Technical Paper

Oxidation of Nb-Mo Alloys Over the Temperature Range of 485 to 935°C

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The oxidation behavior of Nb-2.5, 5.0 and 7.5 a/o Mo alloys was investigated in detail by means of thermogravimetric measurement, X-ray diffraction and metallographic methods. The tests were conducted at temperatures ranging from 485 to 935°C in dry oxygen at a pressure of 0.20 atm. Generally the para-linear or pseudo para-linear type of oxidation curve was obtained. The apparent linear oxidation rate of the alloys was calculated from the post transition part of each oxidation curve and was found to be generally lower than that of pure niobium. Breakaway of a thin protective layer formed at low temperatures was delayed by molybdenum alloying. At temperatures ranging from 635 to 735°C on Nb-5.0 or 7.5 a/o Mo alloy a thin protective layer of NbO₂ was formed to give a high oxidation resistance, under which NbO₂ platelets were formed abundantly. The B-Nb₂O₅ was for the first time identified in the scales on the Nb-Mo alloys at temperatures ranging from 685 to 835°C. Oxidation of Nb-2.5 a/o Mo alloy at 835°C was found to show a peculiar parabolic to plateau-like type rate transition and this was attributed to the T to B structural transition of Nb₂O₅ in scale.

1 Introduction

A considerable effort has been devoted to the problem of developing an oxidation-resistant niobium alloy without the emergence of an alloy of commercial quality. According to preceding papers^{1)~5)} on oxidation resistance of niobium-base alloys, molybdenum is looked upon as one of the elements which make solid solution with niobium over a wide composition range and improve the poor oxidation resistance of niobium. Recently close relationships between the oxidation rate of niobium alloys and the structure of oxide scales formed on the alloys have been clarified^{6)~8)}. The present report will describe an investigation of the high temperature oxidation properties of niobium-molybdenum alloys with emphasis laid on the relation between the oxidation rate and the structure of the scale.

2 Experimental

Three kinds of niobium-molybdenum alloys with nominal molybdenum contents of 2.5 a/o (=atomic%), 5.0 a/o and 7.5 a/o, respectively, were prepared in vacuum in an electron beam melting furnace. The niobium used (original purity 99.9% up) was purified by means of electron beam melting. The reported analytical quality of the niobium was as follows; Ta: 500 ppm, W: 300 ppm, N, O, S and Fe: 100 ppm each, C and Cu: 400 ppm each. The molybdenum

was a semi-sintered rod supplied by the Toshiba Electric Co.. According to the report of the company, the purity of the molybdenum was 99.96% and contents of the oxides of Al, K and Si were less than 20 ppm each. Because of a high rate of gas release from the molybdenum semi-sintered block, the molybdenum was purified in an electron beam melting furnace in advance of alloy preparation. The melting of each alloy specimen was repeated three times after inversion of the specimen each time, in order to ensure complete melting. The Vickers hardness values and the lattice constants of the alloys were in good accordance with corresponding values in references^{9),10)} when the true composition of the alloy was assumed to be given by the nominal value. Hence the nominal composition of the alloy was assumed to be in close proximity to its true composition.

The castings of the Nb-Mo alloys were cut into slabs about 2 mm thick, which were then rolled to 0.2 mm in thickness, all at room temperature. Rectangular specimens of 8 mm×27 mm were cut from the sheets, which were heat-treated in vacuum of 2×10^{-5} torr or less for 2 hours at 1350°C. By this heat treatment the specimens became polycrystalline with an average grain diameter of about 0.1 mm. After heat treatment, specimens were polished electrolytically in a solution of H₂SO₄+10% HF for one minute, with the anodizing voltage of 12 V, then weighed by means of a chemical microbalance.

The apparatus and the experimental method of this research were the same as described in previous paper⁶⁾.

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In this work each sample was oxidized for 2 hours in oxygen at 0.20 atm.

3 Results

3.1 Kinetic studies

The typical results of the oxidation rate measurements are presented in Fig. 1~3. The weight gain curves in these figures generally start out in nearly parabolic form and then straighten out. At the rate transition point or during the rate transition period of each weight gain curve the instantaneous oxidation rate of the specimen either increases (*i.e.* breakaway oxidation), does not change, or decreases, depending upon the temperature and the specimen composition. These three types of the parabolic to linear rate transition are typically shown in the weight gain curves for the oxidation of Nb-2.5 a/o Mo alloy at 585°, 785° and 835°C, respectively, as seen in Fig. 1. In some cases of the breakaway oxidation the weight gain changes nearly sigmoidally following the initial parabolic stage, as typically shown in the curve for Nb-7.5 a/o Mo alloy oxidized at 785°C in Fig. 3. Such a type of oxidation curve is called a pseudo-paralinear type in this paper.

The "apparent" linear rate was calculated from the

Curve no.	Temperature(°C)	Curve no.	Temperature(°C)
1	485	6	735
2	535	7	785
3	585	8	835
4	635	9	935
5	685		

Fig. 1 Weight gain curves for Nb-2.5 a/o Mo alloy

Curve no.	Temperature(°C)	Curve no.	Temperature(°C)
1	485	6	735
2	535	7	785
3	585	8	835
4	635	9	935
5	685		

Fig. 2 Weight gain curves for Nb-5.0 a/o Mo alloy

Curve no.	Temperature(°C)	Curve no.	Temperature(°C)
1	485	6	735
2	535	7	785
3	585	8	835
4	635	9	935
5	685		

Fig. 3 Weight gain curves for Nb-7.5 a/o Mo alloy

Fig. 4 Temperature dependence of apparent linear rate of Nb and three kinds of Nb-Mo alloys

● : Nb, ▽ : Nb-5.0 a/o Mo alloy
○ : Nb-2.5 a/o Mo alloy, △ : Nb-7.5 a/o Mo alloy

post-transition part of each parabolic or pseudo-parabolic type weight gain curve and its logarithmic value is plotted against the reciprocal absolute temperature in Fig. 4. For oxidation of Nb-2.5 a/o Mo alloy three runs were made at most run temperatures each and the mean value of the linear rate and the

mean deviation from it for each three runs were calculated and shown in Fig. 4. The scattering of the linear oxidation rate of Nb-2.5 a/o Mo alloy was considerably large, as seen in Fig. 4. The linear oxidation rates of the three alloys were generally in fair agreement with each other (within or nearly within the scattering range of the rate for Nb-2.5 a/o Mo alloy) for most temperatures investigated, except for 485°C and 835°C, where the linear rate of Nb-2.5 a/o Mo alloy was either higher or lower than either of the rates of the other two alloys by much more than the scattering range of the rate.

In Fig. 4 the apparent linear oxidation rate for pure niobium is also plotted for comparison. From the comparison the linear oxidation rates of Nb-rich Nb-Mo alloys are seen to be generally smaller than the rate of pure niobium. The anomalous temperature dependence observed in the oxidation of pure niobium⁶⁾ was retained in the oxidation of the Nb-Mo alloys investigated.

The oxidation behavior of Nb-2.5 a/o Mo alloy at 835°C was found to be quite peculiar. Its weight gain curve started parabolically, then almost abruptly flattened down to a level line. This anomalous behavior was found to be highly reproducible as three runs of Nb-2.5 a/o Mo alloy made at 835°C showed the quite similar behaviors. The values of the linear oxidation rate k_1 for Nb-2.5 a/o Mo alloy at 835°C is almost as small as zero, so that this value should be shown only by the direction with two arrows in Fig. 4.

3.2 Identification of reaction products

After oxidation, X-ray diffraction patterns from the surfaces of the oxidized specimens were obtained for identification of reaction products with Ni-filtered Cu radiation. The results of the identification are sum-

Table 1 X-ray pattern of oxide scales on Nb-Mo alloys oxidized for two hours

Temp. (°C)	Nb-2.5 a/o Mo alloy	Nb-5.0 a/o Mo alloy	Nb-7.5 a/o Mo alloy
	<u>B-region</u>		<u>A-region</u>
485	$T^+ \div Me^* \gg NbO_z$	Me	$Me \gg (TT)^{**}$
535	$T^+ > Me \gg (NbO_z)$	$Me \geq TT$	$TT \gg (Me)$
585	$T^+ > Me \div NbO_z$	$T^+ \div Me \div NbO_z$	$Me > TT > NbO_z$
			<u>C-region</u>
635	$Me > T^+ > NbO_z$	$Me > NbO_z > NbO_z \geq (T^+)$	$Me \div NbO_z > NbO_z > (TT)$
685	$T^+ = Me > B \div NbO_z$	$Me \div NbO_z > NbO_z \gg (B)$	$Me \geq NbO_z > NbO_z \div B > (TT)$
	<u>D-region</u>		
735	$T \geq B \div Me$	$Me > NbO_z > NbO_z > (B) \div (T)$	$Me \div NbO_z \div NbO_z \div T \div B \div M$
785	$T \geq B$	$Me > B > NbO_z \geq NbO_z \div T \gg (M)$	$M > Me > (NbO_z)$
835	$B > T > M$	$B \div M > T$	M
	<u>E-region</u>		
935	M	M	M

* Me : Metal substrate, ** () : Trace amount

Table 2 Appearance of oxide scales on Nb-Mo alloys oxidized for two hours

Temp. (°C)	Nb-2.5 a/o Mo alloy	Nb-5.0 a/o Mo alloy	Nb-7.5 a/o Mo alloy
	<u>B-region</u>	<u>A-region</u>	
485	dull gray, partly interference color	interference color	interference color
535	dull gray	gray powdery, partly interference color	gray powdery, partly interference color
585	gray powdery	gray powdery, partly interference color	gray powdery, partly interference color
		<u>C-region</u>	
635	interference color, partly dull gray	semi-lustrous black	dark gray
685	dull gray, partly dull black	lustrous black	lustrous black
	<u>D-region</u>		
735	semi-lustrous black	lustrous black	semi-lustrous black
785	semi-lustrous black	semi-lustrous black	dull gray, partly dull black
835	lustrous black	semi-lustrous black	dull dark gray
	<u>E-region</u>		
935	dull gray	dull gray	dull gray

marized in Table 1. In this table the order in the amount of each identified phase is shown qualitatively. Generally the niobium pentoxide Nb_2O_5 was the main reaction product on the Nb-Mo alloys investigated as that on pure niobium^{6,7}, except for A-region in Table 1 where only the substrate peaks (as shown with Me in the Table) were identified with significant peak heights, and further except for C-region where NbO_2 and NbO were the main products.

The niobium pentoxide is known to appear in several polymorphs, such as M, B*, T, TT, etc., according to the notation*2 adopted by Brauer and Schäfer¹³. The polymorph of Nb_2O_5 which was identified in the scales formed on Nb-2.5 a/o Mo alloy at relatively low temperatures exhibited an X-ray pattern which was in accordance with that of T- Nb_2O_5 except the peaks of this polymorph at 28.5° , 37.0° and 50.0° in 2θ which were not so splitted as seen in the normal pattern of T- Nb_2O_5 ¹⁴. These unsplit peaks appear to belong to the pattern of TT- Nb_2O_5 instead of T- Nb_2O_5 . Hence this phase is looked upon as a transient phase between TT-form and T-form of Nb_2O_5 and is designated as T⁺-form in this paper.

Several polymorphs of Nb_2O_5 were identified to appear consecutively in the scales on Nb-2.5 a/o Mo alloy, with raising the reaction temperature, in the following order: T⁺→T→B→M. In the scales formed on Nb-5.0 a/o Mo and Nb-7.5 a/o Mo alloys the

following polymorphs of Nb_2O_5 appeared consecutively in the following orders with raising the temperature: TT→T⁺→T→B→M and TT→T→B→M, respectively.

In B-region in Table 1, TT-form or T⁺-form of Nb_2O_5 was the main product. In D-region, B- Nb_2O_5 was either the main product or was formed almost as much as the main product (i.e. T- Nb_2O_5 on Nb-2.5 a/o Mo alloy at 735° and 785°C). Besides B- Nb_2O_5 , T- Nb_2O_5 was formed in considerable amount in D-region. In E-region, however, M- Nb_2O_5 was the only product that was formed in significant amount.

3.3 Visual inspection

The visual characteristics of the scales formed on the Nb-Mo alloys are summarized in Table 2. At low temperatures thin films having interference color were formed on the alloys. Especially at 485°C only the thin film having interference color was formed all over the surfaces of Nb-5.0 a/o Mo and Nb-7.5 a/o Mo alloys (A-region in Table 2). On the specimens oxidized at a little higher temperatures (B-region), gray scales (frequently powdery) were formed, in most cases besides thin film areas having interference color. At intermediate temperatures (C- and D-regions) lustrous or semi-lustrous black films were formed on the alloys. At high temperatures (E-region) dull gray or dull black scales were formed.

3.4 Metallographic studies

By means of optical microscopic observation of polished cross sections of the specimens it was seen that dull gray or gray powdery scale areas formed on the alloys at temperatures within B-region were comparatively thick and quite porous, as shown in Photo. 1 (a). On the other hand, the thin film areas having

*1 B-form is also designated as δ and γ' according to Laves et al.¹¹ and Terao¹², respectively.

*2 The correspondence relation between the notation employed in the preceding paper⁶ by the present authors and the one originally adopted by Brauer and Schäfer and employed in this paper is as follows: $\delta = \text{TT}$, $\delta \cdot \gamma = \text{T}^+$, $\gamma = \text{T}$, $\alpha' = \text{M}$ and $\alpha = \text{H}$.

Photo. 1 Typical cross sections of Nb-Mo alloys oxidized for two hours

- (a) : Nb-2.5 a/o Mo alloy oxidized at 525°C ($\times 150$)
- (b) : Nb-5.0 a/o Mo alloy oxidized at 685°C ($\times 200$)
- (c) : Nb-2.5 a/o Mo alloy oxidized at 785°C ($\times 100$)
- (d) : Nb-2.5 a/o Mo alloy oxidized at 935°C ($\times 100$)

interference color were too thin to be distinguished on the cross sections of the specimens (A- and B-regions). Thickness of the porous scale was observed to depend upon the orientation of the substrate crystal on which the scale was formed, as seen from Photo. 1 (a). Platelets of NbO_x were seen to be formed in the substrate just under porous scale areas in the form of wedges driven into the substrate from the scale-substrate interface. Orientation of the NbO_x platelets was seen to depend upon the orientation of the substrate crystal into which the platelets intruded.

On Nb-5.0 a/o Mo and Nb-7.5 a/o Mo alloys at temperatures ranging from 635 to 735°C (C-region) comparatively thin surface layers (thickness less than few microns) were formed and in the substrates just under the surface layers NbO_x platelets were formed, as seen in Photo. 1 (b).

At temperatures within D-region comparatively thick scales containing a small number of pores were formed on Nb-2.5 a/o Mo and Nb-5.0 a/o Mo alloys, as seen in Photo. 1 (c), as though on pure niobium at either 785° or 835°C⁶⁾. Thickness of these comparatively compact scales was also seen to depend upon the orientation of the substrate crystal on which the scale was formed.

At high temperatures within E-region thick scales containing a number of pores were formed on the alloys, as seen in Photo. 1 (d).

4 Discussion

In this study B- Nb_2O_5 was identified in the scales formed on the Nb-Mo alloys at temperatures ranging from 685 to 835°C. This polymorph of Nb_2O_5 has not been identified in the scales formed on either pure niobium or niobium-based alloys such as Nb-Zr, Nb-Be or Nb-Al alloys^{6),7)}. In the scales on these specimens, however, other polymorphs such as T- Nb_2O_5 (γ - Nb_2O_5) and M- Nb_2O_5 (α' - Nb_2O_5) were identified, suggesting that B- Nb_2O_5 is probably bypassed in the scales on these specimens. It seems to be for the first time that B- Nb_2O_5 was identified in the oxide scale on any alloy or metal even including Nb-0.4~3.4 a/o Mo alloys¹⁵⁾. The reason why B- Nb_2O_5 appears in oxide scales on merely Nb-Mo alloys, as so far clarified, is unknown at present.

In the course of oxidation of Nb-2.5 a/o Mo alloy at 835°C it was observed that a plateau-like stage appears following the initial parabolic stage. This peculiar rate-transition behavior was ascertained to be highly reproducible in this work. The X-ray pattern of the scale on the specimen which was at the plateau-like stage when taken out from the furnace has revealed that this scale was composed primarily of B- Nb_2O_5 and secondarily of T- Nb_2O_5 , as shown in Table 1. This result suggests that the T to B transition of the structure of Nb_2O_5 most probably proceeded during the oxidation run of the above-mentioned alloy at 835°C. This transition of Nb_2O_5 is presumed to be the cause of the para-plateau type rate transition observed in this work. An investigation to clarify in detail the cause of this anomalous rate transition is in progress in the authors' laboratory and the result of this investigation will be presented in near future.

It was suggested by appearances of the specimens oxidized at temperatures within B-region that the breakaway of a protective thin film having interference color, that is, the nucleation and growth of porous oxide scale (composed of TT- or T⁺- Nb_2O_5) from the thin film, occurred during the oxidation runs. Such a breakaway process usually causes a simple breakaway oxidation curve or a sigmoidal breakaway oxidation curve (pseudo-paralinear type curve), depending on the protective properties of the porous oxide scale formed by the nucleation and growth process. Actually both types of breakaway oxidation curves were obtained at temperatures within B-region.

Scattering of the apparent linear rate of Nb-2.5 a/o Mo alloy (and most probably of the other two Nb-Mo alloys, too) was considerably large. Some part of this scattering should have been caused by the considerably strong dependence of the growth rate of scale upon the orientation of individual substrate crystal on

which the scale is formed, which has been observed for the scales formed at temperatures within B- and C-regions. For temperatures within B-region, in addition to the above reason, variation of the duration of time until breakaway due to differences in the specimen surface condition, the substrate texture etc. is presumed to be another reason for the above scattering of the oxidation rate.

At temperatures within C-region, on Nb-5.0 or 7.5 a/o Mo alloy a black thin layer of NbO_2 was formed, which gave a high oxidation resistance. Under the NbO_2 layer, a number of NbO_x platelets were seen to be formed. This observation is interesting because in the preceding studies of the oxidation of niobium and niobium-based alloys NbO_x platelets were observed to be formed only under porous scale composed of Nb_2O_5 (usually TT- Nb_2O_5)^{6),7)}. The above observation suggests that molybdenum alloying probably suppresses the oxidation of NbO_2 to Nb_2O_5 to a considerable degree by stabilizing NbO_2 and that it probably reduces the deteriorating effect of NbO_x platelets on the dense scale formation as was observed in the oxidation of pure niobium¹⁶⁾.

As described in the result section, the apparent linear oxidation rate of the Nb-Mo alloys was generally smaller than that of pure niobium. In A and B temperature regions, delaying of the start of the breakaway caused by molybdenum alloying appears to be the main reason for this rate decrease. In C-region, the stabilisation of NbO_2 by molybdenum alloying is presumed to be the main reason for this. In D-region, however, the formation of B- Nb_2O_5 seems to be an important factor in the mechanism of this rate decrease. In E-region, dissolution of the hexavalent molybdenum ion into the niobium oxide, which is known to be a *n*-type semiconductor, appears to be

the main reason for this. The rate decrease observed on the Nb-Mo alloys in E-region does not seem to be attributed to the change in the thickness of the compact part of scale in such a way as discussed in previous paper for the case of other alloys⁶⁾, because the cross-sectional structure of the Nb_2O_5 scale formed on the Nb-Mo alloys in E-region, as was observed with an optical microscope in this study, did not look so much different from that on pure niobium.

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