Formation of Void in Oxide Scale on Niobium with High Temperature Oxidation

Michio YAMAWAKI

A mode of formation of void in oxide scale on niobium with oxidation was studied in the temperature range 585-760°C using an observation-in-polarized-light technique. The voids formed in this temperature range have typically the shape of a circular cone with a concaved bottom. Using the above technique reflection from the surfaces of the voids could be clearly observed from outside of the scale. In an early short period of less than 5 or 10 min an initial group of voids are formed and their diameters are expanded with oxidation according to a parabolic time law. After the formation of the initial group of voids, new void formation ceases up to about 30 min. Thereafter, a second group of voids begin to form in the oxide/metal interface region of the specimen. The density of the initial group of voids is highly affected by the surface roughness of the specimen as well as the reaction temperature.

1 Introduction

It has been reported that a number of voids are produced in oxide scale on niobium with high temperature oxidation. In the lower temperature range 400-600°C lines of pores are produced over the NbO2 suboxide platelets, whilst at higher temperatures around 700°C conical-shaped or lenticular voids are produced in otherwise compact scale. The conical-shaped voids act as barriers to oxygen transport in scale and so reduce the weight-increase rate of the specimen. Little was known, however, about the mode of the formation of these voids. Hence, this aspect of the oxidation of niobium has been studied in detail as a part of the series of investigations on the oxidation of niobium and niobium alloys.

2 Experimental

The material used for this investigation was an electron-beam-melted niobium bar with the following maker's analysis: Nb : 99.99% up, Ta : 500ppm, W : 300ppm, N,O, Si and Fe : 100 ppm each, C and Cu : 400 ppm each. The bar was purified by melting in an electron-beam melting furnace. By this melting the hardness of the niobium decreased from 80 to 60 on the Vickers diamond scale. The casting was cold-rolled into sheets about 0.2 mm thick. Rectangular specimens of 2.5 cm x 1.0 cm were cut from the sheets and vacuum-annealed at 1200°C. Most of the specimens were electro-polished in a 90% H2SO4-10% HF solution. Some of the specimens were abraded with up to 1000 grit emery papers. All the specimens were then thoroughly washed and degreased. Oxidation was conducted in a silica-glass system. The finished specimen was suspended inside a reaction tube by a platinum wire and dried air was passed at a rate of 150 ml/min. After oxidation, the surfaces of the specimens were examined in polarized light using an optical microscope. In polarized light reflection from the surfaces of the voids was observed as bright circles, whilst the compact part of the scale was dark. Using this technique the size and the density of the voids in scale were measured from outside of the scale. For some specimens intermittent oxidation runs were conducted so as to directly examine a mode of expansion of the diameter of the voids with oxidation.

3 Results and Discussion

Typical cross section of a void formed in oxide scale on niobium in the temperature range 600-760°C is shown in Photo. 1. While in Photo. 2 and 3, where photomicrographs taken in polarized light are given, circular reflections from the surfaces of the voids are clearly observed. Photo. 1 and 2 (or 3) give cross-sectional and top views of the voids, respectively, from which the typical shape of the voids is deduced to be a circular cone with a concaved bottom.
Photo. 1 Cross section of an abraded Nb specimen oxidized at 735°C for 13 min. The part of scale over the top of the void was removed during metallographical preparation of the specimen.

Photo. 2 Microphotographs taken in polarized light showing expansion of voids in scale on an abraded Nb specimen with oxidation at 735°C (intermittent oxidation run)
   Reaction interval : (a) 4 min, (b) 13 min, (c) 30 min, (d) 50 min

In order to clarify a mode of change in size as well as in density of voids with oxidation, a series of electro-polished specimens was oxidized for various lengths of time at several temperatures ranging from 635 to 760°C. After each run, diameters of the voids were measured using a micrometer-attached microscope. A typical change in the diameter distribution with time obtained for oxidation at 635°C is shown in Fig. 1. The diameter distribution curve for the initial period exhibits a sharp peak in the smaller diameter region. This peak moves rightward with time, indicating a gradual expansion of the diameter of the voids with oxidation. Strictly, the expansion rate is not uniform for all the voids, as shown by the broadening of the peak with time. The diameter distribution curve for 35 min exhibits another peak (or plateau) in the smaller diameter.

Photo. 3 Microphotographs taken in polarized light showing the effect of temperature on the formation of voids in scale on electropolished Nb specimens
   Oxidation time : 15 min for all specimens
   Temperature : (a) 685°C, (b) 635°C, (c) 685°C, (d) 735°C

Fig. 1 Change of the void diameter distribution in the electro-polished specimen oxidized at 635°C with time
region. This peak indicates that a second group of voids began to form at about 30 min.

A mode of change in the density of voids with oxidation is explicitly indicated in Fig. 2, where the density of voids, \( N \), is plotted against time. As can be seen from this figure, a comparatively small number of voids are formed in an early period of less than 5 or 10 min, then further void formation ceases up to about 30 min. Thereafter, a second group of voids begin to form.

In order to estimate a mode of change in the diameter of voids with oxidation the square of the mean diameter, \( D \), of initially-formed voids which was obtained from the abscissa of the corresponding peak in the diameter distribution curve is plotted against time in Fig. 3 for 635 and 735°C. Each curve in Fig. 3 shows that the diameter of initially-formed voids is expanded according to a parabolic time law.

For further confirmation of this result, expansion of the specific voids was followed using an intermittent oxidation run. The square of the mean diameter of voids obtained from this run is plotted against time in Fig. 3, resulting in Curve I. This result confirms a parabolic expansion of the diameter of voids as estimated above. In Photo. 2 some of the microphotographs of the specimen examined in the intermittent run are given.

The mean diameter of voids, \( D \), is also plotted against scale thickness, \( X \), which gives a linear relation, as indicated in Fig. 4. This result shows that the thickness of scale increases according to a parabolic time law as well, in accord with Sheasby's observation\(^{12,13}\). From Fig. 4, the \( D/X \) ratio is calculated as 3.2 for both 635 and 735°C. As the...
scale thickness is approximately equal to the height, \( H \), of the initially-formed voids (as seen from Photo. 1), the above \( D/X \) ratio is nearly equal to the \( D/H \) ratio. At present, however, this value can not be theoretically explained on account of the lack of a proper model of expansion of voids.

Based on a number of cross-sectional observations it was presumed that the voids are nucleated in the oxide/metal interface region, \( i.e. \) at the oxide/metal interface and/or in the innermost part of scale. As the scale is forming continuously at the oxide/metal interface\(^3\), the voids formed at later stages are located in comparatively deep regions of the scale. As a result, the counting of the number of the lately-formed voids was not so easy as that of the initially-formed ones. This is one of the drawbacks of this observation-in-polarized-light technique. Its another drawback is in the fact that on abraded specimens outline of reflection from voids is not so distinct as on electro-polished ones due to the disturbing reflection from various surface defects produced during abrasion.

It was noted that temperature considerably affects the density of voids, as seen from Fig. 2 as well as Photo. 3, where microphotographs, taken in polarized light, of the specimens oxidized for 15 min at various temperatures are shown. The logarithmic value of the density of initially-formed voids in electro-polished specimen is plotted against reciprocal absolute temperature in Fig. 5, which gives a linear relation between \( \log N \) and \( 1/T \) expressed as follows:

\[
N(\text{mm}^{-2}) = 1.82 \times 10^{-22} \exp[4.80 \times 10^4/T(\text{K})]
\]

At 585°C irregular voids were formed in addition to circular ones. The distribution of the areas of different types of voids was intimately related with that of the substrate grains. So the formation of irregular voids is attributed to NbO\(_2\) platelets which can form various types of voids in an anisotropic way on account of the difference in the metal density of NbO\(_2\) and that of Nb (O) substrate\(^3\). The point of 583°C in Fig. 5 indicates the density of voids in a circular void forming area where the effect of NbO\(_2\) platelets is estimated to be minimal. This appears to be the reason why the point is located with a smooth connection with those for temperatures above 600°C.

Besides temperature, the finishing of specimens was observed to affect the density of voids as well. As seen from the comparison of Photo. 2 and 3, an abraded specimen is more prone to nucleation of voids than an electro-polished one. This result is consistent with Sheasby's observation\(^9\). The difference in nucleation densities is attributed to that in the amounts of surface defects which can afford nucleation

\[1/T \times 10^4 (\text{°K}^{-1})\]

Fig. 5 Temperature-dependence of the number density of voids in scale on electro-polished specimens

sites for voids (even though the detailed mechanism of nucleation of voids is not well known at present). The nucleation of lately-formed voids appears not to be related with the surface roughness, but with the accumulation of the growth stresses in scale.

In this paper some of the experimental facts concerning the mode of formation of conical-shaped voids in scale on niobium with oxidation have been presented. As a next step, mechanisms of nucleation and growth of voids are expected to be clarified. A trial to connect the mode of expansion of voids to the weight increase behavior of specimen did not succeed due to the disturbing rapid oxidation at the edges of specimen.

**4 Summary**

A mode of formation of void in oxide scale on niobium with oxidation was studied in the temperature range 585—760°C using an optical microscope and the following results were obtained.

(1) The typical shape of the void formed in this temperature range is a circular cone with a concaved bottom, of which the diameter/height ratio is about 3.2.
A relatively small number of voids form in the initial short period of less than 5 or 10 min, then the formation of voids ceases up to about 30 min. Thereafter, a second group of voids begin to form.

The diameter of the bottom of the voids expands at a parabolic rate, keeping a linear relation with the scale thickness during oxidation.

The number density of the initially-formed voids is highly affected by the temperature as well as the surface roughness of the specimen.

Acknowledgements:

The author wishes to appreciate Professors T. Mukaiho and M. Kanno for their instructive suggestions on this study. Thanks are also due to Miss K. Osada for typing the manuscript.

References:

Technical Paper

Vapor Phase Equilibrium of the Disproportionation Reaction of Indium Dichloride*

Yasuo Kuniya** and Masahiro Hosaka**

Equilibrium of the disproportionation reaction of indium dichloride in the vapor phase, \( \text{InCl}_3(g) \rightleftharpoons \text{InCl}_2(g) + \text{Cl}_2(g) \), has been studied by means of vapor pressure measurements and computer calculations. In the calculations, the vapor phase species of \( \text{InCl}_3(g) \), \( \text{InCl}_2(g) \), \( \text{InCl}_1(g) \), and \( \text{Cl}_2(g) \) were considered and each partial pressure was calculated by using the equilibrium constants previously reported. The temperature dependence of the equilibrium constant for the above reaction was obtained as \( \log K_p = \frac{-7.463 \times 10^4}{T} + 9.658 \). The vapor pressures of \( \text{InCl}_3 \) and \( \text{InCl}_2 \) were also investigated and it was found that the vapor phases from these compounds consist of same species as those from \( \text{In}_2\text{Cl}_4 \).

1 Introduction

With the progress of technique for single crystal growth of III-V compound semiconductors by vapor phase chemical transport, the optimization of yield has been extensively studied by thermodynamic calculations for the vapor phase equilibria in the transport reaction system. In these studies, chemical species in vapor phase in the system should at first be accurately known. Therefore, we have investigated reactions between the metallic element as a constituent of compound semiconductor and halogen, and studied physical and chemical behaviors of the halides in the vapor phase.

In early works on the thermodynamic calculations, only predominant reactions in the system were considered. Although some species of fairly small amounts, e.g. \( \text{As}_2 \), \( \text{P}_2 \), and the like, have been recently taken into account in the calculation, it seems that other species with unexpected high partial pressure have not yet been regarded.

In the studies on the reactions in the system \( \text{InCl}_3 \), the following equilibria were investigated:

\[
\begin{align*}
\text{InCl}_3 (g) & \rightleftharpoons 2 \text{InCl}_2 (g) \quad (1) \\
\text{InCl}_2 (g) & \rightleftharpoons \text{InCl} (g) + \text{Cl}_2 (g) \quad (2)
\end{align*}
\]

Furthermore, in order to discuss the vapor phase reaction in a system containing indium and chlorine, the existence of indium dichloride in the vapor phase should be taken into account, but it has been over-looked in studies by many investigators. In our previous paper, it was pointed out that the compound exists as \( \text{InCl}_3(g) \) rather than \( \text{InCl}_2(g) \), even in the vapor phase, and that it disproportionates with increasing temperature according to the equilibrium:

\[
\text{InCl}_3 (g) \rightleftharpoons \text{InCl}_2 (g) + \text{InCl} (g) \quad (3)
\]

The present work was intended to determine the...