulbransen and Andrew (35), Cathcart, Campbell, and Smith (31), Goldschmidt (19), and Gurlen (36) all did work on the oxidation of niobium in this time period. Hurlen et al. (10) published the most extensive work done up to this time in 1960. They summarized all the

previous research done and used many of the techniques of individual authors before them. Per Kofstad continued the research with this group and published a number of papers (45-49) in the following years. Many other investigators, including a number of Russians, have studied certain aspects of the oxidation of niobium in the first half of the 1960's.

Table 2 summarizes the investigators, the temperature range investigated, the year of publication, the atmosphere used, the specimen shape, the experimental techniques used, any special parameters affecting the oxidation, and the point of interest of the research.

Oxidation/Time Relationships

From the results presented in the majority of the publications, it appears that the weight gain versus time curves may be represented by a common generalized curve shown in Figure 2 (10). This curve indicates that several oxidation stages are observed for niobium. According to the rate equations which best fit the oxidation data, these stages have been called

the linear (I) stage

the parabolic (II) stage

the transition (III) stage

the linear (IV) stage
the parabolic (V) stage, and
the parabolic (VI) stage.

All these types of oxidation stages are not observed at all temperatures and oxygen pressures. At lower temperatures, the linear (I) oxidation stage dominates at low pressures and the parabolic (II) oxidation stage at high pressures. At higher temperatures the linear (IV) or the subsequent parabolic (V or VI) oxidation stages dominate at least at the higher oxygen pressures. The relationship between the rate curves for the various conditions of temperature and pressure does suggest that, in the latter case the oxidation probably passes through the first stages too quickly for these to be observed, and that the oxidation in the former case is too slow for the later stages to be reached within the experimental time applied.

In the temperature range of interest (420 to 430°C), the linear (I) stage exists for less than five minutes, the parabolic (II) stage lasts for about 30 more minutes, the transition (III) stage takes about 20 minutes to pass through, and the linear (IV) stage exists for the remainder of the experiments.

Oxidation/Temperature Relationships

The effect of temperature on the occurrence and the extension of the various oxidation stages found for niobium has already been described in the preceding section.

The effect of temperature on the linear IV oxidation rate which is the predominate oxidation rate above 500°C can be presented simply by an oxidation rate versus temperature curve. Figure 3 is such a curve representing the results reported by most investigators at atmospheric pressure (10,12). It can be seen that the oxidation rate increases with temperature from $300-575^{\circ}\text{C}$, goes through a maximum around 575°C , and then decreases to approximately 650°C . The oxidation rate passes through a minimum at 650°C and then increases with temperature to about 900°C . At 900°C the rate goes through a second maximum, experiences a slight drop, goes through a minimum around 1000°C and then increases again to 1400°C .

This second reversal in the oxidation rate was usually associated with the transformation of niobium pentoxide from a low temperature to a high temperature form; called M-T or $\gamma-\alpha$. The first reversal in the oxidation rate has been the subject of investigation of many researchers (12,24,26,29,48,50,55). The strongest evidence between oxidation rate and

possible causes appears to be the correlation between the reversal in the oxidation rate and the change in the innermost oxide from NbO_2 to NbO as reported by Doyle (12). A closely related proposal was given by Kofstad (48) in that he believes the reversal in the linear oxidation rate is caused by competition between the rate of nucleation and the rate of growth of NbO on NbO_2 .

Oxidation Products

Oxygen contamination of underlying metal

Oxygen contamination of underlying metal can be followed by microhardness measurements. Tottle (72), Seybolt (1), Di Stefano (73), and Lenel and Hulsizer (6) measured the diamond pyramid hardness of niobium as a function of the weight of oxygen introduced into the metal and obtained similar results. Tottle's data is shown in Figure 4. From this microhardness versus oxygen content curve, data obtained from the literature presenting hardness versus distance penetration into the metal can be correlated to percent oxygen versus distance into metal. Hurlen et al. (10), Klopp et al. (43), and Kolski (50) have included curves of hardness versus distance from oxide/metal interface in their publications. The curves are difficult to compare because the authors used varying hardness measurements,

temperatures, and times of oxidation. The general trend is that the hardness near the metal/oxide surface increases respectively with increasing temperature while the hardness level at the center remains nearly constant. After longer times, the hardness level at the center also increases respectively with increasing temperature. An example showing that the depth of contamination in niobium by oxygen is proportional to time and temperature is shown in Figure 5 as reported by Klopp et al. (43).

An important point to observe from Figure 5 is that if the curve is converted to oxygen content versus distance from surface using Figure 4, the oxygen content near the surface considerably exceeds the solubility limit of oxygen in niobium for a specified temperature.

Ordering of interstitial oxygen

Ordering of interstitial oxygen was observed by Van Landuyt (74) as an oxidation phenomenon in the solid solution period of the process. He believed this ordering represented an intermediate stage in the transformation to the other oxide phases. He reported that the process started by a nucleation mechanism whereby nuclei consisting of small parallel domains were formed. These nuclei have been observed on foils oxidized

at temperatures of 600°C in reduced pressure of air, and the transformation sequence could be followed also by heating the foils in the electron microscope.

On further heating more small domains were added to the nuclei and they grew in the length directions in such a way that after prolonged treatment whole areas were covered with a cross-hatched pattern having the appearance of a grain structure. The growth of the domains proceeded in strict crystallographic directions being in the $\langle 110 \rangle$ directions on a (100) oriented foil. By the ordering of the interstitials a superlattice with an axis of two times the niobium axis originates as is evidenced by the supplementary spots in the electron diffraction patterns presented by Van Landuyt (74). He also observed the small domains nucleate preferentially at dislocation lines although the presence of dislocations is not a condition for the nucleation process to take place. Van Landuyt emphasized that the nucleation process under consideration takes place in the interior of the metal so that nuclei were observed over the whole length of the dislocation lines. He determined the habit planes of the domain walls and the internal twins observed to be of the (110)-type or (112)-type. He suggested that these domains were of the same nature as the

larger domains he observed in niobium foils treated as bulk material. These domains were revealed by the fringe pattern at the boundaries and by the supplementary spots in the electron diffraction images he presented.

Van Landuyt proposed that theoretically it should be possible to calculate the expected habit plane for the transformation Nb(O) ordered phase. Therefore one could assume the transformation to proceed crystallographically as a martensitic transformation. Although the lattice of the ordered phase is hitherto not completely determined, the appearance of the domains suggests strongly that such a mechanism may be accounted for by the martensitic process.

This work by Van Landuyt corresponds with observations made by numerous other authors (10,50) who reported that interference colors were observed early in the low temperature oxidation of niobium but that no X-ray diffraction lines could be observed other than those attributed to the expanding niobium metal lattice.

Adherent inner oxide layer

An adherent inner oxide layer which was not removed on wire brushing the underlying metal core has been studied using metallographic, X-ray diffraction, and electron diffraction

techniques. Doyle (12) and Hurlen et al. (10) have found the lower oxide NbO_x as a very thin layer on the metal in the temperature range 400 to 475°C . Both observed NbO_x metallographically and Hurlen et al. identified it by X-ray diffraction data. Doyle and Hurlen et al. have also found the lower oxide NbO_2 as thin platelets or needles penetrating the metal in the temperature range 500 to 575°C .

In the temperature range 625 to 700°C , Doyle (12) found by metallographic examination a very thin layer of NbO .

Hurlen et al. (10) found by metallographic examination and X-ray diffraction data that NbO was formed during oxidation at oxygen pressures of 10^{-2} torr or lower in this temperature range. He also found NbO_2 diffraction lines at oxygen pressures of 1 torr or lower. Klopp et al. (43) also found a thin layer of NbO in this temperature range.

From 700 to 850°C , T of $\gamma\text{-Nb}_2\text{O}_5$ was identified by a number of investigators using all three previously mentioned techniques. In fact, Arkharov et al. (25), Burova et al. (30), Hurlen et al. (10), Klopp et al. (43), Kofstad et al. (46), and Kolski (50) have identified a thin, black, adherent layer present at all temperatures in the range of 400 to 1325°C to be strongly oriented T or $\gamma\text{-Nb}_2\text{O}_5$.

From 825°C and above Kolski (50) found a similar oriented oxide which he identified as H or α -Nb₂O₅.

Outer oxide layers

The outer oxide layers have been observed, investigated, and identified by almost all of the investigators of niobium oxidation using all of the varying techniques mentioned previously. There is unanimous agreement in all data with the exception of the temperature range around 850°C. In the temperature range of 400 to 700°C, only T or γ -Nb₂O₅ oxide was present although it did change in quality from a porous powder at 400°C to very non-adherent scales at 600°C to more-adherent scales at 700°C. Above 700°C traces of poorly crystalline H or α -Nb₂O₅ were observed along with the T or γ -Nb₂O₅. This trend continued with increasing amounts of H or α -Nb₂O₅ to 825°C. From 850 to 950°C the outer oxide was substantially layered scales of imperfectly crystalline H or α -Nb₂O₅. Above 975°C, the outer scale was crystalline H or α -Nb₂O₅ which was voluminous and porous. Table 3 summarizes these results.

Break-away phenomena

A "break-away" phenomena in the temperature range of 400 to 450°C was observed and studied by Harvey and Draper (37) and Pawel et al. (60) using optical and electron microscopy,

electron and X-ray diffraction, volumetric weight gain measurements, and capacity measurements. The oxidation proceeded as follows: The initial process was the formation of a thin, coherent, protective, amorphous oxide film, accompanied by dissolution of oxygen in the metal. The kinetics of film growth during this period followed a logarithmic rate law which was governed by metal ions moving outward through the film. There then followed a faster growth rate where crystal nuclei form at the metal/oxide interface and the presence of crystalline pentoxide was detected. The rate was increased because this nucleation has led to a shortening of the intergranular diffusion paths. The final "break-away" stage was caused by further growth of the nuclei causing cracking of the overlying amorphous film and continued growth by inward migration of oxygen. This entire process is then repeated in a cyclic manner causing a layered oxide structure.

Stress Measurements

History

It was originally postulated by Pilling and Bedworth (75) that the majority of oxide films should form in a state of compression since the volume of the oxide is greater than the metal oxidized. Exceptions to this rule would occur in cases

like magnesium where the volume of the oxide is less than that of the metal. At the time when Pilling and Bedworth put forward their hypothesis it was thought that metal oxide films grew by the inward diffusion of oxygen. Now, it is known that in most cases they grow by outward metal ion migration which process should give rise to a stress-free film.

In 1950, Dankov and Churaev (76) showed that if a thin layer of metal was evaporated onto one side of a strip of mica, subsequent oxidation caused the mica to bend, the direction of the bending depending on whether the volume ratio was greater or less than unity. These experiments were carried out at room temperature and in the case of iron and nickel, bending occurred in a direction which indicated a volume ratio greater than unity, while in the case of magnesium it indicated a value less than unity.

Jaenicke and Leistikow (77) carried out similar experiments on silver-plated copper in the range 300-500°C in 1964. They used a long, thin strip of copper bent into the form of a helix which unwound upon oxidizing. However, at the higher temperatures serious difficulties were encountered due to the diffusion of oxygen through the silver layer.

In 1965 Tylecote (78) extended the range of temperature

of the work on copper although perhaps less quantitatively. He used discs of metal placed on the top end of a vertical mullite tube through which a protective atmosphere of H_2 , N_2 , and Ar passed. Thus when only the top side of the metal disc oxidized, the disc "domed" and the height increase was followed with a cathetometer. Conversion of the height of the dome data to stress values was not made, but the dome data was used in a qualitative manner. Tylecote carried out a limited amount of work on nickel and titanium using the same experimental techniques.

Bollenrath and Buresch (79) in 1966 studied the effect which oxygen under a pressure of 0.1 mm Hg or air under atmospheric pressure exert on the state of internal stresses caused in the zirconium by the pressure due to the growth of the oxide film. Their tests were carried out in a temperature range from 400 to 800°C using rods and tubing of zirconium. They measured the dilation of these test pieces with time by means of a dilatometer. Their calculations showed that from the start of the corrosion, the zirconium metal was subjected to multiaxial stresses which can surpass the elastic limit, and thus result in plastic deformation.

In 1968 Stringer (80) published a paper primarily con-

cerned with the geometrical effects on the oxidation of tantalum but from which some rough stress calculations were made. He oxidized tantalum specimens in the form of short tubes at 825 and 930°C in oxygen at a pressure of approximately 400 torr. Stringer kept the external diameters of all the specimens the same, but varied the internal diameter. He found the oxidation rate of the inner surface decreased with decreasing radius of curvature, but the rate on the outer surface remained constant and was approximately the same as that on the inner surface for the thinner-walled tubes.

Stringer found that the metal tubes dilated during oxidation because of the stresses generated at the oxidizing surfaces. His results suggested that the major source of this stress was in the adherent part of the oxide scale rather than in the surface layers affected by solution of oxygen. Using a measured value of dilation as a strain measurement, Stringer roughly calculated the compressive stresses in the adherent pentoxide layer to be in the order of 5×10^5 p.s.i.

The next apparent application of Dankov and Churaev's original technique was made by Pawel, Cathcart, and Campbell (81) in 1963. They used thin rectangular specimens of tantalum which were protected on one side by vapor-deposited

aluminum. A quartz fiber was hung onto the specimen with the end through an "eye" located at the bottom end of the aluminum-coated side. The fiber extended so that deflection measurements could be made through a quartz window in the part of their apparatus beneath the furnace. Deflections were measured with a cathetometer and from geometrical considerations, radii of curvature of the specimen were calculated. Using these radii of curvature calculations and the simple flexure formula for a beam, bending stresses were determined. These bending stresses were correlated with known oxidation rate behavior and oxide morphology. They found the simplest stress model, that of a uniform film on a substrate, to be an inadequate description of the stress source, thus reflecting the complexity of the tantalum-oxygen reaction. A model relating the stress gradient to the oxygen concentration gradient was tested and shown to be reasonably consistent with the experimental data. The stress value due to this oxygen concentration gradient was calculated to be approximately 50,000 psi compression.

In a subsequent paper published in 1966, Pawel and Campbell (61) expanded their earlier studies on tantalum to higher temperatures and longer times. They also made some rough

measurements on niobium sheet specimens which will be further discussed later. For tantalum they found that for longer times at lower temperatures and for higher temperatures the attribution of the compressive stress to the oxygen concentration gradient alone no longer was valid. A thin-film contribution must be considered. They did not suggest any value for a compressive thin-film stress for tantalum.

Elastic strains may arise during oxidation as a result of any of several possible mechanisms when one solid phase is forming on another under isothermal conditions. For niobium oxidation, these sources of strain may be classified generally as those associated with (a) the establishment of defect gradients, (b) epitaxial effects, and (c) volume changes during the reaction.

Defect gradients

Theoretical The relationship between defect gradients and stress gradients has been treated by Richmond et al. (82) for the case of an impurity gradient in the surface region of a metal. They used a thermoelastic analogy to derive an equation for the greatest compressive surface stress in the metal which corresponds to the beginning of impregnation when the solute is limited to an infinitesimal surface layer.

$$S = \frac{\beta E C_o}{1 - \nu} \quad (1)$$

where for niobium at 425°C, S = greatest compressive surface stress (psi), β = lattice dilation coefficient = 0.0012 (at. %)⁻¹, E = Young's modulus = 14.5x10⁶ psi., ν = Poisson's ratio = 0.34, and C_o = surface concentration of oxygen. As an example, take C_o = 1.0 at. % (0.17 wt. %), then the calculated stress S is 29,000 psi. A plot of Richmond's oxygen solution stress versus oxygen content is given in Figure 6. Equation 1 is derived in detail in their paper.

Experimental Pawel, Cathcart, and Campbell (81) derived an equation for the surface stress in a metal due to oxygen solution as a function of bending stress. As shown more extensively in their paper, their oxygen-solution model was based on a diffusion treatment. The surface stress as derived by Pawel et al. (81) is:

$$\sigma_I = 2\sigma_s \frac{h^2}{d(3h-2d)} \quad (2)$$

where σ_s = maximum bending stress, h = specimen thickness, and d = a distance parameter determined from diffusivity data.

Pawel and Campbell (61) measured macroscopic bending stress by means of flexure experiments and applied the simple "cantilever beam" flexure formula (83) to estimate the maximum

bending stress, σ_s , derived in Crandall and Dahl (83):

$$\sigma_s = \pm \frac{Eh}{2\rho} \quad (3)$$

where E = Young's modulus of the metal, h = specimen thickness, and ρ = radius of curvature of the specimen. The surface stress which Pawel and Campbell calculated from their measurements and these relations ranges from 29,000 psi. at the start of oxidation to 35,000 psi. for 10 to 40 minutes of oxidation time at 425°C.

These values of surface stress based on experimental measurement agree very well with the theoretical calculation.

Epitaxial stresses

Theoretical If the oxide grows coherently and epitaxially upon the metal substrate, the oxide film upon a single metal grain would be so highly oriented as to be a virtual single crystal. If the spacing of atoms in the oxide and metal are different, then atomic interactions across the metal/oxide interface cause epitaxial strains in both the metal surface and oxide surface.

Experimental Neither single crystal oxide growth, distortion in the metal surface layer, nor distortion in the oxide surface layer have been observed for the oxidation of niobium. Therefore, epitaxial strains in the oxidation of

niobium are most likely absent or insignificant.

Volume changes during reaction

Theoretical Case I: The case where anion diffusion predominates and the oxide is formed isotropically and is adherent to the metal. When a segment of the metal lattice at the metal/oxide interface is converted to oxide, three-dimensional expansion of the metal lattice is required to bring the metal ions into their new positions in the oxide. This expansion is resisted by the overlying layers of previously formed oxide and can occur only through the distortion of this layer. For a three-dimensional expansion of the metal lattice to the niobium pentoxide lattice (oxide/metal volume ratio = 2.68), the linear expansion ratio would be the cube root of 2.68, or 1.39. Under the condition of complete constraint, the compression of the oxide to 1.00 elastically, gives a unilateral strain of 0.39 which times the Young's modulus for the niobium pentoxide ($E = 4 \times 10^6$ psi. for Nb_2O_5 with 10% porosity (84)) gives a compressive stress of 1.56×10^6 psi. If the condition for complete constraint does not hold but instead there is a sharing of strain equally between the oxide and metal, the unilateral strain would be 0.195. This strain times the Young's modulus for niobium pentoxide gives

a compressive stress of 753,000 psi. Therefore, a compressive stress in the niobium pentoxide layer based upon the Pilling-Bedworth ratio would be extremely high and should be easily measured by flexure experiments.

The preceding example was given for the better known case of niobium pentoxide in the amorphous state. Other calculations can be less rigorously made on the lower oxides and suboxides of niobium. Using the Pilling-Bedworth ratio (85):

$$\frac{\text{Volume of oxide}}{\text{Volume of metal}} = \frac{Md}{amD} \quad (4)$$

where M = molecular weight of the oxide, D = density of the oxide, m = atomic weight of the metal, d = density of the metal, and a = number of atoms of metal per molecule of oxide with oxide formula Me_aO_b and data extrapolated from known oxide density data as shown in Figure 7, the unilateral strain and thus compressive stress in the oxide can be estimated. The calculated molecular weights, extrapolated densities, calculated Pilling-Bedworth ratios, extracted unilateral strains, and estimated compressive stresses for various oxides are tabulated in Table 4.

An important suboxide to notice is the case for Nb_5O , a probable and compromising formula for NbO_x . Calculating a

Pilling-Bedworth ratio of 1.068 using 8.28 g/cm^3 as the extrapolated density, the unilateral strain is 0.021 which times the Young's modulus for the metal (an approximation to that for Nb_5O) gives a compressive stress of about 300,000 psi. If the calculated unilateral strain were shared between the suboxide and the oxygen-saturated niobium, the estimated value of compressive stress in the suboxide and tensile stress in the metal would be about 150,000 psi.

Case II: The case where anion diffusion predominates but the oxide grows anisotropically and is not coherent with the metal substrate. The oxygen diffuses across the inner layer of oxides but does not diffuse into the metal to the pentoxide positions but instead there is a considerable reshuffling of metal and oxygen atoms at the metal/oxide phase boundary which results in completely anisotropic growth. Therefore, no strains in the oxide or the adjacent metal are produced and the oxide film can grow freely with no expected compressive stress build-up.

Case III: In systems where the reaction occurs by cation diffusion, the oxide is formed at the oxide/oxygen phase boundary. Therefore, no restraints act upon the newly formed oxide and it remains adherent and strain-free even for very large oxide/metal volume ratios.

Experimental Pawel and Campbell (61) attempted to measure the film stresses produced during the oxidation of niobium by means of flexure experiments. They used an equation given by Dankov and Churaev (76) for thin-film stresses as a function of maximum bending stress, σ_s , to calculate the stress in the oxide layer, σ_F .

$$\sigma_F = \frac{1}{3} \sigma_s \frac{h}{w} \quad (5)$$

where h = metal thickness and w = oxide thickness. Neither paper presented a derivation of this equation, but I believe it came from an analogy to Timoshenko's (86) treatment of a bi-metallic strip subjected to a temperature change. Equation 5 is derived from Timoshenko's work in Appendix A.

Pawel and Campbell state that while accurate quantitative values of film stresses cannot be extracted from the data they have obtained so far, the data do indicate that these stresses will be quite high, perhaps approaching 100,000 psi.

Pawel and Campbell's data showing maximum bending stress versus time for niobium specimens oxidized at 400 and 425°C is shown in Figure 8. Their calculated data for oxygen solution stress, σ_I , and thin-film stress, σ_F , computed from bending stress data is shown along with the oxygen consumed curve at 425°C in Figure 9.

Since the maximum bending stress is easily determined from flexure measurements, an indication of how isotropic or anisotropic the oxide grows can be easily extracted and a prediction of which case, outlined above, is operating can be made.

Mechanical Properties of Niobium

The first systematic study of the mechanical properties of niobium as influenced by temperature and oxygen content was done by Tottle (72) in 1956. A plot of his data on the effect of oxygen content on the room temperature tensile properties of niobium is shown in Figure 10. His data indicate that the ultimate tensile strength at room temperature reaches a maximum at an oxygen content of about 3150 ppm and drops slightly at his highest oxygen content of 4100 ppm. Tottle explained that the irregularities in his elongation data were due to some specimens breaking in the grips.

McCoy and Douglass (87) studied the effect of oxygen on the room temperature bend properties of niobium. Because of the differences in material and test procedure and the limitations of their work, a comparison between their data and Tottle's is only approximate. The trend appears to be that bend test data give higher proportional limits and higher

maximum stresses for a given deflection than tensile test data.

A number of authors (72,88,89,90,91) have looked at the effect of temperature on the mechanical properties of niobium with varying degrees of purity. Most of these samples tested were commercially pure but many had lesser amounts of interstitial impurities. The effect of oxygen as well as temperature on the mechanical properties of niobium has been investigated and reported in a scattered manner. Vaughan and Rose (91) studied the effect of oxygen on the ultimate strength of niobium at various temperatures but unfortunately report data for no temperature near 425°C . The closest data which can be extrapolated to the desired temperature and oxygen contents were reported by Enrietto, Sinclair, and Wert (92) and are reproduced in Figure 11. Extrapolating from the data of Enrietto et al., the ultimate tensile strength of niobium at 425°C varies from about 42,000 psi. for a specimen with an oxygen content of 200 ppm. to 48,000 psi. for an oxygen content of 4300 ppm., this latter value applying to a specimen which has fractured in a brittle manner.

Oxide Wedge Formation

Kolski (50) reported a phenomenon in the oxidation of niobium which was unreported by previous investigators. He found niobium oxide "spikes" which penetrated deeply into the metal after oxidation. The sample which showed this spiking was a coupon specimen oxidized at 400°C for 168 hours. Kolski offered no explanation of why this phenomenon occurred.

Doyle (12) found spikes to occur in specimens oxidized around 425°C and which had some initial curvature. Since Doyle's main interest in the investigation was the reason for the region of decreasing oxidation rate, they primarily studied subscales and only had time to briefly consider these spikes.

Fox¹ roughly scanned the effects of specimen curvature, surface preparation, and residual stresses on the occurrence of oxide spikes in niobium oxidized at 425°C in air. Fox found that in all cases of oxidizing bent specimens they opened upon oxidizing and there were spikes formed on the inside or concave side of the specimens. He also noticed

¹Fox, D. B. Oxide penetration in niobium. Private communication. Ames Laboratory, Iowa State University, Ames, Iowa. 1965.

that the density of the oxide spikes increased with decreasing initial radius of curvature of the specimens. Fox also noticed that cold-working a sample before oxidation increased the severity of spiking. The surface preparation of the sample before oxidation was found to have no effect on the occurrence or density of oxide spikes.

Fox suggested that the oxide spikes were associated with the concave geometry of the specimens.

OBJECTIVES OF THE INVESTIGATION

Occurrence and Importance of Oxide Wedges

Enough theoretical and experimental information is known about the kinetics of the oxidation of niobium in the vicinity of 425°C to predict with some certainty the oxidation rate, and hence, the lifetime of a part made from niobium sheet.

Initially it was expected that these calculations should apply to curved sheets and tubing as well as niobium sheet. Testing these calculations with tube specimens shows that the overall reduction of the wall thickness of the tube with time does proceed in an approximately linear manner and at the expected oxidation rate, but there are areas of localized attack which cause premature failure of the tube. The complete penetration of the tube wall in a local area can occur in as little as one-tenth of the lifetime calculated from thin sheet data. The reason for the premature failure of these tubes is the phenomenon originally called 'oxide spiking' after the shape observed in a metallographic section of the deeply penetrating oxide. Rather than 'oxide spikes', a better terminology would be 'oxide wedges'; since rather than having a needle-like shape, they have depth such as a knife edge.

This phenomenon may be unique to niobium but because of

the similarities in the oxidation characteristics between niobium and tantalum, tantalum probably is susceptible to oxide wedge formation also.

The phenomenon appears to be restricted to niobium pieces with some curvature, especially tubing.

Oxide Wedge Formation Hypothesis

The hypothesis for oxide wedge formation and growth is proposed as follows:

A compressive stress in the oxide along with a geometrical constriction of the growing oxide cause a tensile strain in the surface layer of the metal on the inside of a tube. When this tensile strain surpasses the ultimate strain for the embrittled metal, the metal substrate cracks. As oxidation continues, oxygen penetrates into the crack and from the crack tip and sides diffuses into the metal causing an embrittled zone. Also, the sides of the crack oxidize with impingement of the two growing surfaces causing additional stress at the crack tip as well as aiding the outer film growth in opening the tube. As the tube continues to open, the crack propagates into the hardened niobium zone and the oxide wedge continues to grow into the metal substrate.

Proposed Work

Flexure measurements

An effect hypothesized to aid in the formation of oxide wedges is the tensile strain imposed upon the embrittled niobium surface due to the compressive stress in the growing niobium pentoxide. Since the Pilling-Bedworth ratio predicts very high compressive stresses for the niobium pentoxide formation, these compressive stresses should be measureable.

The stress due to the niobium pentoxide formation will be separated from the stresses due to an oxygen concentration gradient and/or a niobium suboxide concentration gradient and/or a niobium suboxide thin film. Separation of these stresses will be made by applying the measured data to the theoretical concentration gradient and thin-film equations for stresses and by applying the boundary conditions of known oxidation mechanisms and products, then choosing the results which are most reasonable.

Oxide wedge formation

A second effect hypothesized to aid in the formation of oxide wedges is an additional tensile strain imposed upon the embrittled niobium surface due to the opening of the niobium tube caused by the geometrical constriction of the growing

oxide on the inside of the tube. This tensile strain can be simulated by applying a constant stress to a niobium sheet tensile specimen while oxidizing. By varying the initial oxygen content of the tensile specimen, a plot of tensile stress needed for a given initial specimen oxygen content to form oxide wedges can be obtained.

The combination of the data from these two types of measurements along with the given data for the compressive yield strength of niobium pentoxide, should give the quantitative parameters needed to explain the phenomenon of oxide wedge formation.

PRELIMINARY EXPERIMENTS

To test the oxide wedge formation hypothesis in a qualitative manner, a series of preliminary experiments was performed.

Materials

Niobium tubing was purchased from Kawecki Chemical Co. The tubing had an outside diameter of 0.375" and a wall thickness of 0.020". The purity was given as 'reactor grade'; the chemical analysis as given by the supplier is shown in Table 5.

Preparation

Samples 1.1 cm long were cut from the tube and placed in a small lathe so the inside diameter could be polished with 240, 400, and 600 grit silicon carbide paper. This process removed all scratches and extrusion marks parallel to the cylinder axis and gave an acceptable surface finish. The ends of the sample were ground flat to give a sample length of 1 cm. The samples were stress-relieved at 1000°C for 1 hr. in a vacuum of 10^{-5} torr or better. The final microstructure was still that of the cold-worked state.

Experiments

A series of these samples was run at 425, 500, 600, and 700°C in dry, flowing air. The oxidation kinetics were followed by weight gain measurements and the data plotted as weight gain per unit surface area versus the time of oxidation. Upon removing the samples from the furnace, they were immediately mounted on end in Precisonite, sectioned, and mechanically polished. Observations were made and photographs taken of the final curvature of specimens and the existence of oxide wedges. Microhardness measurements were made across the section of the mounted and polished specimen and plotted as a function of oxygen penetration distance.

Results

The series at 425°C was oxidized for 24, 30, 36, 42 and 48 hours respectively. The oxidation kinetics are shown in Figure 12 and correspond closely to curves reported in the literature for coupon samples. The 24, 30, and 36 hour samples showed uniform oxide layers while retaining their circular shape. They showed no oxide wedge formation. The 42 hour sample showed signs of buckling on two ends to give an elliptical cross section. There were numerous oxide wedges on the outside curvature in these areas where the metal has been

subjected to a high tensile stress. There were also a few small cracks and oxide wedges on the inside curvature or concave side of the sample. The 48 hour sample which had broken and opened somewhat showed numerous oxide wedges on its concave side.

Since it was observed that the niobium tube oxidized for 48 hours at 425°C broke open, the question arose: Are these oxide wedges actually needle-like spikes or do they run the length of the tube like a knife edge? Figures 13a and 13b show an area of a severely oxidized sample which has been mounted with its concave side at the mount's surface. It can be seen that the "spikes" do actually have depth and may run the entire length of the sample.

A series of samples was oxidized at 500°C in air for 8, 16, 24, 32, and 36 hours respectively. The progress of this oxidation is shown in Figures 14a thru 14d. The oxidation kinetics are shown in Figure 12 and correspond closely to curves reported in the literature for coupon samples. The 8, 16, and 24 hour samples oxidized uniformly and held their circular shape. The 32 hour sample which had broken and opened slightly showed a few small cracks on the concave side but no oxide wedges were observed. The 36 hour sample which opened

further than the previous sample contained a few oxide wedges, one running across the entire metal substrate.

The oxidation kinetics for a series of niobium tubes oxidized at 600°C for 2, 6, 10, 14, 18, 22, and 26 hours respectively is shown in Figure 12. The oxidation rate was observed to be about one-half as fast as that reported in the literature for coupon specimens. During the oxidation of this set of samples, it was found that the oxide spalled so frequently that the oxide never built-up enough volume to break open the samples. No oxide wedges or cracks were observed in any of these samples.

The progress of the oxidation of a series of samples at 700°C for 2, 4, 5, 6 and 8 hours is shown in Figures 15a thru 15e respectively. The oxidation kinetics for this set are shown in Figure 12 and correspond closely with curves reported in the literature for niobium coupon samples. Figure 15c shows that the tube oxidized at 700°C for 5 hours has already broken and opened somewhat. Figures 15d and 15e show that continued oxidation consumes the sample uniformly, opening it until it approaches flatness. However, no cracks or oxide wedges are observed in any of these samples.

The reason for oxide wedge formation at 425 and 500°C and

no formation at 700°C may be associated with the oxygen concentration profiles at these respective temperatures. Figures 16, 17, and 18 give the diamond pyramid hardness versus the penetration distance of the oxygen into the metal after various oxidizing times at 425, 500, and 700°C respectively. Figures 16 and 17 show that the microhardness and thus oxygen content increased from the center towards the surface reaching a maximum at the metal/oxide interface. Figure 18 also shows the hardness and thus oxygen content increased from the center towards the surface but reached a maximum about 0.5 mil from the surface and then the hardness decreased indicating a second phase was present which reduced the hardness of the substrate.

EXPERIMENTS

Stress Measurements

In this section attempts to measure the stresses involved in the oxidation of niobium, and in particular the stress due to the niobium pentoxide film, will be discussed.

Materials

The niobium used in this section of the investigation was obtained from the Fansteel Metallurgical Corporation in the form of a single annealed 0.010 in. sheet. The supplier's maximum impurity limits are given in Table 5.

Preparation

The preparation of niobium samples for stress measurements depended somewhat on the oxygen content desired in the specimen. In general the preparation proceeded as follows. A niobium specimen was cut from the 0.010 in. sheet as a rectangular coupon 1x4.5 cm. This coupon was then polished on both sides with 600 grit silicon carbide paper to remove the surface scale. The polished coupon was placed in a furnace at 425°C and oxidized to a predetermined oxygen weight gain. The specimen supporting a thin, adherent niobium pentoxide layer

was vacuum annealed at temperatures from 500 to 1200°C for times up to 14 or 3 days respectively.

Upon cooling of the specimen subsequent to the vacuum anneal, the remaining niobium oxide scale detached from the metal substrate in most cases. For the lower-temperature anneals (500 and 600°C) where the scale remained adherent, a two hour submersion in 25% hydrofluoric acid in water solution removed the scale. Dissolution in acid tests as well as X-ray diffraction studies indicates this black, compact scale was mainly niobium dioxide with some remaining niobium pentoxide.

The oxygen-saturated coupon was again polished on both sides with 600 grit silicon carbide paper and subsequently one side only was further polished with 15 micron, 1 micron, and 0.3 micron levigated alumina. A 0.5 cm piece was cut off from one end to be vacuum-fusion analyzed for oxygen, nitrogen, and hydrogen content. The remaining coupon was cleaned for five minutes in a solution containing 50 parts lactic acid, 30 parts nitric acid, 2 parts hydrofluoric acid, and the balance water.

A support yoke of 0.032 in. Nichrome wire was discharge-welded on the alumina-polished side of the coupon, at the end which contains a small notch. See Figure 19. At the other

end of the coupon and on the same side, a straight piece of 0.032 in. Nichrome wire was discharge-welded across the tip. A 0.021 in. hole was drilled through the middle of this straight Nichrome wire to form a small "eye". The specimen was cleaned again in the lactic, nitric, hydrofluoric solution for five minutes.

The specimen was placed in a vacuum evaporator with Nichrome wire side up, and aluminum was plated onto this one side to a thickness of approximately 6 microns. For specimens with lower oxygen contents where a smooth, polished surface could be obtained for the aluminum deposition, this as-deposited aluminum layer was sufficient to resist oxidation. For specimens with higher oxygen contents where polishing was difficult, a subsequent vacuum annealing at 600°C for 24 hours formed a diffusion bond between niobium and aluminum which made an excellent protective film. The specimen was then ready for flexure measurements.

Oxidation flexure measurements

A schematic drawing of the apparatus constructed for flexure measurements is shown in Figure 20. The prepared specimen was suspended in the apparatus by inserting the Nichrome yoke attached to the specimen into two holes in a

stainless steel sleeve and positioning the specimen with set screws. See Figure 19. This stainless steel sleeve attached to the end of a stainless steel support rod and was positioned by a set screw. A quartz fiber, 235 mm long, was hung onto the specimen with its hook in the small notch at the top end of the specimen and its free end threaded through the "eye" located at the bottom end of the aluminum-coated side. The purpose of the eye was to restrict lateral motion of the fiber along the edge of the specimen as bending proceeded. The fiber extended so that deflection measurements could be made through the quartz window in the part of the apparatus beneath the furnace. Deflections were measured with a traveling microscope which was converted to an X-Y cathetometer. A total deflection of about 4 cm could be measured with the accuracy of individual readings being ± 0.05 mm.

With the specimen in position, the system was evacuated to a pressure of approximately 2×10^{-6} mm Hg by means of an oil diffusion pump backed up by a mechanical roughing pump. A liquid nitrogen cold trap was placed between the flexure apparatus and the oil diffusion pump. The temperature was slowly raised to 300°C and the system allowed to outgas for a few hours. Upon reaching a vacuum below 3×10^{-6} mm Hg, the temper-

ature was raised to within five degrees centigrade of the desired reaction temperature. The specimen temperature was monitored by two chromel-alumel thermocouples placed close to the specimen but at different heights. The two thermocouples gave temperature readings within one centigrade degree of each other in vacuum. When the oxygen was introduced into the system, the thermocouple which was higher and farther from the specimen gave a reading of five centigrade degrees higher than the other.

Small and reproducible fiber deflections were monitored during the heating period. After temperature was reached, the fiber remained essentially steady except for occasional mechanically-produced vibrations. A "zero" reading was taken immediately before the flexure apparatus was isolated from the vacuum system. A stopcock was opened allowing oxygen to leak into the system. The oxygen was dried by passing it through a sulfuric acid bubbler and a column of calcium sulfate. The oxygen was preheated in a container filled with alumina chips which was mounted above the specimen on the edge of the furnace hot zone as shown in Figure 20. As the preheated oxygen first entered into the system, the temperature of the specimen quickly rose five degrees centigrade to the desired oxidation

temperature. The oxygen flow rate was maintained at 1.5 l/min.

As the specimen oxidized on the clean side, it bent with the aluminum on the concave side. The quartz fiber maintained a position corresponding to the chord of the arc of the deflecting specimen and thus the end of the fiber deflected proportionately with the curvature of the specimen as shown schematically in Figure 21. The slight deviation of the quartz fiber from a straight line as it became non-vertical was determined by a previous calibration and this deviation was taken into account in subsequent calculations of deflection. Cathetometer readings were taken intermittently for the duration of the experiment. In this manner, a plot of fiber deflection versus oxidation time was obtained.

From the geometry of the specimen-fiber relationship, Figure 21, the deflections were related to the radii of curvature of the specimens using the following equation (83)

$$\rho = \frac{\Delta S}{\Delta \theta} \quad (6)$$

where ρ is the radius of curvature of the specimen, ΔS is half the length of the chord of the arc of the specimen and $\Delta \theta$ is the angle between the initial and final positions of the fiber and is determined using the equation

$$\Delta \theta = \frac{\delta}{l} \quad (7)$$

where δ is the deflection of the fiber tip measured by the cathetometer and l is the length of the quartz fiber.

The strict applicability of the above equations to the specimen-fiber relationship is based on the assumption that the bending specimen is forming an arc of a circle. Indices measured from a photograph of a curved specimen plotted into the equation of a circle gave a variation in the radius of approximately plus or minus two percent. This radius calculated from the equation of a circle corresponded closely with the radius of curvature calculated from deflection measurements.

Since the bending specimen closely approaches the arc of a circle, the calculated radii of curvature can be substituted into Equation 3 and the maximum bending stresses determined. The result was a plot of maximum bending stress versus oxidation time for the oxidation process.

Cooling flexure measurements

Upon conclusion of the time desired for oxidation, the oxygen flow into the system was stopped and the system was evacuated. Simultaneously, the power to the furnace was cut off so that specimen cooling began. Cathetometer readings were taken intermittently for the duration of the cooling.

From these readings, a plot of maximum bending stress versus temperature was obtained for the cooling process.

When the sample had reached room temperature and the final deflection noted, the specimen was removed from the apparatus and from the holder and a photograph was taken at approximately 2.5 magnification to show the specimen curvature.

The weight of the specimen was measured before and after the oxidation process in order to determine the amount of oxygen added. Since the surface area of the specimen which was oxidized was known, the thickness of niobium pentoxide formed can be calculated using the measured weight gain of oxygen and the following equation which is developed in Appendix B.

$$\chi(\text{microns}) = W_o \times 1.8604 \quad (8)$$

where χ is the thickness of the niobium pentoxide in microns, W_o is the weight gain of oxygen in milligrams and 1.8604 is a constant determined from density values. Figure 22 is a plot of thickness of niobium pentoxide as a function of weight of oxygen.

Using Timoshenko's (86) derivation for the cooling of a bimetallic strip and applying boundary conditions for the present niobium-niobium pentoxide composite, the following

equation was derived as shown in Appendix C.

$$1/\rho = 3/2(\alpha_n - \alpha_o)T \frac{2h_o}{h_n^2} \quad (9)$$

where $1/\rho$ is the reciprocal of the radius of curvature of the composite, α_n is the thermal expansion coefficient of niobium, α_o is the thermal expansion coefficient of niobium pentoxide, T is the change in temperature, h_n is the thickness of the niobium and h_o is the thickness of the niobium pentoxide as calculated from Equation 8.

Using the radii of curvature calculated from these weight gain measurements, the maximum bending stresses for cooling were calculated from Equation 3. Figure 23 shows the plot of weight of oxygen gained versus the maximum bending stress for cooling. These values for maximum bending stress for cooling were then compared with the values calculated from the fiber deflection measurements during cooling.

Dissolution flexure measurements

The specimen was attached by its Nichrome wire yoke to a nylon sleeve. This nylon sleeve was attached to a nylon support rod which was centered in a supporting rubber stopper, see Figure 24. A 0.020 in. molybdenum wire 150 mm long was suspended from the specimen analogously to the quartz fiber.

The stopper also supported a Teflon funnel and contained a gas escape hole. This supporting stopper was then placed on top of a Plexiglass cylinder with the specimen and molybdenum wire suspended beneath. A solution of 25% hydrofluoric acid in water was poured through the funnel to a level just beneath the specimen. A "zero" reading was taken with the cathetometer before introducing more hydrofluoric acid. Upon submersing the specimen with hydrofluoric acid solution, the aluminum layer immediately dissolved away. A cathetometer reading showed this removing of the aluminum affected the specimen curvature very slightly, about one percent of the total value. Hydrofluoric acid dissolves niobium pentoxide with relative ease but only slightly attacks niobium and does not dissolve niobium dioxide significantly (93). As the hydrofluoric acid dissolved the niobium pentoxide scale, the specimen bent back towards straightness. The dissolution process proceeded slowly for a time as the acid attacked the oxide/solution surface and also the oxide/metal interface. When enough oxide was dissolved at the oxide/metal interface to prevent adequate mechanical bonding of the oxide, the scale flaked off the metal substrate. As this scale flaked off, the specimen straightened rapidly. This procedure was followed

quantitatively by measuring the amount of deflection of the molybdenum wire with time. Using Equations 6 and 7, the deflections were converted to specimen radii of curvature from which bending stresses could be calculated. The maximum bending stresses were attributed to negative sign for this dissolution process because the specimen was unbending, causing the fiber to deflect in a direction opposite to that previously taken as the positive direction. Inserting a negative deflection into Equation 7 gives a negative value for $\Delta\theta$ which when inserted into Equation 6 gives a negative value for ρ . Since ρ is used in Equation 3 to obtain the maximum bending stress, this stress will have a negative sign. The result was a plot of negative maximum bending stress versus dissolution time for the dissolution process.

When the scale had essentially all flaked off and the rate of deflection of the molybdenum wire had become very slow, the sample was removed and thoroughly rinsed with cold water and dried with alcohol. A photograph was taken at 2.5 magnification to show the present state of curvature of the specimen.

Annealing flexure measurements

After the niobium pentoxide dissolution process, the specimens still retained some curvature. If this retained

curvature was due to a defect concentration gradient, such as an oxygen concentration gradient; the remaining curvature could be eliminated by vacuum annealing the specimen to remove the gradient. If this retained curvature was due to plastic deformation of the surface of the metal, vacuum annealing at 550°C (recrystallization temperature equals 1400°C) would not appreciably affect the specimen curvature.

The specimen was replaced in the stainless steel sleeve and placed in the controlled atmosphere furnace system already mentioned. The system was evacuated to a pressure of 2×10^{-6} mm Hg and the temperature slowly raised to 300°C to let the system outgas. When the pressure was again acceptably low, the temperature was quickly raised to 550°C and a "zero" reading taken with the cathetometer. Three days at 550°C was usually sufficient to return the specimen to its original shape of straightness. Intermittent readings were taken with the cathetometer for the duration of the annealing process. Similarly to the dissolution flexure measurement, during the vacuum annealing the fiber continued to deflect in the assigned negative direction. The result was a plot of negative maximum bending stresses versus annealing time.

For completeness, the specimen was removed and a final

photograph taken at the same magnification to show the return of the specimen to straightness.

This entire procedure for stress measurements from specimen preparation through vacuum annealing was followed concurrently by specimen weight measurements. These measurements were made on an analytical balance to an accuracy of ± 0.05 mg.

Results

The purpose of the flexure measurements was to obtain a value for the compressive stress in the niobium pentoxide film. Specimens were oxidized and cooled and the resulting curvature was measured and photographed. A dissolution treatment then removed the niobium pentoxide layer causing a reduction in curvature which was measured and photographed. An annealing returned the specimen to straightness with the reduction in curvature being measured and photographed.

The curvature measurements were converted to bending stresses and thus the oxidation and cooling bending stresses due to increasing curvature should equal the dissolution and annealing bending stresses due to decreasing curvature.

Table 6 lists the conditions for specimen preparation and oxidation for the first group of flexure measurement specimens. The purpose of this group of specimens was to show the repro-

ducibility of the data for a given set of conditions. Figure 25 shows the reproducibility of the oxidation flexure measurements for specimens oxidized 180 minutes. Figure 26 shows an example of the specimen curvature from this set. Figures 27, 28, 29, and 30 show the reproducibility of the oxidation, cooling, dissolution, and annealing measurements respectively for specimens oxidized for 240 minutes. Figure 31 shows an example of the corresponding curvatures for this set of specimens. The measurements were observed to be reproducible to within three percent. Also, the total positive bending stress was within two percent of the total negative bending stress as shown in Table 7. Equation 2, as derived by Pawel and Campbell and called the oxygen solution stress, σ_I , gives the surface bending stress in a metal due to an oxygen concentration gradient as a function of oxidation bending stress, σ_S . A parameter needed in this calculation was the diffusion coefficient for oxygen in niobium. A wide divergence of the values was found in the literature (95). The case of Klopp et al. (43) for oxygen diffusion was similar to the present case. Their value [$D = 4.07 \times 10^{-3} \exp(-24,900/RT)$ cm²/sec] gave a diffusion coefficient whose value lay between the other reported values. Using this diffusion coefficient, the

oxidation bending stresses, σ_s , obtained from Figures 25 and 27 were substituted into Equation 2 and the oxygen solution stress, σ_I , was plotted as a function of oxidizing time as shown in Figure 32.

The data plotted as expected starting out level during the oxygen solution time and increasing when the niobium pentoxide formation began. Comparing the measured values of stress on the level portions of the curve, σ_I , with the theoretical calculations of Richmond et al. (82) for a bending stress due to an oxygen concentration gradient as shown in Figure 6, gave oxygen concentrations of 2650 and 2900 ppm above the 1300 ppm initial oxygen content.

The thin film stress, Equation 5, derived in Appendix A, gives the lateral compressive stress in a thin oxide film. A parameter needed in this calculation was the thickness of the niobium pentoxide which forms on an oxidizing specimen. Unfortunately, simultaneous flexure measurements and weight gain due to oxygen pickup can not be made with the apparatus employed. However, specimens prepared similarly can be oxidized in a thermogravimetric balance system obtaining continuous weight gain curves. These curves were reproducible to within a few percent and compared favorably to similar

data observed by Hurlen et al. (10) and Doyle (12). The weight gain increased to an approximate value of 0.5 mg at an oxidation time of 30 minutes for a temperature near 425°C (also measured intermittently on a microbalance with 0.01 mg accuracy) and then increased in a linear manner to the stop point. Making use of this knowledge, the curves of Figure 33 were drawn by reproducing the data for weight gain to the oxidation time of 30 minutes and then drawing a line between this value of 0.5 mg and the final weight gain value as measured after oxidation.

This did introduce an error into the calculations because the true weight gain of the flexure specimens probably did not match the corresponding simulated weight gains at all oxidizing times. However, since the simulated weight gain at the oxidation stop point was the true measured weight gain, the difference between the calculated and true weight gain values approached zero and the error in the thickness calculation became zero.

These simulated values of weight gain were converted to niobium pentoxide thicknesses through the use of Figure 22 as derived in Appendix B. These niobium pentoxide thicknesses were substituted along with the oxidation bending stresses

obtained from Figures 25 and 27 into Equation 5 and the thin film stress in the oxide, σ_F , plotted as a function of oxidizing time as shown in Figure 34. The values for specimens 66, 67, and 68 fell between the limits shown by specimens 64 and 65. The data for σ_F showed a good reproducibility with the final values falling between 72,000 and 83,000 psi.

The σ_F stresses as a function of time plotted as would be expected. At early oxidation times when no niobium pentoxide has been observed to form, the calculated film thicknesses for the small weight gains due to oxygen were very small. However, the oxidation bending stress during this period was appreciable. Therefore, substituting these values of w and σ_S into Equation 5 gave very high values for σ_F , around 600,000 psi which indicated that some other flexure producing process was operative. The values for σ_F drop to more reasonable magnitudes corresponding with the oxidizing times for observed niobium pentoxide formation. The σ_F stress levels off corresponding with the observed process of niobium pentoxide film growth.

Another characteristic of the oxidation of niobium in the temperature range near 425°C which must be taken into account was the formation of a niobium suboxide, designated

NbO_x , during early oxidation times. Upon removing specimens from the thermogravimetric system after oxidizing from ten to twenty minutes near 425°C , they were examined by X-ray diffraction. A similar occurrence to that found by Hurlen (10) and Goldschmidt (20) was observed in that small peaks appear adjacent to the niobium X-ray diffraction peaks. Upon further oxidation, these extra peaks disappeared most likely due to the formation of niobium pentoxide on top of the NbO_x .

In order to make a thin film analysis for NbO_x similar to that used for Nb_2O_5 , two important parameters must be known so that an 'effective' oxide film thickness can be calculated from the weight gain due to oxygen. The term 'effective' is used because even though the NbO_x suboxide was known to exist near the surface of an oxidizing piece of niobium metal, it was not known with certainty if it existed as a separate layer or in another form.

The first parameter which needed to be known was the formula for NbO_x or, more precisely, the oxygen content of NbO_x . The formulae reported in the literature are Nb_6O , Nb_5O , and Nb_4O which gave oxygen contents of 2.70, 3.23, and 4.00 weight percent respectively. Since these values are not greatly variant, the intermediate formula of Nb_5O with oxygen

content of 3.23 weight percent was chosen for the purpose of calculation.

The second parameter which was used in the calculation of the effective thin film thickness was the density. This value has not been measured experimentally but a reasonable assumption of its approximate magnitude can be made from the following considerations. First, Magneli et al. (96,97) have studied the change in density with oxygen content for the TiO_x , VO_x , ZrO_x , and HfO_x systems. The titanium, zirconium, and hafnium systems have a hexagonal crystal structure and the vanadium system a body-centered tetragonal crystal structure near the metal-rich end of the system with the oxygen occupying the interstitial positions. The solubility of oxygen in these metals is high, the values of x in MeO_x being 0.5, 0.33, 0.4, and 0.26 for TiO_x , VO_x , ZrO_x , and HfO_x respectively. They found that the density rose slightly with increasing oxygen content until the first stable oxide was formed and then the density fell off in an approximately linear manner. The percent density increase from the pure metal to the value of MeO_x of 0.2 for the four systems is: 3.2 for TiO_x , 2.5 for VO_x , 1.5 for ZrO_x , and 0.25 for HfO_x . Thus, in these systems, moving to the right or moving down

the periodic table from titanium caused a reduction in the effect of increasing density due to oxygen in the interstices. Extrapolating these results to the body-centered tetragonal system for niobium (moving down and to the right on the periodic table from titanium to niobium) would mean that the effect of increasing oxygen in niobium would raise the density only slightly if at all. The approximate density for NbO_x from this consideration would be that of niobium, 8.57 gm/cc.

A second consideration was from some data reported by Brauer et al. (8,9). They found a tetragonal niobium suboxide with the unit cell dimensions $a_0 = 3.39\overset{\circ}{\text{\AA}}$ and $c_0 = 3.27\overset{\circ}{\text{\AA}}$ and an oxygen content of about 2.5 weight percent. Using these values, a theoretical density of 8.42 gm/cc was calculated. Thus, for the approximate niobium suboxide Nb_6O the calculated theoretical density is 8.42 gm/cc.

Thirdly, once a stable oxide forms in a system, the density fell off in an approximately linear manner with increasing oxygen content. Therefore plotting the known densities of niobium oxides and extrapolating in a linear manner gave a curve such as shown in Figure 7. The values of density taken from this curve for the niobium suboxides Nb_6O , Nb_5O , and Nb_4O are 8.33, 8.28, and 8.20 gm/cc respectively.

The difference between this value for Nb_6O , 8.33 gm/cc, and the value from Brauer's X-ray data, 8.42 gm/cc, was 1.3% which was well within the usual limit of error for X-ray density data.

A combination of values for Nb_5O of 3.23 weight percent oxygen and a density of 8.28 gm/cc was used for the calculation of film thickness of Nb_5O as a function of weight gain due to oxygen. The equation was derived similarly to that for Nb_2O_5 shown in Appendix B and is:

$$x(\text{mil}) = W_o(\text{mg}) \times 0.3499 \quad (10)$$

Using the other combinations for oxygen content and density for the niobium suboxides Nb_6O and Nb_4O gave a variation of film thickness of plus 18% and minus 18% respectively from the value for Nb_5O . The main contribution to this difference was the difference in oxygen contents and not the value taken for density.

The weight gains due to oxygen from Figure 33 were used with Equation 10 to calculate an effective Nb_5O film thickness with oxidizing time. These calculated values were used with the measured oxidation bending stresses, σ_s from Figures 25 and 27 to calculate thin films stresses, σ_F , using Equation 5 as shown in Figure 35.

The σ_F stresses for Nb_5O as a function of time plotted as expected for a thin film stress analysis where the film was important early in the oxidation and became masked when niobium pentoxide formation was predominant. The σ_F stresses would be 18% higher if the film analysis was made with values for Nb_4O and 18% lower for Nb_6O .

When specimens prepared similar to those in the preceding section were oxidized in air for times up to 12 hours near 425°C , the aluminum layer became ineffective as a protective coating. A better coating was developed by vacuum annealing a specimen with an approximately 8 micron layer of aluminum at 600°C for 24 hours. The remaining flexure measurement specimens have been treated in this manner.

This next group of niobium specimens had a nominal initial oxygen content of 1500 ppm and were oxidized in oxygen at 420° , 425° , and 430°C . The conditions for specimen preparation and oxidation for this group of specimens are listed in Table 8. Figures 36, 37, 38, and 39 show the oxidation, cooling, dissolution, and annealing deflections and bending stresses for these specimens. The entire set of figures was shown to illustrate the variant shapes of the curves for similar specimens which have been oxidized at different tem-

peratures. The immediate observation was that for specimen 69 which was oxidized at 425°C in oxygen for 240 minutes, the oxidation bending stress during the first 30 minutes was higher than the comparable values for specimens 65 through 68, oxidized at 425°C . This indicated that the annealed aluminum coating was more protective than the unannealed coating because a reaction on the aluminum side was not suppressing the bending caused by oxidation on the other side. A summary of the final bending stresses of the four processes is shown in Table 9. Comparing the total bending stresses in the positive direction with those in the negative direction showed a good agreement. Figure 40 shows macrographs of specimen 71 showing curvature after oxidizing and cooling, after the dissolution treatment, and after annealing.

An observation from Figure 40 was that after the niobium pentoxide film was removed, the specimen still retained an appreciable curvature.

As previously mentioned, no detailed study has been made of the oxygen solubility in niobium for the temperature range from 425 to 500°C . If the solubility curves, as shown in Figure 1, are extrapolated to 500°C , the value for oxygen solubility in niobium falls between 900 and 1000 ppm.

The initial oxygen content of this second group of specimens was around 1500 ppm indicating that they should have been oxygen saturated. Any oxygen added during the oxidation flexure measurement should have been used to form a niobium pentoxide layer and not an oxygen concentration gradient. When the pentoxide layer was removed, the specimen should have returned to straightness.

σ_I as a function of oxidizing time was calculated and plotted as shown in Figure 41 from the oxidation bending stresses shown in Figure 36 and Equation 2. Comparing the σ_I 's obtained with Richmond's theoretical calculations gave oxygen concentrations of 3200 and 3650 ppm above the initial oxygen concentration of 1500 ppm.

Using the weight gain due to oxygen from Figure 42 along with the oxidation bending stresses from Figure 36, gave a plot of σ_F from Equation 5 as shown in Figure 43. The shape of the plot was much as that discussed for the previous group of specimens but the leveling off and final thin film stresses were higher.

Treating the oxidation bending stresses of Figure 36 as due to a thin film of Nb_5O , the plots shown in Figure 44 for σ_F in Nb_5O were obtained. The oxidation bending stress in-

creased at 10 minutes oxidation time from 1300 psi at 420°C to 1675 psi at 430°C or a 29 percent increase. However, the weight gain due to oxygen pickup and thus Nb₅O thickness increased proportionately so that the thin film stress, σ_F , for Nb₅O remained approximately constant at 10 minutes oxidation time.

A listing of σ_I , C_O , σ_F for Nb₂O₅ and σ_F for Nb₅O is given in Table 10 for this second group of specimens.

The last group of flexure measurement specimens were prepared with an annealed aluminum coating and nominal initial oxygen contents of 2850, 3550, and 4000 ppm. The primary result wanted from this group, was the effect of oxygen content on the amount of retained curvature after the dissolution treatment.

Table 8 lists the conditions for specimen preparation and oxidation for this group. Figure 45 shows that the shape of the oxidation bending stress curves are similar for a given oxidation temperature but the magnitudes reduced somewhat with increasing oxygen as determined in the first 30 minutes of oxidation time. Figures 46, 47 and 48 show examples of macrographs of a specimen from each oxygen content set. Figure 48 shows that even for a specimen with

an initial oxygen content of 4000 ppm, some curvature was retained after the niobium pentoxide layer was removed.

Table 9 lists the bending stresses for this last group of specimens.

The oxidation bending stresses, σ_S , as shown in Figure 45 were used in Equation 2 and along with weight gain due to oxygen from Figure 49 were used in Equation 5 to calculate σ_I , σ_F in Nb_2O_5 and σ_F in Nb_5O as a function of oxidation time respectively. The σ_I plots shown in Figure 50 did not level off during early oxidation times as they should for an oxygen solution stress analysis. Values of σ_I were chosen at 30 minutes of oxidation time, the usual time for a level curve, for the sake of comparison and are shown in Table 10. According to Richmond, the corresponding values for oxygen concentrations needed above the initial oxygen contents to give such σ_I stresses are also shown in Table 10. A result implied from the σ_I stresses for the specimens with an initial oxygen content of 4000 ppm was that a five centigrade degree rise in the oxidation temperature caused the oxygen concentration near the surface of the metal to increase by 600 ppm. This does not agree with oxygen solubility increases with temperature as shown in Figure 1.

The thin film stress, σ_F , plots for niobium pentoxide as shown in Figures 51a and 51b are similar in shape and magnitude to the corresponding curves of the second group of specimens. The σ_F stresses again bracketed the 100,000 psi stress level.

The thin film stress, σ_F , plots for Nb_5O are shown in Figure 52. The important observation was that the σ_F stresses at 10 minutes oxidation time did steadily drop with an increasing specimen oxygen content but remained fairly constant for a given specimen oxygen content.

The summary of the results for this last group of flexure measurement specimens is given in Table 10.

The macrophotograph of specimen 79 showing its curvature after oxidizing and cooling as shown in Figure 46 was used to make an enlargement to 8X. Coordinate measurements from this enlargement were substituted into the equation of a circle and the radius of curvature was calculated. These radii of curvature calculations varied by at most one percent (4.60 to 4.65") which gave credence to the assumption that the specimens curved as an arc of a circle. The total deflection measured for the oxidation and cooling of specimen 79 was 38.6 mm. Substituting this value into Equation 7 and using Equation 6,

the measured radius of curvature calculated was 4.79". Comparing this value with those calculated from the enlargement gave a variance of from 3 to 4 percent. However, the calculations from the photograph include an additional slight curvature due to the small transverse bending of the specimen which the deflection did not measure. Taking this into account gave an even better correspondence of the two values and added credence to the bending stress calculations.

To conclude the results of the flexure measurement specimens, some sample photographs are shown of specimens which were protected on one side by an annealed aluminum coating and subsequently oxidized to a further degree in the thermogravimetric balance system. Figures 53 and 54 show macrophotographs of pure 10-mil niobium specimens oxidized at 425°C in air for 24, 30, 36, and 48 hours respectively. Specimens which were oxidized at 500°C in air for 6, 6.5, 7, and 8 hours respectively showed very similar curvature. Figure 53 shows that a specimen oxidized for 30 hours at 425°C formed an apparently symmetrical tube thus lending credence to the earlier evidence that oxidized specimens form an arc of a circle. Calculating a bending stress from the radius of the closed tube (3/8"), gave a value of approximately 200,000 psi

which of course far surpassed the elastic limit of relatively pure niobium as the microstructure indicated. Figure 55 shows an end view of a 10-mil niobium specimen oxidized for 8 hours at 425°C in air. The purpose of the photograph was to show the curvature in the transverse direction. Figure 56 shows a microphotograph of a 10-mil niobium specimen oxidized at 425°C in air for 24 hours. The microhardness readings indicated that a very small amount if any oxygen penetrated through the protective aluminum layer because no hardness increase was measureable. When the specimens shown in Figure 54 were mounted and sectioned, oxide wedges were observed on the outer or convex side of the specimens. Thus, a flat piece of niobium sheet can be oxidized in such a way to cause the formation of oxide wedges.

Interpretation and discussion

The group of flexure measurement specimens most nearly like the specimens of Pawel and Campbell (61) were specimens 62 through 68. The main difference was that their 13-mil specimens were essentially oxygen-free whereas specimens 62-68 had a 10-mil thickness and were supposedly oxygen saturated.

The maximum bending stress curves of Pawel and Campbell are shown in Figure 8. The comparable curves for this study

are shown in Figures 25 and 27. For the oxidizing temperature of 425°C , the general shape of the respective curves was similar. A gradual decrease in the rate of bending was observed until about 40 minutes of oxidation time at which point an increased rate which became approximately linear was observed. The magnitude of the bending stress for Pawel and Campbell during the early oxidation times was about 25 percent lower than the bending stress from this study at a comparable time. At oxidation times after the initial region where niobium pentoxide formation is dominant, the difference in magnitudes of oxidation bending stresses is reduced.

The analysis of the thin film stress in the oxide layer, σ_F , made by Pawel and Campbell was appreciably different than that of this study. They used niobium monoxide, NbO , as the major oxide instead of niobium pentoxide, Nb_2O_5 , as done in this study. Their plot of the thin film stress in NbO is shown in Figure 9. The plots of thin film stress in Nb_2O_5 as obtained in this study are shown in Figure 34. The general shape of the σ_F curves is very similar showing the high values at early oxidation times and dropping to more reasonable values with the onset of niobium pentoxide formation. The σ_F in NbO which Pawel and Campbell obtained was about 100,000 psi

and they indicated the values of σ_F for Nb_2O_5 would be about 40 percent higher, or 140,000 psi. Their curve for σ_F as shown in Figure 9 terminates at 80 minutes oxidation time. The σ_F in Nb_2O_5 from this study for an oxidation time of 80 minutes as shown on Figure 34 is approximately 90,000 psi. This termination time is somewhat early in that it was observed the σ_F values drop significantly with oxidation times of slightly longer duration and then level off appreciably.

A summary of thin film stress, σ_F , for niobium pentoxide at 150 minutes of oxidation time and for the final oxidation time for specimens with annealed aluminum coatings is shown in Table 10. Average values of the thin film stress, σ_F , for 150 minutes and final oxidation times were 103,540 and 100,140 psi respectively. These results correlated with the observations made from Figures 54, 51a and 51b that the curves bracketed the 100,000 psi level. The σ_F stresses for 80 minutes of oxidation time fell between 110,000 and 160,000 psi in better agreement with the 140,000 psi value of σ_F in Nb_2O_5 reported by Pawel and Campbell.

The thin film stress, σ_F , of 100,000 psi was the value for lateral compressive stress in the niobium pentoxide film if a transverse constraint was absent. Figure 55 shows that

there was a transverse constraint which acted to give a transverse bending when niobium pentoxide was formed on a thin rectangular sheet. The thin film stress equation, Equation 5, must be adjusted for this transverse bending moment as shown in Appendix A. The corrected thin film stress equation becomes

$$\sigma_T = \frac{1}{3} \sigma_S \frac{h}{w} \frac{1}{(1-\nu)} \quad (11)$$

where ν is the Poisson's ratio for niobium pentoxide. The value for Poisson's ratio for most 'single oxides' falls in the range of 0.2 to 0.3 (98). Poisson's ratio for niobium pentoxide has not been measured. Therefore, the value for the thin film stress, σ_T , for niobium pentoxide could vary from 125,000 to 143,000 psi. Manning et al. (99) measured Poisson's ratio in some rare earth oxides as a function of porosity. They found it to decrease from about 0.29 for no porosity to about 0.26 for about 18 percent porosity. Thus, for purposes of illustration a value of 0.25 was chosen as Poisson's ratio for niobium pentoxide with around 16 percent porosity (porosity level having been discussed in Appendix B).

The scale on the right of Figures 34, 43, 51a and 51b was determined using 0.25 for ν to correct σ_F which gave σ_T . The thin film stresses, σ_T , for the niobium pentoxide were tabu-

lated in Table 10. The average value calculated for σ_T was 133,500 psi.

There was one final correction to the thin film stress which must be made. The values for σ_F and σ_T as calculated and plotted as a function of oxidizing time, used the magnitudes of the oxidation bending stresses, σ_S , which contained both the contribution from the thin film of niobium pentoxide and the contribution from the additional oxidation stresses. These contributions could not be separated as a function of oxidizing time but were separated after the oxidation and cooling process by the dissolution and annealing treatment. Therefore, the additional contribution to the maximum bending stress which was not attributable to the niobium pentoxide film was that bending stress removed by annealing. Dividing this 'annealing bending stress' by the total bending stress in the positive direction gave a percent correction for the effect not due to niobium pentoxide. These percent corrections along with the corrected final values of σ_F and σ_T were listed in Table 11. The average values computed were 70,370 and 93,820 psi for the corrected σ_F and σ_T respectively. Thus, the final corrected value for the total lateral compressive stress in a thin film of niobium pentoxide forming on niobium

in oxygen near 425°C was about 94,000 psi.

This value compared well with the value of 117,000 psi measured by Douglass (33) as the compressive strength of niobium pentoxide at room temperature. The agreement between the measured lateral stress and the ultimate compressive stress suggested that in this 'break-away' oxidation range, the individual niobium pentoxide nuclei grow until they impinge upon one another in a lateral direction. The compressive stress builds up to the point when the compressive strength is surpassed and the oxide fractures or 'breaks-away'. Since this is happening on an individual basis in a random manner over the specimen surface, the overall compressive stress approaches that of the ultimate compressive strength.

The final statement made by Pawel et al. (60) in summarizing the results they found on the 'break-away' phenomena in niobium was as follows: "Evidence of the development of severe stresses within the oxide film was observed, and it is believed that these internally generated stresses play a dominant role in the break-away process."

In the early oxidation times, the oxidation bending stresses for 425°C measured by Pawel and Campbell and shown in Figure 8 were about 25 percent lower than the oxidation

bending stresses measured in this study and shown in Figures 25 and 27. However, the thicknesses of the specimens of the two studies varied so that a better comparison is made by using σ_I , the surface bending stress due to an oxygen concentration gradient as derived by Pawel et al. (81) and repeated here for clarity

$$\sigma_I = \sigma_S \frac{2h^2}{d(3h-2d)} \quad (2)$$

where $d = 2\sqrt{Dt}$, a diffusivity parameter and h is the specimen thickness. D , the diffusion coefficient of oxygen in niobium at 425°C , is taken as the same for both studies. Since the specimen thickness of Pawel and Campbell was 13.4 mil compared to 10 mil for this study, the second term in Equation 2 is about 34 percent higher for Pawel and Campbell. Therefore, a 25 percent decrease in σ_S times a 34 percent increase in the second term gives an overall increase in the σ_I for Pawel and Campbell of less than one percent over σ_I for this study.

These measured σ_I stresses can be compared to the theoretical oxygen solution stresses due to an oxygen concentration gradient calculated by Richmond et al. (82) as given in Equation 1 to obtain C_0 , the surface concentration of oxygen.

The σ_I reported by Pawel and Campbell (61) for oxygen-free niobium oxidized at 425°C was approximately 35,000 psi.

A σ_I of 35,000 psi in Richmond's theoretical calculations gave a C_0 of 2200 ppm. Since their specimens were oxygen free, this C_0 can be compared to the oxygen solubility limit of oxygen in niobium at 425°C. They took a solubility limit of 1700 ppm which then compared well with their C_0 of 2200 ppm.

However, as shown previously the oxygen solubility limit as determined from extrapolated values to 500°C was about 1000 ppm of oxygen. The C_0 of 2200 ppm of Pawel and Campbell does not compare well with the 1000 ppm oxygen solubility limit. Adding the initial oxygen content of 1300 ppm for specimens in this study to the C_0 of 2200 ppm gives a surface oxygen concentration of 3500 ppm which compares even more poorly to the solubility limit of oxygen in niobium at 425°C, 1000 ppm.

These comparisons of measured σ_I with theoretical σ_I to get C_0 's were made using the diffusion coefficient which Pawel and Campbell chose. Using the intermediate diffusion coefficient as chosen for this study for σ_I calculations, gave comparative theoretical σ_I 's and C_0 's which were higher than those just discussed. Therefore, because similar σ_I 's supposedly due to an oxygen concentration gradient were obtained for oxygen-free and oxygen-saturated specimens and because

the compared theoretical σ_I 's gave surface oxygen concentrations considerably above the oxygen solubility limit, another stress source must be contributing to the bending of the specimens during early oxidation times.

This contributing stress source was believed to be the formation of a thin niobium suboxide, NbO_x , film. The contribution to the oxidation bending stress, σ_S , due to a thin film formation of Nb_5O and the contribution due to an oxygen concentration gradient can be compared in a relative manner by holding all the oxidation conditions for the oxidation process constant except the temperature. In the equation derived by Richmond et al. for the theoretical oxygen solution stress, σ_I , Equation 1, the only term which would increase perceptively with a ten centigrade degree rise would be the surface oxygen concentration, C_0 . From Figure 1, the rise in the solubility limit of oxygen in niobium in the temperature range near $500^\circ C$ is at most 20 ppm for a 10 centigrade degree rise. An increase in the C_0 of Equation 1 of 20 ppm would cause an increase of about 300 psi in the theoretical σ_I . Therefore, for values of σ_I above 30,000 psi, the increase due to a 10 centigrade degree rise would be less than one percent.

Taking the measured σ_I in Equation 2 from Pawel and

Campbell as increasing by less than one percent for a 10 centigrade degree oxidation temperature rise, the change in oxidation bending stress, σ_S , needed to compensate for the change in the second term due to the increase in D , the oxygen diffusion coefficient, is obtained. Independent of the diffusivity values used for oxygen diffusion near 425°C , a 10 centigrade degree rise causes a 33 percent rise in the value of D . The thickness and relative time are held constant, so the decrease in the value of the second term in Equation 2 is governed by the diffusion coefficient change through d . The decrease in the second term is about 13 percent for a 33 percent increase in D due to the 10 centigrade degree rise. The decrease of 13 percent of the second term in Equation 2 would cause the oxidation bending stress, σ_S , to increase about 13 percent in order to maintain the increase in σ_I for a 10 centigrade degree rise in oxidation temperature as less than one percent. Therefore, a 13 percent increase in the oxidation bending stress, σ_S , during early oxidation times can be accounted for as due to an oxygen concentration gradient increase caused by an oxidation temperature rise of 10 centigrade degrees.

The oxidation bending stress contribution due to the

formation of a thin film of NbO_x , example Nb_5O used, can be looked at by using Equation 5 reproduced here for clarity

$$\sigma_F = \frac{1}{3} \sigma_S \frac{h}{w} \quad (5)$$

As shown previously for the thin film stress, σ_F , for Nb_2O_5 , the thin film stress, σ_F , for NbO_x should reach a constant stress level. This stress level should not vary appreciably with a small temperature change. The magnitude of w , the thin film thickness, of Equation 5 varies linearly with the weight gain of a specimen due to an oxygen pickup. Therefore, holding the specimen thickness, h , and the thin film stress, σ_F , constant in Equation 5, an increase in the weight gain due to an increase in the oxidation temperature at a relative oxidation time gives a proportional increase in the oxidation bending stress, σ_S , necessary to maintain the σ_F constant. Thus, for an increase in the weight gain due to oxygen pickup of 33%, the oxidation bending stress, σ_S , would increase 33%. Changes of this order of magnitude for weight gain at 10 minutes of oxidation time for changes in oxidation temperature of 10 centigrade degrees have been observed. The change needed for the example of Nb_5O from 420 to 430°C oxidation temperature is only 0.03 mg (0.09 to 0.12 mg). The changes needed for the examples of Nb_4O and Nb_6O would be plus or

minus 18 percent respectively from this 0.03 mg value. Therefore, an increase in the oxidation bending stress, σ_S , during early oxidation times of at least 33 percent, and perhaps greater, can be accounted for as due to an increase in the thin film thickness of NbO_x caused by an oxidation temperature rise of 10 centigrade degrees.

As shown in Figure 36 for specimens 71 and 70, a 10 centigrade degree rise in the oxidation temperature has caused increases in the oxidation bending stress, σ_S , of 29, 27 and 25 percent for oxidation times of 10, 15, and 20 minutes, respectively. Similarly shown in Figure 45 for specimens 77 and 79, a 10°C rise in the oxidation temperature caused increases in σ_S of 36, 31 and 26 percent for comparative oxidation times. For specimens 85 and 86, a 5°C rise caused increases in σ_S of 24, 25 and 27 percent for comparative oxidation times.

These results show that for an increasing initial oxygen content in a specimen, the increase in the oxidation bending stress, σ_S , caused by an increase in the oxidation temperature becomes larger. The magnitudes of the σ_S increases became increasingly larger than that explainable by a bending stress increase due to an oxygen concentration gradient increase

(13%). These results indicate that with increasing initial oxygen contents in the specimens, for a given weight gain increase due to an oxidation temperature increase less oxygen is going into solution and more is being used to form the thin film of NbO_x . Since then the thickness of the NbO_x film for a given oxidation time is increasing with increasing initial oxygen content, the oxidation bending stress will increase in a similar manner.

Therefore, during early oxidation times, the cause of the oxidation bending stress, σ_s , at increasingly higher initial oxygen contents can be accounted for better by a thin film formation of NbO_x than by the formation of an oxygen concentration gradient.

The results and conclusions have been discussed in a relative manner for the niobium suboxide NbO_x using the example Nb_5O . These results and conclusions would be just as valid for the other suboxides Nb_6O and Nb_4O because the relative values would remain approximately constant even though the absolute magnitudes vary by plus or minus 18 percent.

To obtain an approximate thin film stress for Nb_5O the equation for the thin film stress, σ_F , Equation 5 must be corrected similarly to that for the niobium pentoxide case. The

correction, Poisson's ratio for Nb_5O , is not known but a reasonable value can be chosen. As previously mentioned, Poisson's ratio for most single oxides varies between 0.2 and 0.3. The value for most dense, hard oxides approaches 0.3 (98). The value of Poisson's ratio for niobium is 0.38.

Taking a value of Poisson's ratio of $1/3$ for Nb_5O makes the values for the Nb_5O thin film stress, σ_T , one and a half times greater than the σ_F values. This is the scale used for σ_T in Figures 35, 44, and 52 and in Table 10. Using the values for σ_F from specimens 85 and 86 with oxygen contents of 4000 ppm, gave values of σ_T for Nb_5O of 160,000 and 150,000 psi respectively.

Looking at Figures 41 and 49, the largest oxygen solution stress, σ_I , that is indicated before the oxygen solution model breaks down completely is approximately 60,000 psi. This says that the compressive stress in the very surface of the metal caused by the solution of oxygen is 60,000 psi.

The surface oxygen concentration, C_0 , above the initial oxygen content which would be responsible for a σ_I in the metal of 60,000 psi is 3700 ppm. Since the initial oxygen content was at least 1300 ppm, the total oxygen concentration at the surface would be at least 5000 ppm. The solubility

limit of oxygen in niobium around 425°C is thought to be around 1000 ppm. The indication is then that a second phase has formed. In this temperature range, it is thought that oxygen goes into the interstitial positions in the body-centered cubic structure of niobium in an oriented manner forming a body-centered tetragonal structure. The tetragonality increases with increasing oxygen content until the suboxide unit cell is formed. This is also thought to happen in areas of clusters rather than as a distinct outer region near the metal surface. Because of the gradual transition and because of the random clustering, a distinct second phase is hard to see optically but indications are there from electron microscopy (74).

If this oxygen going into solution had formed a distinct unit cube of niobium pentoxide, the theoretical stress in the niobium pentoxide would be, according to the Pilling-Bedworth calculations, at least 1,560,000 psi using Young's modulus for niobium pentoxide from Durbin et al. (84) and could be up to 9,400,000 psi using that from Douglass (33). The measured compressive stress in the niobium pentoxide film was about 94,000 psi or from only one to six percent of the theoretical value. Therefore, the oxidation process to form niobium pen-

toxic does not happen in this theoretical manner but rather is a considerable redistribution of the atoms at the metal-oxide interface. For the temperature range of study, this redistribution is through the niobium suboxide, NbO_x , phase.

Although the niobium pentoxide does not form in an epitaxial manner upon the oxygen-hardened niobium substrate, it does have some physical coherency. This coherency would tend to produce a tensile strain in the attached substrate proportional to its compressive stress; the proportionality being the relation of the Young's Moduli of the two materials. The cooling flexure measurements showed that curvature changes calculated from the fiber deflections were within a few percent of theoretical curvature changes calculated from Equation 9 using an E_M/E_0 of two as discussed in Appendix C. Using this proportionality of two, the tensile stress acting upon the substrate due to the niobium pentoxide film would be about 188,000 psi.

Using the oxygen solution model, the compressive stress in the substrate surface would be about 60,000 psi. Thus, the resulting tensile stress on the metal substrate due to the oxidation process would be about 128,000 psi.

Using the 'effective' thin film model for NbO_x , the compressive stress in the substrate surface would be at least

125, 150 and 177 thousand psi for Nb_6O , Nb_5O , and Nb_4O respectively. The resulting tensile stress on the substrate surface would be at most 63, 38, and 11 thousand psi for Nb_6O , Nb_5O , and Nb_4O , respectively. These values appear more reasonable. In fact, since the niobium pentoxide is not completely coherent with the substrate and does fracture, it probably slips and deforms to reduce the actual tensile stress towards a value in closer agreement with the minimum value of 11,000 psi.

Oxide Wedge Formation

Materials

The material used in this section on the study of oxide wedge formation was obtained from the Fansteel Metallurgical Corporation in the form of one fully annealed 20-mil niobium sheet. The maximum impurity limits as given by the supplier along with the gaseous interstitial contents determined by vacuum fusion analysis in this laboratory are shown in Table 5.

Preparation

The 20-mil niobium sheet was cut into strips and machined to form sheet tensile specimens with a 4-cm gauge length and a 1-cm width. The surfaces were polished using 600 grit silicon carbide paper. The specimens were suspended from the thermogravimetric balance into a furnace and oxidized at 430°C in air to an approximate weight gain of 50 mg. This procedure

formed a thin adherent layer of niobium pentoxide on the niobium specimens. These specimens were then annealed in a vacuum approaching 2×10^{-7} torr at temperatures between 600 and 1100°C. The annealing time at a given temperature was at least ten times longer than calculated for 95% saturation. Upon conclusion of the annealing, the cooling produced a spalling of the remaining oxide which was determined to be mainly niobium dioxide. The microstructures of specimens prepared in such a manner are shown in Figures 57 through 62. The nominal oxygen contents obtained for these specimens by vacuum fusion analysis are also indicated and vary from 1000 ppm to 3750 ppm for 600 to 1100°C annealing temperatures, respectively. These oxygen contents were confirmed by microhardness readings using Figure 4. No oxygen concentration gradients could be detected by hardness testing.

The specimens were given a final polish with 600 grit silicon carbide paper. The thickness and width were then measured to obtain the cross-sectional area.

Stress-strain measurements

In order to obtain background data on the tensile properties of niobium as a function of initial oxygen content, stress-strain measurements were made at room temperature and

at 425°C in helium. The purpose of this background data was threefold. First, to obtain the yield point and fracture stress of niobium as a function of oxygen content at 25 and 425°C. Second, to observe if an oxygen concentration would be reached whereby further adding of oxygen into solution did not raise the yield point or fracture stress appreciably but did reduce the amount of elongation before fracture. Third, to know the amount of oxygen needed in a specimen in order to apply a constant tensile stress and remain in the elastic region of the specimen.

The true stress, σ , versus true strain, ϵ , curves were obtained using the following equations

$$\sigma = P/A_i \quad (12)$$

$$\epsilon = \ln l_i/l_o = \ln A_o/A_i \quad (\text{before necking}) \quad (13)$$

$$\epsilon = \ln A_o/A_i \quad (\text{after necking}) \quad (14)$$

where P is the applied load, l_o and l_i are the original and instantaneous specimen gauge length, and A_o and A_i are the original and instantaneous specimen cross-sectional area. At room temperature, the true strain was calculated from measurements of both length and cross-sectional area up to the necking point. The results agreed within plus or minus two percent.

At higher temperatures, tests became more difficult because of problems with measurement techniques. A simple arrangement was developed to function as a high-temperature extensometer. Knife edges were secured to the specimen at the set gauge length with extension rods protruding down out of the furnace to which the extensometer was fastened. A helium atmosphere was used to reduce the specimen contamination at temperature.

True stress versus true strain curves were plotted to the necking point using Equation 13. After necking, the curves were assumed to be linear between the ultimate and fracture stress.

The engineering stress-engineering strain curves as a function of oxygen content at 25 and 425°C are shown in Figures 63a and 64a respectively. The true stress-true strain curves as a function of oxygen content at 25 and 425°C are shown in Figures 63b and 64b respectively. A tabulation of the data from these specimens is given in Table 12. Figure 65 shows a plot of upper yield point, ultimate tensile stress, true fracture stress, and elongation as a function of oxygen content for the data taken at room temperature. The data shown in Figure 65 show very good agreement with the data

taken by Tottle (72) shown in Figure 10. Figure 66 shows a plot of upper yield point, ultimate tensile stress, true fracture stress, and elongation as a function of oxygen content for the data taken at 425°C. These data can be only roughly compared with that taken by Enrietto et al. (92) shown in Figure 11. The values at lower oxygen contents were approximately in agreement but at high oxygen contents this study showed considerably higher values of ultimate tensile stress. However, above 0.3 weight percent oxygen, the magnitudes of ultimate tensile stress in this study were dropping and thus are approaching agreement at 0.43 weight percent oxygen with the data of Enrietto et al.

The curve for true fracture stress in Figure 66 showed an increase with oxygen content up to about 0.25 weight percent. At this point it began leveling off and reached a maximum stress at about 0.31 weight percent oxygen after which the magnitude decreased. Therefore, the magnitude of the fracture stress in high oxygen content niobium is around 80,000 psi. This fracture appeared to happen in an increasingly brittle manner with increasing oxygen content because the amount of plastic deformation or total elongation decreased.

If oxide wedges form by brittle fracture of the oxygen-

saturated layer, these tensile test data show that an applied stress of around 80,000 psi is required at an oxidizing temperature of around 425°C to form them.

Constant stress measurements

When flexure specimens which are not oxygen saturated are oxidized, any wedges which form do so under conditions of varying stress and varying oxidation gradient. Moreover, the total strains required to produce wedges in a flexure test exceed the yield strain, making both measurement and analysis difficult. Constant stress measurements were designed in order to form wedges at uniform stress and oxygen level.

Coupon specimens of niobium were suspended from the thermogravimetric balance into a furnace and oxidized at 430°C in air for varying times. Upon completion of the desired oxidation time, they were sectioned and mounted and the resulting thicknesses measured with a filar eyepiece in a microscope. Figure 67 shows the resulting thickness of original 20-mil niobium specimens oxidized at 430°C in air as a function of time. The linearity of the plot was expected because of the linearity of the oxidation rate with time in this temperature range.

The desired experiment was to oxidize niobium tensile

specimens near 425°C in air while maintaining a constant applied tensile stress. In order to maintain a constant applied tensile stress upon a specimen oxidizing linearly with time, it was necessary to decrease the applied load proportionately with time.

A system was built to perform this function. Figure 68 is a schematic diagram of this apparatus. The tensile specimen is attached by wedge grips between support rods on the specimen side of a creep machine (left side of the schematic drawing). A load cell was suspended between the tensile specimen and the lever arm of the creep machine. Signals from the load cell were fed back into the console of a Budd Universal Testing Machine from which the existing load could be read off of a tape strip or could be plotted on a strip chart recorder. A glass sleeve containing alumina chips was placed around the tensile specimen inside the furnace. The alumina chips were used to preheat air circulated into the bottom of the glass sleeve and out a window across the specimen.

The load was suspended from the other end of the pivot arm (the right side of the schematic drawing). Water was used as the loading medium. In order to siphon the water off at a

constant rate, a constant pressure head must be maintained. A smaller can was placed atop the main loading bucket and fitted with an overflow tube and a tap off tube. Water was siphoned from the bucket and circulated through a centrifugal pump to the small can. The water level in the small can was thus maintained at the height of the overflow tube and this pressure head stayed constant. The water flow tapped from the bottom of the small can was adjusted through a variable stop-cock and metered by a flowmeter.

The loading system shown at the far left of the schematic drawing was a safety device to stop the swinging lever arm when a tensile specimen broke.

A magnitude of tensile stress to be applied was chosen and the needed load calculated. The load reduction needed with oxidizing time was calculated from curves of specimen thickness reduction such as Figure 67. After oxidation of the specimen, the final thickness was measured and the actual stresses calculated as a function of oxidizing time. Figure 69 shows an example of an applied tensile load and thickness reduction of a niobium tensile specimen oxidized at 435°C in air. Figure 72 shows the calculated applied tensile stresses on this oxidized specimen.

Results

In order to test the mechanics of the constant applied tensile stress apparatus built, a niobium specimen with an initial oxygen content of about 1000 ppm (which happened to be made from a piece of cold worked niobium sheet) was oxidized at 430°C in air while maintaining an approximate constant tensile stress of 15,000 psi. The intention was to oxidize the specimen for one week but it failed on the fifth day. Upon sectioning and mounting the specimen, numerous oxide wedges were observed. To check the validity of this result, two specimens (which were prepared as discussed from annealed sheet) were oxidized in air at 440 and 435°C respectively while maintaining a constant tensile stress of approximately 15,000 psi. Figure 71 shows examples of the oxide wedges formed in the specimen oxidized at 435°C . The final niobium thickness was actually measured to be slightly greater than predicted so that the tensile stress could not have surpassed the 15,000 psi level. This result was in direct conflict with my hypothesized value of 80,000 psi needed for oxide wedge formation. The only plausible answer to this phenomenon appeared to be the existence of a stress raiser at the metal-oxide interface. The thought was that perhaps the

thin adherent film of oxide on niobium (either NbO_x or the oriented mixed NbO and Nb_2O_5) cracked under the applied tensile stress causing a stress amplification of four or five. The specimens were carefully polished and the niobium-oxide interface observed on a metallograph at 1400X. Microcracks were not observed in the thin adherent oxide layer but niobium suboxide needles were observed penetrating into the metal.

Figure 72 shows the microstructure of the metal-oxide interface of a niobium specimen oxidized at 430°C in air for 48 hours. Note the layering of the grayish niobium pentoxide upon the clear, light niobium. Figure 73 shows the microstructure of the metal-oxide interface of a niobium specimen oxidized at 500°C in air for 24 hours. Again the gray niobium pentoxide was layered upon the light niobium, but there was an additional phenomenon not observed at 430°C . These needles have been observed previously (10,12) at oxidation temperatures from about 475 to 650°C . They were designated as a suboxide of niobium called NbO_z (10).

Further observation of the suboxide needles in the specimens oxidized while being subjected to a tensile stress, showed that a number of these needles had microcracks associated with them. As shown in Figure 75, some cracks were

within the needles, some were propagated from the needles base, some from the needle tip, and some occurred between a few needles. It was thus suspected that the oxide wedge formation was initiated by the microcracks associated with the niobium suboxide needles. Further evidence of this was shown by Figures 76 and 77. Figure 76 is a microphotograph of a niobium pentoxide wedge in niobium at a magnification of 1400X. A point to observe was the initial direction of the oxide wedge formation before propagating more perpendicularly into the niobium. This direction was similar to that for most niobium suboxide needles indicating that the oxide wedge may have started from a microcrack inside of a suboxide needle. Figure 77 shows an area in the niobium pentoxide layers directly adjacent to the oxide wedge shown in Figure 76. The trail of pores and slight oxide discoloration observed were similar to those associated with niobium suboxide needles as shown in Figure 74. There thus was evidence of a direct relationship between niobium suboxide needles, microcracks associated with them, and niobium pentoxide wedges.

To obtain a more complete understanding of the oxide wedge formation phenomenon, niobium tensile specimens with varying initial oxygen contents were oxidized at various tem-

peratures around 425°C while maintaining various applied constant tensile stresses. The results from these experiments can be best handled as three groups. The first group was made up of specimens which had been prepared simultaneously with those used for the stress-strain measurements. They were used for a first, general analysis of the effects of oxygen content, temperature, and stress level. The results from this group are shown in Table 13. Except for specimens 30_B and 31_B which have already been discussed, the results for the most part showed that the temperatures and stress levels used were too low to form wedges in specimens with initial oxygen contents of 1300 to 3750 ppm. Specimen 55_B with an initial oxygen content of around 3150 ppm did show a few suboxide needles and a few oxide wedges. Specimen 58_B with an initial oxygen content of around 3750 ppm contained a few suboxide needles and only one small oxide wedge which appeared to lead to the early failure of this highly brittle tensile specimen.

The second group of specimens was prepared in a manner to produce a nominal initial oxygen content of 1300 ppm. Table 16 summarizes the results for these tensile specimens. The oxidizing temperature at which most positive data were obtained was 435°C . Table 14 indicates that specimens oxi-

dized at 435°C in air while maintaining stress levels of 25, 20, 15, and 10 thousand psi were subject to suboxide needle formation as well as oxide wedge formation. Figures 78 through 81 show the effects of the applied tensile stresses on these specimens in regard to suboxide needle formation. The frequency increased and length decreased with increasing applied tensile stress. The angle the needles made with the niobium-oxide interface remained essentially the same regardless of the crystal grain they were observed in. This angle was always approximately 45° or the angle of intersection of the metal-oxide interface and the crystal planes upon which the shear stress would be maximum. The niobium pentoxide wedge formation frequency increase corresponded with the frequency increase of niobium suboxide needles with increasing applied tensile stress.

The third group of specimens was prepared in a manner to produce a nominal initial oxygen content of 1950, 2550, and 3150 ppm. The oxidizing temperature was mainly chosen as 435°C and the applied tensile stress was varied. Table 15 summarizes the results of this group of specimens. The results again showed a correspondence of suboxide needle formation and oxide wedge formation. The frequency of oxide

wedges increased with the frequency of suboxide needles observed. An important result was that there existed a minimum applied tensile stress at a given oxygen content which was required for the formation of suboxide needles and subsequently oxide wedges. This minimum applied tensile stress varies from about 10,000 psi at 1300 ppm to 43,000 psi for 3150 ppm of oxygen. The upper yield point in this range varied from about 24,000 psi for 1300 ppm to 61,000 psi for 3150 ppm. Therefore, the difference between the upper yield point and the minimum stress required to form needles was about 14, 18, 15 and 18 thousand psi for initial oxygen contents of 1300, 1950, 2550 and 3150 ppm, respectively. These data for the oxidation of niobium tensile specimens at 435°C in air as a function of initial oxygen content and applied tensile stress are best shown in Figure 82.

A specimen with initial oxygen content of 1950 ppm was oxidized at 430°C in air while maintaining a constant applied tensile stress of 30,000 psi. This specimen showed the formation of a few niobium suboxide needles along with a few oxide wedges. A similar specimen oxidized under similar conditions but at 435°C, showed many more suboxide needles and oxide wedges than the specimen oxidized at 430°C. Therefore,

reducing the temperature means the minimum applied tensile stress must be increased to produce niobium suboxide needles and subsequently oxide wedges. The results from these specimens indicate that the minimum applied stress needed for suboxide needle formation for specimens oxidized at 430°C in air would be only about 5,000 psi below the upper yield point as a function of oxygen content as compared to about 16,000 psi below for 435°C .

Figure 83 shows the profiles of diamond pyramid hardness and oxygen content as a function of distance from the oxide-metal interface. These results indicate that for oxidation times of sufficient length (approximately 24 hours) the surface oxygen concentration is approximately the same irrespective of the initial oxygen contents of the specimens or the slight variations of temperature (plus or minus 10°C). Therefore, the oxygen concentration profile would be the same for a given set of specimens with the same initial oxygen contents oxidized at the same temperature for the same oxidation time. Therefore, the existence as well as the frequency and length of the suboxide needles would be only a function of the applied tensile stress in specimens under these conditions as was observed in Figures 78 through 81.

A final point was that the first tensile specimen oxidized which was made from a cold-worked niobium sheet, showed many more oxide spikes than specimens made from the annealed sheet which were oxidized at the same temperature and had about the same initial oxygen content. This result agrees with the observation of Doyle (12) that cold working a specimen reduces the temperature for suboxide needle formation.

Interpretation and discussion

A detailed study of the formation of these niobium suboxide needles in niobium has not been made. Van Landuyt and Wayman (13) did perform a detailed study of the suboxide needle formation in tantalum. As outlined in a previous section, the formation of tantalum suboxide, TaO_y , needles was shown to proceed in a martensitic manner. A subsequent overgrowth of another suboxide, TaO_z , then made the needles more readily visible in optical microscopy. They indicated that the actual details of formation of the TaO_y plates are still largely conjectural, but certain pieces of evidence obtained shed additional light on the situation. Firstly, the TaO_y plates do not form until a certain incubation period has passed. Secondly, their work established that the TaO_y plates form only near the surface. They postulated that since it

appeared that during the incubation period the oxygen concentration in a surface layer is building up, when this becomes high enough the oxygen saturated Ta transforms to the orthorhombic suboxide plates, TaO_y .

Since the oxidation characteristics of niobium and tantalum are very similar, the assumption that the niobium suboxide needles are also forming in a martensitic manner would not seem too unreasonable. Adding to this agreement is the observation that an incubation time is also needed in niobium to allow the surface oxygen concentration to build up. Also, tetragonal suboxides of niobium, NbO_x and NbO_z , have been observed which correspond to the tetragonal suboxides of tantalum, TaO_x and TaO_z . However, one correspondence which has not been observed is the existence of an orthorhombic niobium suboxide, NbO_y , similar to the orthorhombic tantalum suboxide, TaO_y . Since the existence of these orthorhombic suboxides is very critical to the argument favoring the mechanism of martensitic formation, a doubt exists as to the applicability of the mechanism of martensitic formation in the niobium system. Adding to this doubt are observations made in this study which appear to suggest another possible mechanism.

The observation was made that in most cases the suboxide

needles were associated with surface irregularities in the metal which may have been rounded by subsequent oxidation. A surface slip trace may have been produced by a slipping of the metal on a shear plane. The slipped metal would be more susceptible to oxidation than the surrounding matrix, so it would oxidize first, perhaps as a plate, and propagate itself along ahead of the metal-oxide interface.

Adding to this confusion is the information reported on the indices of the plane on which these NbO_z plates lie. Norman (101) reported that the (100) plane of the suboxide, NbO_z , was parallel to one of the (100) planes of the metal lattice. This would agree with the {100} indices observed by Van Landuyt and Wayman (13) for the habit plane of TaO_z , the overgrowth phase. However, the actual martensite phase underneath this overgrowth was the orthorhombic, TaO_y , with {320} habit planes.

Hurlen et al. (10) indicated that the diffraction lines received from the suboxide phase, NbO_z , were reflections from the 110 planes of the niobium metal lattice. This orientation would agree with the {110} indices for the slip planes found in niobium at room temperature (102).

As indicated by Van Landuyt and Wayman (13) the problem

is not that easily analyzed because of the closeness of the $\{110\}$ and $\{320\}$ planes in a body-centered cubic system to each other and to the theoretical shear plane. Also, the overgrowth of one oxide upon another adds confusion.

Therefore, because of the ambiguities of the proposed mechanism with observations, exactly which mechanism is causing the suboxide needle formation can not be determined without further study. The best study to begin with would be an electron microscopy study such as that of Van Landuyt and Wayman (13). An observation to be made would be the existence or non-existence of an orthorhombic niobium suboxide. Then further, the parent-oxide orientation relationship, the variants of the habit plane, the orientation relationship and the plane and direction of the inhomogeneous shear must be observed and related to prove or disprove the postulation of a martensitic mechanism. Once this is done, light will have been shed on the other possible mechanism.

The difference in frequency and length of the suboxide needles as observed in specimens with only the applied tensile stress varied, also can not unambiguously be explained. However, a possible explanation may be a nucleation and growth model. A higher applied tensile stress causes the nucleation

sites (observed dislocation lines (74)) to increase and thus the frequency of needles increases. The nucleation of suboxide needles which have a smaller spacing at this increased stress causes a reduction in the driving force in their immediate vicinity therefore causing a reduction in growth, or length.

Irregardless of the nucleation and growth or the formation mechanism of these suboxide plates, the important aspect for this dissertation was that under the proper conditions of oxygen concentration gradient, temperature and stress these plates do form. Once they are formed, in areas where the local frequency is high, only a very small applied tensile stress (less than 10,000 psi) is needed to produce a microcrack. Once this microcrack is formed it further oxidizes to form an oxide wedge. If the conditions of oxygen concentration gradient, temperature, and stress are not right to form suboxide plates, no microcracks or oxide wedges are observed. The important correlation then is the existence of niobium suboxide plates to subsequently make possible the formation of an oxide wedge.

COMBINED RESULTS

As shown in the section on flexure measurements, combining the tensile stress on the metal substrate due to the formation of niobium pentoxide with the compressive stress in the substrate surface due to an oxygen concentration gradient gives a resulting tensile stress of about 128,000 psi on the oxygen hardened substrate. As shown in the section on stress-strain measurements, this high a tensile stress acting upon the surface of oxygen-hardened niobium would cause plastic flow and subsequent metal fracture. These results were not observed due to the oxidation process alone. Therefore, the oxygen solution model is incorrect for these oxygen-saturated niobium specimens.

Combining the tensile stress on the metal substrate due to the formation of niobium pentoxide with the compressive stress in the substrate surface due to the formation of an 'effective' thin film of NbO_x gives a resulting tensile stress of about 10,000 to the very most of about 60,000 psi on the oxygen-hardened substrate. This magnitude of tensile stress due to the oxidation process alone can be supported by the oxygen-hardened substrate without causing plastic flow or metal cracking. Therefore, an 'effective' thin film model

appears to be reasonably correct for these oxygen-saturated niobium specimens.

No matter what the actual tensile stress is on the oxygen-saturated surface of the metal due to the oxidation process alone near 425°C , this stress would be approximately the same for the case of oxidizing niobium tubes, coupon specimens, flexure specimens or sheet tensile specimens. It is the addition of an applied tensile stress either by bending (as in the case of tubes or flexure specimens) or by pulling (as in the case of tensile specimens) on the oxygen-saturated metal surface which cause the formation of suboxide needles, subsequent cracking of the metal in some localized areas where there is a high frequency of needles, and a final formation of an oxide wedge.

The applied stress needed to form suboxide needles was observed to decrease with a decreasing initial oxygen content of the specimens and with an increasing temperature. Thus, as has been observed at low initial oxygen concentrations, a high enough oxidation temperature will in time produce a stress state which will cause the suboxide needles to form without any additional applied stress.

However, neither microcracks nor oxide wedges are ob-

served in these specimens so that some applied tensile stress is still needed for microcrack and subsequent oxide wedge formation. As mentioned previously, for these low initial oxygen contents, this applied tensile stress is less than 10,000 psi.

The cold-worked tensile specimen indicated that the temperature and stress level needed for niobium suboxide formation and subsequent oxide wedge formation were reduced by cold work.

The results of this study have serious implications from a materials design point of view. Many uses of niobium involve parts which are made from drawn tubing or formed sheet of commercial purity which are not further annealed. (Because of the low neutron cross-section of niobium, it has been suggested as a possible containant for the liquid sodium or potassium coolant in a fast breeder reactor.) The material would then be in a cold-worked state with a fairly low initial oxygen content. If the part were used in an atmosphere which contained oxygen in a temperature range of approximately 425 to 650°C, the oxygen concentration of the surface of the metal could build up to the level needed for niobium suboxide needle formation. If the temperature were such that needles formed

or were aided in formation by an applied stress of fairly small magnitude, then a subsequent stress of no larger than 10,000 psi would be needed to form microcracks and subsequent oxide wedges which would cause premature failure of the part.

Since the oxidation characteristics of niobium and tantalum are very similar and since suboxide needles are observed to form in tantalum, oxide wedge formation may take place in tantalum also.

SUGGESTIONS FOR FURTHER RESEARCH

As a result of discussions on the Young's Modulus of niobium pentoxide as a function of temperature and porosity, Bill Manning of the Ceramic Engineering Department at Iowa State University has already begun preliminary experiments on the mechanical properties of niobium pentoxide. A publication by Durbin et al. (84) indicated that Young's Modulus increased by a factor of four near a temperature of 800°C . If this phenomenon is indeed true, W. Manning and Dr. O. Hunter, Jr. believe it contains the possibility of a start on a research problem for a doctoral dissertation.

An electron microscopy study of the formation of niobium suboxide, NbO_2 , needles similar to that done by Van Landuyt and Wayman (13) on the tantalum system would be a difficult but interesting research problem. The results would directly relate to the studies of this paper on oxide wedge formation as governed by the suboxide needle formation.

The direct observation of suboxide needle formation as a function of temperature and stress applied using a metallographic hot stage is another possibility for further research.

And finally, but perhaps the most difficult, a complete and thorough examination of the niobium-oxygen system near

the metal rich end using techniques and analyses similar to those developed by Magneli et al. (96,97) for titanium, vanadium, zirconium and hafnium.

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APPENDIX A. THIN-FILM STRESS MODEL

An example of the bending of a beam of two different materials is the case of a bimetallic strip built up of materials of different E's. Timoshenko (86) considered the case due to bending from a temperature change. A schematic diagram of the case under consideration is shown in Figure 7b

The internal forces over any cross section of the beam must be in equilibrium; therefore

$$\Sigma F = 0 = P_M - P_O, P_M = P_O = P \quad (a)$$

$$\Sigma M = 0 = M_O + M_M = P \frac{h_M}{2} + P \frac{h_O}{2} \quad (b)$$

Using a moment form of the flexure beam formula:

$$M_O = E_O I_O / \rho \quad \text{and} \quad M_M = E_M I_M / \rho \quad (c)$$

Substituting these relations into Equation b gives

$$P/2(h_O + h_M) = E_O I_O / \rho + E_M I_M / \rho, \text{ simplified}$$

$$P = \frac{2}{\rho} \left(\frac{E_O I_O + E_M I_M}{h_O + h_M} \right) \quad (d)$$

The normal stress in the oxide is obtained by adding to the compressive stress produced by the force P, the tensile stress due to curvature $1/\rho$:

$$\sigma_N = \text{force/area (for P)} + \text{strain} \times E(\text{for curvature})$$

$$\sigma_N = \frac{P}{b h_O} + \frac{h E_O}{2\rho} \quad (e)$$

Substituting for P from Equation d

$$\sigma_N = \frac{2}{\rho b h_0} \left(\frac{E_O I_O + E_M I_M}{h_0 + h_M} \right) + \frac{h_0 E_O}{2\rho} \quad (f)$$

The moments of inertia are:

$$I_O = b h_0^3 / 12 \quad \text{and} \quad I_M = b h_M^3 / 12 \quad (g)$$

Substituting the moments of inertia in Equation f gives

$$\sigma_N = \frac{2}{\rho b h_0} \left(\frac{b h_0^3 E_O + b h_M^3 E_M}{12(h_0 + h_M)} \right) + \frac{h_0 E_O}{2\rho} \quad (h)$$

Since for the case in point, $h_M \approx 10$ mil and $h_0 < 0.5$ mil; h_0^3 is negligible compared to h_M^3 and $h_0 + h_M \approx h_M$. Thus, Equation h becomes

$$\sigma_N \approx \frac{h_M^2 E_M}{6\rho h_0} + \frac{h_0 E_O}{2\rho} \quad (i)$$

Since $h_M \gg h_0$; h_0 is negligible compared to h_M^2/h_0 and thus the tensile stress due to the curvature $1/\rho$ is eliminated.

$$\sigma_N \approx \frac{E_M h_M^2}{6\rho h_0} \quad (j)$$

This is the equation used by Dankov and Churaev (76) to calculate the normal compression in an oxide layer formed from a metal plated on a thin substrate of mica.

Substituting into this equation, the expression for the maximum bending stress as given by Equation 2 gives

$$\sigma_F = \frac{1}{3} \sigma_S \frac{h_M}{h_0} \quad (5)$$

This form of Equation j was used by Pawel and Campbell (61) to calculate the surface stresses due to a thin-film of niobium monoxide.

Equation 5 was derived from the assumption that the compressive stress is produced only by a force, P , acting in the normal direction. In fact, this is an incorrect assumption. There is a force, P , acting in the transverse direction producing a transverse bending moment and causing a compressive stress in the transverse direction of equal magnitude to that in the normal direction. This transverse compressive stress influences the normal compressive stress in an additive manner. This additive term can be most easily visualized and added through the maximum bending stress term.

The maximum bending stress, σ_s , as derived by Crandall and Dahl (83) to give Equation 2 was actually for the case of a slender beam where the only non-zero stress was in the normal direction. For the case of a thin plate, there is an additional arc of curvature, $-(1/\rho)$, in the transverse direction. Thus, using Hooke's law

$$\epsilon_x = 1/E [\sigma_x - \nu (\sigma_y + \sigma_z)] = -y/\rho \quad (k)$$

Since the plate is thin, assume

$$\sigma_x = \sigma_y = \sigma \quad \text{and} \quad \sigma_z = 0, \text{ then}$$

$$\epsilon_x = 1/E (1 - \nu) \sigma = -y/\rho, \text{ or}$$

$$\sigma = - \frac{E y}{\rho (1 - \nu)} \quad (l)$$

At the top or bottom surfaces of a beam of height h , $y = \pm h/2$ and the stress would be at its maximum. The maximum bending stress, σ_M , is

$$\sigma_M = \pm \frac{E h}{2 \rho (1 - \nu)} \quad (m)$$

Substituting this value for the maximum bending stress, σ_M , into Equation 5, gives the total compressive stress in the thin oxide film, σ_T .

$$\sigma_T = 1/3 \sigma_M \frac{h_M}{h_0}, \text{ or} \quad (n)$$

$$\sigma_T = \frac{E_M h_M^2}{6 \rho h_0 (1 - \nu)}, \text{ or} \quad (o)$$

$$\sigma_T = 1/3 \sigma_S \frac{h}{w} \frac{1}{(1 - \nu)} \quad (11)$$

APPENDIX B. CALCULATION OF NIOBIUM PENTOXIDE THICKNESS
FROM OXYGEN WEIGHT GAIN

The assumption made in this calculation is that the oxygen added to the oxidizing specimen is primarily used for forming niobium pentoxide layers on the surface of the specimen.

Since for most specimens the initial oxygen content was higher than the oxygen solubility limit in niobium at 425°C, there should not be any oxygen going into solid solution. There is a possibility of the oxygen being used to form a niobium suboxide film but since this film would be only a couple of microns thick, the oxygen used to form it is negligible.

The thickness of oxide on the top surface of the niobium specimen is the desired quantity so that the oxygen used to form pentoxide layers on the sides of the specimen must be factored out from the total. The ratio of the area of the sides to the top of the specimen is five percent.

From the Handbook of Chemistry and Physics (93), the densities are:

oxygen 1.429 g/cc

niobium 8.57 g/cc

$$2\text{Nb} = 2 \times 8.57 \text{ g/cc} = 17.14 \text{ g/cc}$$

$$5 \text{ O} = 5 \times 1.429 \text{ g/cc} = 7.14 \text{ g/cc}$$

$$\text{Nb}_2\text{O}_5 = 24.28 \text{ g/cc}$$

$$\text{O w/o} = 7.14/24.28 \times 100\% = 29.4 \text{ w/o in Nb}_2\text{O}_5$$

$$\text{Nb w/o} = 17.14/24.28 \times 100\% = 60.6 \text{ w/o in Nb}_2\text{O}_5$$

$$\text{Weight of oxygen} \times 3.40 = \text{Weight of niobium pentoxide}$$

The density of niobium pentoxide as formed on a specimen oxidizing at 425°C in air is not so firmly set. However, a good value can be arrived at by looking at existing data.

The theoretical value of the low-temperature form of niobium pentoxide is given as 5.17 g/cc (18). If the porosity of the niobium pentoxide layer formed at 425°C is taken as 16 percent in agreement with a porosity of 19 percent measured by Aylmore et al. (27) for niobium pentoxide formed at 500°C which is slightly more porous, the value for the density would be 4.34 g/cc. This value also compares favorably with a value of 4.36 g/cc reported for the density of an amorphous film of niobium pentoxide formed on niobium when oxidized at temperatures approaching 435°C (18).

$$\text{niobium pentoxide (16\% porosity)} \quad 4.34 \text{ g/cc}$$

$$\begin{aligned}\text{Volume of oxide} &= \text{length} \times \text{width} \times \text{thickness} \\ &= \text{weight of oxide} \div \text{density}\end{aligned}$$

$$\text{length} = 4 \text{ cm}$$

$$\text{width} = 1 \text{ cm}$$

$$\text{thickness} = x$$

$$V_{\text{Nb}_2\text{O}_5} = 4\text{cm}^2 \times x = W_{\text{Nb}_2\text{O}_5} / \rho_{\text{Nb}_2\text{O}_5}$$

$$x = \frac{W_{\text{Nb}_2\text{O}_5} \times 0.95}{\rho_{\text{Nb}_2\text{O}_5} \times 4\text{cm}^2} = \frac{W_o \times 3.40 \times 0.95}{4.34 \text{ g/cc} \times 4\text{cm}^2}$$

$$x = W_o(\text{gm}) \times 0.18604 \text{ cm}$$

$$x(\text{cm}) = W_o(\text{mg}) \times 0.18604 \times 10^{-3}$$

$$x(\text{microns}) = W_o(\text{mg}) \times 1.8604 \quad (8)$$

$$x(\text{mil}) = W_o(\text{mg}) \times 0.07325$$

The accuracy of this calculation was checked on a few coupon specimens of niobium oxidized for 24 and 48 hours in air at 425°C. The variation in oxide film thickness along a longitudinal section bracketed the calculated value to within five percent.

APPENDIX C. COOLING OF A BIMETALLIC STRIP

Let a narrow strip consisting of two metals welded together be uniformly cooled from $t^{\circ}\text{C}$ to $t_0^{\circ}\text{C}$. If the coefficient of linear expansion of these metals be different the cooling will produce bending of the strip. Let

α_M = the coefficient of thermal expansion of the metal M

α_0 = the coefficient of thermal expansion of the metal O

E_M = the modulus of elasticity of metal M

E_0 = the modulus of elasticity of metal O

h_M = the thickness of metal M

h_0 = the thickness of metal O

h = the total thickness of the strip

b = the width is unity.

The following analysis has been made by Timoshenko (94) assuming that the cross-sections of the strip originally plane and perpendicular to the axis remain plane during bending and become perpendicular to the curved axis of the strip. Consider an element cut out from the strip as shown in Figure 7b.

The internal forces over any cross section of the strip must be in equilibrium; therefore as shown in Appendix A in Equations a through d the result was

$$P = \frac{2}{\rho} \left(\frac{E_O I_O + E_M I_M}{h_O + h_M} \right) \quad (d)$$

Another equation for calculating P and ρ will be obtained from the consideration of deformation. On the bearing surface of both metals the unit elongation occurring in the longitudinal fibers of metals M and O must be equal, therefore

$$\alpha_O(t_O - t) + \frac{P_O}{E_O h_O} + \frac{h_O}{2\rho} = \alpha_M(t_O - t) - \frac{P_M}{E_M h_M} + \frac{h_M}{2\rho} \quad (p)$$

or, using Equations a and d from Appendix A

$$\frac{h}{\rho} + \frac{2(E_O I_O + E_M I_M)}{h\rho} \left(\frac{1}{E_O h_O} + \frac{1}{E_M h_M} \right) = (\alpha_M - \alpha_O)(t_O - t) \quad (q)$$

Simplifying,

$$\frac{1}{\rho} = \frac{(\alpha_M - \alpha_O)(t_O - t)}{\frac{h}{2} + \frac{2(E_O h_O + E_M I_M)}{h} \left(\frac{1}{E_O h_O} + \frac{1}{E_M h_M} \right)} \quad (r)$$

Letting,

$$\frac{h_O}{h_M} = m, \quad \frac{E_O}{E_M} = n \quad \text{and} \quad (t_O - t) = T$$

and taking the moments of inertia from Appendix A, Equation g, the following general equation for the curvature of a bimetal strip will be obtained

$$\frac{1}{\rho} = \frac{6(\alpha_M - \alpha_O)T (1+m)^2}{h[3(1+m)^2 + (1+mn)(m^2 + 1/mn)]} \quad (s)$$

At this point, Timoshenko applied the solution to a case for the two metals having the same thickness; whereas, in the

present case one metal had a thickness considerably greater than the other.

Substituting the thicknesses back into Equation s and simplifying for the case where $h_M \gg h_0$, Equation s became

$$\frac{1}{\rho} = \frac{6(\alpha_M - \alpha_0)T}{(4 + 1/n)h_M + 10 h_0 + h_M^2/h_0} + \frac{12(\alpha_M - \alpha_0)T h_0/h_M}{(4 + 1/n)h_M + 10 h_0 + h_M^2/h_0(1/n)} \quad (t)$$

Looking at the second part of Equation t, for $h_M \gg h_0$

$$h_M^2/h_0(1/n) \gg (4 + 1/n)h_M + 10 h_0. \quad (u)$$

Using the simplification of Equation u, the second part of Equation t became zero. Using Equation u on the first part of Equation t, it became

$$\frac{1}{\rho} = \frac{6(\alpha_M - \alpha_0)T}{h_M^2/h_0(1/n)} \quad (v)$$

Or, in another form

$$\frac{1}{\rho} = \frac{3}{1/n} (\alpha_M - \alpha_0)T \frac{2h_0}{h_M^2} \quad (w)$$

This equation was arrived at by taking only the boundary conditions $h_M \gg h_0$. If a value for n is substituted in,

$$n = E_0/E_M = 1/2, \quad 1/n = 2$$

$$\frac{1}{\rho} \approx \frac{3}{2} (\alpha_M - \alpha_0) T \frac{2h_0}{h_M^2} \quad (9)$$

An analogy between Timoshenko's two derivations for bimetallic strips of similar thicknesses and the present solutions for bimetallic strips of greatly different thicknesses gave the following

Timoshenko

$$\sigma_{\max} = E/3\rho (h)$$

$$\frac{1}{\rho} = \frac{3}{2} (\alpha_M - \alpha_0) (1/n)$$

Weirick

$$\sigma_{\max} \approx E/3\rho (h_M^2/2h_0)$$

$$\frac{1}{\rho} \approx \frac{3}{2} (\alpha_M - \alpha_0) \frac{2h_0}{h_M^2}$$

Thus, Equation 9 was used for the theoretical calculation of cooling bending stress.

If the value for the Young's Modulus of niobium pentoxide as measured by Douglass (33) was corrected for the chosen 16% porosity of the present film, the value of n would be approximately one. Equation 9 would thus be corrected by a factor of two.

Table 1. Summary of conditions for data on oxygen solubility in niobium

Ref. No.	Name	Year	Temp. range °C	Specimen	Exp. technique			Equil. phase
1	Seybolt	1954	755-1100	20 mil sheet	X.D.		M.E.	O ₂
2	Elliot	1959	500-1915	Nb-Nb5%O buttons	V.F.		M.E.	NbO
3	Bryant	1962	700-1550	125 mil sheet	V.F.			NbO
4	Lenel	1962	650-1250	2 mil sheet	X.D.		M.E.	O ₂
5	Gebhardt	1963	500-1900	30 mil sheet	X.D.	E.C.	M.H.	NbO
6	Lenel	1965	850-1250	40 mil sheet	V.F.		M.H.	NbO
7	Taylor	1957	1000-2200	10 mil wire	C.A.	X.D.	M.E.	NbO

Key

X.D. - X-ray diffraction
 M.E. - Metallographic examination
 V.F. - Vacuum fusion
 E.C. - Electrical conductivity
 M.H. - Microhardness
 C.A. - Chemical analysis

Table 2. Summation of previous work

No.	Ref. No.	Name	Year	Temp. range	Atmosphere	Specimen	Exp. technique		Range of study	Special parameters
1	(21)	Arbuzov	1955	500-1000	Air	Coupon	G.W.G.	M.E.	Overall kinetics and high minimum	Structure of Nb ₂ O ₅
2	(24)	Argent	1950	400-1050	Dry and moist O ₂	Coupon Cube	G.W.G.	M.E.	Overall kinetics and low minimum	Purity, pretreatment
3	(25)	Arkharov	1961	700-1200	Dry and moist Air	Coupon Cylinder	G.W.G.	X.D.	High temperature kinetics and oxides	Moisture specimen shape
4	(26)	Alymore	1959	500	Dry O ₂	Coupon	G.W.G.		Porosity of oxides on various metals	
5	(27)	Alymore	1960	350-750	Dry and moist O ₂	Coupon	G.W.G.	S.S.	Kinetics and specific surface	Moisture purity
6	(28)	Blackburn	1962	400-950	H ₂ O vapor O ₂	Coupon	G.W.G.	X.D.	Kinetics and oxides in water vapor	Surface preparation moisture
7	(E)	Brauer	1957	330	Air	Coupon	X.D.		Oxides at 330°C	
8	(29)	Bridges	1956	400-800	O ₂ , 14.7-600 psia.	Coupon	G.W.G.	M.E.	Effect of O ₂ pressure on kinetics	Hi O ₂ pressure
9	(30)	Burova	1964	1000-1200	Air	Coupon	E.D.	X.D.	Layer beneath the scale	Ti, Mo alloys
10	(31)	Cathcart	1958	325-450	Dry O ₂	Coupon	E.M.	X.D.	Microtopography	Pretreatment
11	(32)	Cox	1963	350-650	O ₂ , H ₂ O and steam	Coupon Disc	G.W.G.	X.D.	Effect of H ₂ O and steam	Moisture surface preparation
12	(33)	Douglass	1963	20-	-	-	-	-	Thermal expansion of Nb ₂ O ₅	-
13	(12)	Doyle	1963	400-700	Dry air	Coupon	M.E.	X.D.	Kinetics and oxides of low minimum	-
14	(5)	Gebhardt	1963	1060-1650	Dry O ₂	Wire	E.R.		-	Lo O ₂ pressure

Table 2. (Continued)

No.	Ref. No.	Name	Year	Temp. range	Atmosphere	Specimen	Exp. technique	Range of study	Special parameters
15	(19)	Goldschmidt	1959	400-1250	Air	Powder Wire	X D.	Transformation of Nb ₂ O ₅	Pre-oxidation treatment
16	(20)	Goldschmidt	1965	300-600	Dry O ₂	Coupon Powder	X D.	X-ray diffraction of Ta, Nb, and Nb alloys	-
17	(34)	Gulbransen	1949	400-900	Dry O ₂	Coupon	G.W.G. X.D.	Kinetics	Sample size
18	(35)	Gulbransen	1958	375-700	Dry O ₂	Coupon	G.W.G. X.D.	Kinetics	Sample size
19	(36)	Gurlen	1954	150-1000	Dry O ₂	Casting	M.E. E.M.	Overall kinetics	O ₂ pressure
20	(37)	Harvey	1964	300-600	Air	Coupon Disc	CAP E.D. M.E.	Break-away phenomena	Surface preparation
21	(39)	Hicks	1961	500-935	Dry O ₂	Cube	Movies	Outer oxide	-
22	(40)	Hicks	1962	450-1200	Dry O ₂	Cube	G.W.G. M.E.	Effect of grain size on oxide penetration	Grain size
23	(10)	Hurlen	1959	150-1000	Dry O ₂	Coupon	G.W.G. X.D. E.D. V.W.G. E.M. M.E.	Overall kinetics and oxides	-
24	(41)	Inouye	1953	400-1200	Wet and dry air	Coupon	G.W.G. X.D. M.E.	Overall kinetics and outer oxide	Moisture
25	(42)	Kilpatrick	1965	1050-1500	Steam	Rod	V.W.G. X.D.	Kinetics and oxides	Moisture
26	(43)	Klopp	1957	600-1200	Dry O ₂ and air	Coupon Rod	V.W.G. M.H. G.W.G.	Overall kinetics	Specimen shape
27	(44)	Kjoellesdal	1960	500-1200	Dry O ₂	Coupon	M.E.	Hi-temp. oxides	-
28	(47)	Kofstad	1960	500-1200	Dry O ₂	Coupon	G.W.G. M.E. E.M. X.D. E.D. M.H.	Overall kinetics and oxides	O ₂ pressure

Table 2. (Continued)

No.	Ref. No.	Name	Year	Temp. range	Atmosphere	Specimen	Exp. technique		Range of study	Special parameters
29	(48)	Kofstad	1962	500-700	Dry O ₂	Coupon	M.E.	E.M.	Low minimum	-
30	(49)	Kofstad	1965	1200-1700	Dry O ₂	Coupon	G.W.G. M.E.	X.D.	Overall kinetics and oxides	O ₂ pressure
31	(50)	Kolski	1962	400-1325	Dry O ₂	Coupon	G.W.G. M.E.	X.D. M.H.	Overall kinetics and oxides	-
32	(51)	Krobokov	1963	400-1100	Dry O ₂	Coupon	X.D.	E.D.	Phase composition of oxides	-
33	(53)	Lorant	1963	400-700	Dry O ₂	Coupon	G.W.G.	E.D.	Lo-temp. kinetics and oxides	-
34	(54)	Mukaibo	1965	485-735	Dry air	Coupon	G.W.G. M.E.	X.D.	Lo-T kinetics and outer oxide	V alloy
35	(55)	McLintock	1962	620-810	Dry O ₂ and N ₂	Coupon	V.W.G.		Effect of N ₂ content on linear oxidation	N ₂ content
36	(56)	McLintock	1963	450-1050	Dry O ₂	Coupon	V.W.G.		Overall kinetics and O ₂ pressure effect	O ₂ pressure
37	(58)	Ong	1962	-	-	-	-	-	Theoretical oxidation kinetics	-
38	(59)	Pasternak	1964	50-1900	Dry O ₂	Ribbon	V.W.G.		Sorption of O ₂	H ₂ vacuum N ₂
39	(60)	Pawel	1961	400-425	dry O ₂	Coupon Sphere	V.W.G. E.M.	M.E.	Break-away phenomena and orientation	Polycrystal and single crystal
40	(61)	Pawel	1966	400-425	Dry O ₂	Coupon	B.S.M.	M.E.	Stress measurements	Ta, Al coated
41	(62)	Prohoshkins	1963	700-1200	Dry air	Coupon	X.D.	M.E.	Outer oxide	-
42	(63)	Raghaven	1962	500-700	Dry O ₂	Coupon	G.W.G.		Effect of dissolved O ₂ on kinetics	-

Table 2. (Continued)

No.	Ref.	Name	Year	Temp. range	Atmosphere	Specimen	Exp. technique		Range of study	Special parameters
43	(64)	Revyakin	1961	500-	Dry O ₂	Coupon	G.W.G.	M.E.	Kinetics	
44	(65)	Rhodin	1961	700- 1300	Dry O ₂ and Argon	Coupon	G.W.G. M.H.	M.E. X.D.	Overall kinetics and oxides of Nb and Ti, Cr alloys	Ti, Cr alloys
45	(66)	Stuckens	1963	25- 1500	Dry O ₂ air	Coupon	V.W.G. X.D.	M.E.	Overall kinetics and oxides	N ₂ , CO ₂ purity
46	(67)	Trillat	1963	500- 1000	Air	Coupon Film	E.D.		Transmission work General-area diffraction.	O ₂ pressure
47	(13)	Van Landuyt	1965	600	Lo pressure O ₂	Film	E.M.		Transmission work	-
48	(68)	Voytovich	1962	200- 800	Air	Coupon	G.W.G.		Effect of work hardening	Specimens pretreatment

E.M. - Electron microscope
 CAP - Capacity measurements
 V.W.G. - Volumetric weight gain
 E.R. - Electrical resistance measurements
 M.E. - Metallographic examination
 G.W.G. - Gravometric weight gain
 X.D. - X-ray diffraction
 M.H. - Microhardness
 S.S. - Specific surface measurements
 E.D. - Electron diffraction
 B.S.M. - Bending stress measurement

Table 3. Oxide phases formed on niobium metal at various temperatures

Outer scale	Temp. °C	Adherent inner layer
T - Nb ₂ O ₅	400	NbO _x + oriented T - Nb ₂ O ₅
	475	
	500	NbO ₂ + oriented T - Nb ₂ O ₅
	575	
	600	NbO + oriented T - Nb ₂ O ₅
	675	(NbO ₂ at low O ₂ pressures - 1 torr)
T - Nb ₂ O ₅ + small amounts of poorly crystalline H - Nb ₂ O ₅	700	oriented T - Nb ₂ O ₅
	825	
imperfectly crystalline H - Nb ₂ O ₅	850	oriented T - Nb ₂ O ₅ + oriented H - Nb ₂ O ₅
	1000	
	1025	oriented T - Nb ₂ O ₅ + oriented H - Nb ₂ O ₅
	1250	
H - Nb ₂ O ₅	1250	(at very low O ₂ pressure - 10 ⁻³
	1700	NbO + NbO ₂

Table 4. Compressive stresses in niobium oxides calculated from Pilling-Bedworth ratios

	Name	Mol. wgt.	Density g/cc	Pilling- Bedworth ratio	Cube root of P-B ratio	Unilateral strain ^a	Compressive stress ^b x10 ³ psi
1	Nb	92.91	8.55	-	-	-	-
2	Nb ₆ O	573.46	8.33 ^c	1.057	1.018	0.009	130.5
3	Nb ₅ O	480.55	8.28 ^c	1.068	1.021	0.0105	152.5
4	Nb ₄ O	387.64	8.20 ^c	1.080	1.026	0.013	188.5
5	Nb ₂ O	201.82	7.90 ^c	1.170	1.054	0.027	391.5
6	NbO	108.91	7.30	1.370	1.110	0.055	797.5
7	NbO ₂	124.91	5.98	1.920	1.243	0.123	1783.5
8	Nb ₂ O ₅	265.82	5.17	2.366	1.333	0.167	2421.5

^aCase for strain equal in metal and oxide.

^bUse $E = 14.5 \times 10^6$ psi.

^cDensity taken from Figure 7.

Table 5. Chemical analysis of niobium sheet and tube

Impurity	Tube suppliers limits ppm	Sheet suppliers limits ppm	10-mil sheet vac. fus. analysis ppm	20-mil sheet vac. fus. analysis ppm
O ₂	300	500	650-800	250-350
N ₂	300	500	250-350	30-40
H ₂	50	-	1-10	1-10
C	100	200		
Fe	500	200		
Mo	500	200		
Ni	200	100		
Si	300	100		
Ta	1000	800		
Ti	500	200		
Zr	500	200		
W	500	100		

Table 6. Conditions for flexure measurement specimens (62-68) (6-8 micron aluminum coating)

Specimen No.	O ₂ added mg.	Anneal temp. °C.	O ₂ content ppm	Oxdn. temp. °C	Oxdn. time min.	O ₂ added mg.	Cal. cool. bend. stress x10 ³ psi
62	0.5	500	1197	425	270	10.0	5.10
63	1.1	500	1244	425	180	6.9	3.50
64	1.2	500	1314	425	180	6.4	3.20
65	1.6	500	1306	425	240	8.0	4.05
66	1.6	500	1295	425	240	8.3	4.20
67	2.0	500	1296	425	240	8.9	4.50
68	2.0	500	1318	425	240	8.6	4.35

Table 7. Summary of data for flexure measurement specimens (62-68) (6-8 micron aluminum coating)

Specimen No.	Oxdn. B.S. x10 ³ psi	Cool. E.S. x10 ³ psi	Total x10 ³ psi	HF B.S. x10 ³ psi	Anneal. B.S. x10 ³ psi	Total x10 ³ psi	Diff. %
62	14.86	5.10	19.96	16.35	4.01	20.36	2.0
63	12.38	3.45	15.83	11.77	4.20	15.97	0.9
64	10.60	3.35	13.95	10.02	4.13	14.15	1.4
65	14.56	4.14	18.70	14.00	5.00	19.00	1.6
66	13.08	3.95	17.03	12.36	4.67	17.03	-
67	14.97	4.34	19.31	14.15	4.85	19.00	1.6
68	14.66	4.15	18.81	14.40	4.60	19.00	1.0

Table 8. Conditions for flexure measurement specimens (69-86) (6-8 micron annealed aluminum coating)

Specimen No.	Thickness mil	Anneal temp. °C	Oxygen content ppm	Oxdn. temp. °C	Oxdn. time min.	Oxygen added mg.	Cal. cool. bend. stress 10 ³ psi
69	10.00	500	1292	425 ^a	240	7.3	3.70
70	9.75	500	1415	430	120	4.3	2.25
71	9.75	500	1432	420	240	4.1	2.15
72	9.75	500	1483	430	150	5.7	3.00
73	9.75	500	1521	425	180	6.1	3.20
77	9.50	800	2825	420	240	4.5	2.45
79	9.00	800	2931	430	150	3.9	2.25
81	9.50	1000	3566	425	180	4.4	2.40
83	9.50	1000	3436	430 ^b	150	5.1	2.80
85	9.50	1200	4008	425	180	4.7	2.55
86	9.50	1200	3985	430	150	5.8	2.95

^aStart temperature was high.

^bStart temperature was low.

Table 9. Summary of data for flexure measurement specimens (69-86) (6-8 micron annealed aluminum coating)

Specimen No.	Oxdn. B.S. x10 ³ psi	Cool. B.S. x10 ³ psi	Total positive x10 ³ psi	HF B.S. x10 ³ psi	Anneal B.S. x10 ³ psi	Total negative x10 ³ psi	Diff. %
69	13.95	3.74	17.69	13.00	5.05	18.05	1.9
70	9.67	2.20	11.87	8.10	4.02	12.12	2.1
71	9.47	2.28	11.75	7.80	3.90	11.70	0.4
72	11.82	3.04	14.86	10.46	4.65	15.11	1.7
73	11.47	3.16	14.63	12.21	2.55	14.76	0.9
77	11.05	2.35	13.40	9.05	4.45	13.50	0.7
79	11.30	2.25	13.55	9.20	4.10	13.30	1.8
81	10.94	2.51	13.45	9.14	4.31	13.45	-
83	11.50	2.72	14.22	9.64	4.46	14.10	0.8
85	10.27	2.52	12.79	10.07	2.80	12.87	0.6
86	12.73	2.97	15.70	12.50	3.20	15.70	-

Table 10. Summary of results for flexure measurement specimens (69-86)

Specimen No.	σ_I 10 ³ psi	C _O ppm O ₂	Nb ₂ O ₅			Nb ₅ O	
			σ_F	σ_F	σ_T^a	σ_F	σ_T^b
			150 min 10 ³ psi	final 10 ³ psi	final 10 ³ psi	initial 10 ³ psi	initial 10 ³ psi
69	-	-	92.38	86.91	115.85	135.75	203.62
70	59.0	3650	-	100.72	134.26	129.65	194.48
71	52.0	3200	103.50	102.48	136.64	134.17	201.25
72	58.5	3600	99.60	92.16	122.88	128.15	192.25
77	57.0	3500	117.93	106.16	141.54	123.68	185.52
79	58.5	3600	118.67	118.67	158.22	120.03	180.45
81	-	-	110.58	107.49	143.32	118.82	178.23
83	-	-	97.48	97.48	129.97	113.13	169.70
85	(45.1) ^c	2800	96.88	94.46	125.94	106.59	159.89
86	(55.2) ^c	3400	94.88	94.88	126.50	99.55	149.33
Total Avg.			103.54	100.14	133.51		

^a ν for Nb₂O₅ with 16% porosity taken as 0.25.

^b ν for Nb₅O taken as 1/3.

^c No horizontal portion of curve, value taken at 30 minutes.

Table 11. Summary of corrected results for flexure measurement specimens (69-86)

Specimen No.	Percent correction	σ_F corrected 10 ³ psi	σ_T corrected 10 ³ psi
69	28.5	62.14	82.83
70	33.6	66.88	89.15
71	33.2	68.46	91.28
72	31.3	63.31	84.42
77	33.2	70.91	94.55
79	30.3	82.71	110.28
81	32.0	73.09	97.46
83	31.4	66.87	89.16
85	21.9	73.77	98.36
86	20.4	75.52	100.69
Total avg.		70.37	93.82

Table 12. Mechanical properties of niobium as a function of oxygen content at 25 and 425°C

Specimen No.	Oxygen content ppm	Upper yield point 10 ³ psi	Ultimate tensile stress 10 ³ psi	Total elong. %	True stress at fracture 10 ³ psi	True strain at fracture
25°C						
18	300	18.5	27.5	50	42.0	52.5
28	1000	40.0	55.5	33	77.0	37.0
32	1200	43.0	57.4	32	80.0	36.5
36	1950	70.0	81.5	28	110.0	35.0
48	2550	83.5	98.5	27.5	130.5	33.0
52	3150	98.5	116.4	27	153.5	30.5
56	3750	104.0	105.0	(1.5) ^a	(106.5) ^a	(1.5) ^a
425°C						
29	1000	20.0	37.8	19	49.5	28.5
33	1200	22.0	41.1	19	53.5	30.0
37	1950	33.7	58.5	19	72.0	16.5
49	2550	49.5	66.0	15	80.5	14.0
53	3150	61.5	75.0	9	83.5	8.5
57	3750	62.0	71.5	7	80.5	6.7

^aSpecimen fractured at knife edge.

Table 13. Results for constant stress tensile specimens (30B-59B)

Specimen No.	Oxygen content ppm	Oxdn. temp. °C	Oxdn. time hrs.	Stress start 10 ³ psi	Stress finish 10 ³ psi	Suboxide needles	Oxide wedges
30B	1000	440	36	15	17	Yes	Yes
31B	1000	435	48	15	16	Yes	Yes
34B	1200	420	48	15	12	No	No
35B	1200	410	48	15	13	No	No
38B	1950	425	48	15	15	No	No
39B	1950	420	48	20	20	No	No
50B	2550	425	59	20	22	No	No
51B	2550	420	72	30	28	No	No
54B	3150	420	20	50	50	No	No
55B	3150	435	36	40	45	Few	Few
58B	3750	420	46	40	37	Few	One
59B	3750	420	20	50	50	No	No

Table 14. Results for constant stress tensile specimens (64B-71B)

Specimen No.	Oxygen content ppm	Oxdn. temp. °C	Oxdn. time hrs.	Stress start 10 ³ psi	Stress finish 10 ³ psi	Suboxide needles	Oxide wedges
64B	1300	420	72	20	18	No	No
65B	1300	415	72	25	23	No	No
66B	1300	435	48	25	25	Yes	Yes
67B	1300	435	48	20	21	Yes	Yes
68B	1300	435	48	15	15	Yes	Yes
69B	1300	420	48	10	9	No	No
70B	1300	435	48	10	10	Few	Few
71B	1300	435	46	20	22	Yes	Yes

Table 15. Results for constant stress tensile specimens (72B-82B)

Specimen No.	Oxygen content ppm	Oxdn. temp. °C	Oxdn. time hrs.	Stress start 10 ³ psi	Stress finish 10 ³ psi	Suboxide needles	Oxide wedges
72B	1950	435	46	30	30	Yes	Yes
73B	1950	435	46	20	20	Yes	Yes
74B	1950	435	48	15	15	Few	Few
75B	1950	430	40	30	30	Few	Few
76B	3150	435	48	15	14	No	No
77B	3150	435	48	20	18	No	No
78B	3150	435	48	20	19	No	No
79B	3150	435	48	30	28	No	No
80B	2550	435	48	30	30	No	No
81B	2550	435	20	40	41	Yes	Yes
82B	2550	435	36	35	35	Few	Few

Figure 1. Solubility of oxygen in niobium as a function of temperature

Figure 2. The generalized oxidation-time curve for niobium

Figure 3. Linear oxidation rate of niobium in air at one atmosphere pressure

Figure 4. Diamond pyramid hardness versus oxygen content in niobium

Figure 5. Knoop microhardness versus depth of contamination in niobium by oxygen

Figure 6. Richmond's oxygen solution stress versus oxygen content in niobium

Figure 7. Density of niobium oxides versus oxygen/niobium ratio

Figure 7b. Schematic drawing of forces and bending moments acting on a section of a slender beam

Figure 8. Pawel and Campbell's bending stress curves for 400°C and 425°C

Figure 9. Pawel and Campbell's oxygen solution stress, σ_I , thin-film stress, σ_F , and oxygen consumed curves for 425°C

Figure 10. Effect of oxygen content on room temperature tensile properties of niobium

Figure 11. Ultimate strength of niobium as a function of temperature for various oxygen contents

Figure 12. Reaction of niobium with air at one atmosphere for various temperatures

Figure 13. Horizontal oxide 'spike' growth

a. 8 hrs.

b. 16 hrs.

Figure 14. Cross-sections of 3/8" O.D. x 0.020" wall niobium tubes oxidized at 500°C in air; 7X

b. 16 hrs.

c. 24 hrs.

d. 32 hrs.

Figure 14. Cross-sections of 3/8" O.D. x 0.020" wall niobium tubes oxidized at 500°C in air; 7X
b. 16 hrs.

a. 2 hrs.

b. 4 hrs.

c. 5 hrs.

Figure 15. Cross-sections of 3/8" O.D. x 0.020" wall niobium tubes oxidized at 700°C in air; 7X

d. 6 hrs.

e. 8 hrs.

Figure 15. Cross-sections of 3/8" O.D. x 0.020" wall niobium tubes oxidized at 700°C in air; 7X

Figure 16. Diamond pyramid hardness versus oxygen penetration distance for 425°C

Figure 17. Diamond pyramid hardness versus oxygen penetration distance for 500°C

Figure 18. Diamond pyramid hardness versus oxygen penetration distance for 700°C

Figure 19. Schematic drawing of flexure measurement specimen

$1'' = 4''$

Figure 20. Schematic drawing of flexure measurement apparatus

Figure 22. Weight of oxygen gained versus thickness of niobium pentoxide scale formed for 425°C

Figure 23. Weight of oxygen gained versus calculated cooling bending stress for cooling from 425° to 25°C

Figure 24. Schematic drawing of dissolution apparatus

Figure 25. Oxidation deflection and bending stress curves for 10-mil niobium oxidized at 425°C ; specimens 62, 63 and 64

Figure 26. Macrophotographs of specimen 63 showing curvature after oxidizing and cooling, after dissolution and after vacuum annealing; 2.5X

Figure 27. Oxidation deflection and bending stress curves for 10-mil niobium oxidized at 425°C ; specimens 65, 66, 67 and 68

Figure 28. Cooling deflection and bending stress curves for specimens 65, 66, 67 and 68 compared to final calculated cooling bending stress

Figure 29. Dissolution deflection and bending stress curves for specimens 65, 66, 67 and 68

Figure 30. Annealing deflection and bending stress curves for specimens 65, 66, 67 and 68

Figure 31. Macrophotographs of specimen 65 showing curvature after oxidizing and cooling, after dissolution and after vacuum annealing; 2.5X

Figure 32. Oxygen solution stress, σ_I , curves for specimens 64 and 68

Figure 33. Weight gain due to oxygen versus time for specimen 63, 64, 65, 66, 67 and 68

Figure 34. Thin-film stress curves, σ_F and σ_T , for niobium pentoxide on specimens 63, 64 and 65.

Figure 35. Thin-film stress curves, σ_F and σ_T , for niobium suboxide (Nb₅O) on specimens 64 and 68

Figure 36. Oxidation deflection and bending stress curves for specimens 69, 70, 71 and 72

Figure 37. Cooling deflection and bending stress curves for specimens 69, 70, 71 and 72 compared to final calculated cooling bending stress

Figure 38. Dissolution deflection and bending stress curves for specimens 69, 70, 71 and 72

ANNEALING DEFLECTION (235 MM FIBER)

Figure 39. Annealing deflection and bending stress curves for specimens 69, 70, 71 and 72

Figure 40. Macrophotographs of specimen 71 showing curvature after oxidizing and cooling, after dissolution and after vacuum annealing; 2.5X

Figure 41. Oxygen solution stress curves, σ_I , for specimens 70 and 71

Figure 42. Weight gain due to oxygen versus time for specimens 69, 70, 71 and 72

Figure 43. Thin-film stress curves, σ_F and σ_T , for niobium pentoxide on specimens 69, 70 and 71

Figure 44. Thin-film stress curves, σ_F and σ_T , for niobium suboxide (Nb_5O) on specimens 69, 70 and 71

Figure 45. Oxidation deflection and bending stress curves for specimens 77, 79, 81, 83, 85 and 86

Figure 46. Macrophotographs of specimen 79 showing curvature after oxidizing and cooling, after dissolution and after vacuum annealing; 2.5X

Figure 47. Macrophotographs of specimen 81 showing curvature after oxidizing and cooling, after dissolution and after vacuum annealing; 2.5X

Figure 48. Macrophotographs of specimen 86 showing curvature after oxidizing and cooling, after dissolution and after vacuum annealing; 2.5X

Figure 49. Oxygen solution stress curves, σ_I , for specimens 77, 79, 85 and 86

Figure 50. Weight gain due to oxygen versus time for specimens 77, 79, 81, 83, 85 and 86

Figure 51a. Thin-film stress curves, σ_F and σ_T , for niobium pentoxide on specimens 77, 81 and 83

Figure 5lb. Thin-film stress curves, σ_F and σ_T , for niobium pentoxide on specimens 79, 85 and 86

Figure 52. Thin-film stress curves, σ_F and σ_T , for niobium suboxide (Nb_5O) on specimens 77, 79, 81, 83, 85 and 86

Figure 53. 10-mil niobium specimen oxidized on one side at 425°C in air for 24 and 30 hours respectively

Figure 54. 10-mil niobium specimen oxidized on one side at 425°C in air for 36 and 48 hours respectively

Figure 55. End view of 10-mil niobium specimen oxidized for 8 hours at 425°C in air

Figure 56. Cross section of 10-mil niobium specimen oxidized at 425°C in air for 24 hours; 250X

Figure 57. Microstructure of 20-mil niobium tensile specimen annealed at 600°C to give an oxygen content of 1000 ppm; 250X and 1400X respectively

Figure 58. Microstructure of 20-mil niobium tensile specimen annealed at 700°C to give an oxygen content of 1300 ppm; 250X and 1400X respectively

Figure 59. Microstructure of 20-mil niobium tensile specimen annealed at 800°C to give an oxygen content of 1950 ppm; 250X and 1400X respectively

Figure 60. Microstructure of 20-mil niobium tensile specimen annealed at 900°C to give an oxygen content of 2550 ppm; 250X and 1400X respectively

Figure 61. Microstructure of 20-mil niobium tensile specimen annealed at 1000°C to give an oxygen content of 3150 ppm; 250X and 1400X respectively

Figure 62. Microstructure of 20-mil niobium tensile specimen annealed at 1100°C to give an oxygen content of 3750 ppm; 250X and 1400X respectively

Figure 63a. Engineering stress versus engineering strain as a function of oxygen content at 25°C

Figure 63b. True stress versus true strain as a function of oxygen content at 25°C

Figure 64a. Engineering stress versus engineering strain as a function of oxygen content at 425°C in helium

Figure 64b. True stress versus true strain as a function of oxygen content at 425°C in helium

Figure 65. Upper yield point, ultimate tensile stress, true fracture stress and elongation versus weight percent oxygen at 25°C

Figure 66. Upper yield point, ultimate tensile stress, true fracture stress and elongation versus weight percent oxygen at 425°C in helium

Figure 67. Thickness of original 20-mil niobium specimen oxidizing at 430°C in air with time

Figure 68. Schematic drawing of constant applied tensile stress apparatus

Figure 69. An example of applied tensile load and thickness reduction of niobium specimen oxidizing at 435°C in air with time

Figure 70. Calculated applied tensile stress on niobium specimen oxidizing at 435°C in air with time

Figure 71. Oxide wedges formed in niobium tensile specimens oxidized at 435°C in air while a constant tensile stress of approximately 15,000 psi was applied; 100X

Figure 72. Microstructure of niobium-oxide interface of niobium specimen oxidized at 430°C for 48 hours; 1400X

Figure 73. Microstructure of niobium-oxide interface of niobium specimen oxidized at 500°C for 24 hours. Note the addition of NbO₂ needles; 1400X

Figure 74. Suboxide needles formed in niobium tensile specimens oxidized at 435°C in air while a constant tensile stress of approximately 15,000 psi was applied; 1400X

Figure 75. Four examples showing cracks associated with niobium suboxide needles; 1400X

Figure 76. Oxide wedge in niobium tensile specimen; 1400X

Figure 77. Holes in niobium pentoxide associated with oxide wedge shown above; 1400X

Figure 78. Suboxide needles formed in a niobium tensile specimen oxidized at 435°C in air while a constant tensile stress of 25,000 psi was applied; 1400X

Figure 79. Suboxide needles formed in a niobium tensile specimen oxidized at 435°C in air while a constant tensile stress of 20,000 psi was applied; 1400X

Figure 80. Suboxide needles formed in a niobium tensile specimen oxidized at 435°C in air while a constant tensile stress of 15,000 psi was applied; 1400X

Figure 81. Suboxide needles formed in a niobium tensile specimen oxidized at 435°C in air while a constant tensile stress of 10,000 psi was applied; 1400X

Figure 82. Plot of applied tensile stress versus initial oxygen content for niobium tensile specimens oxidized at 435°C in air indicating the formation of oxide wedges

Figure 83. Diamond pyramid hardness and oxygen content versus distance from metal/oxide interface for hardened niobium oxidized near 425°C