Research Paper

The High Temperature Oxidation Properties of Nb-Al and Nb-Be Alloys in the Temperature Range 485°–1035°C

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The thermal oxidation properties of Nb-1.0 to 4.0 a/o Al alloys, Nb-0.8 to 9.8 a/o Be alloys as well as pure niobium were investigated in details by means of thermogravimetric measurements, X-ray diffraction and metallographical methods. The tests were conducted at temperatures ranging from 485° to 1035°C in dry oxygen at a pressure of 0.2 atm.

Five modifications of the dominant product Nb_2O_5 , i.e. δ , δ' , γ , α' , and α were identified and the transition temperature of the structure of each modification was observed to be gradually raised with increasing Al content in the substrate of Nb-Al alloys, even though it was scarcely influenced with increasing Be content in the substrate of Nb-Be alloys.

Transitions from parabolic to linear kinetics were observed to occur in scaling of each specimen at lower temperatures. The linear oxidation rates of Nb-Al alloys were lower than the ones of niobium below 585°C, but above 635°C the former became higher than the latter. The linear rates of Nb-Be alloys were higher than the ones of niobium at all temperatures investigated. Such behaviors were explained in connection with the change in a tendency of the scale to cracking caused by alloying. On the other hand the parabolic rate constants calculated were hardly affected by alloying niobium with Al as well as Be.

1 Introduction

The poor oxidation resistance of niobium is a major obstacle to its use in high-temperature applications. There is, however, some possibility of improving the oxidation behavior of niobium to a great extent by alloying it with other elements. The authors have studied the oxidation behaviors of Nb-V¹⁾ as well as Nb-Zr alloys²⁾ at elevated temperatures. The present report will describe an investigation on the oxidation behaviors of Nb-Al and Nb-Be alloys in purified oxygen gas at temperatures ranging from 485° to 1035°C. The oxidation of pure niobium has also been investigated with emphasis laid on the effect of Al or Be alloying.

Both aluminum and beryllium are interesting as alloying elements to niobium because of their highly stable oxides, Al_2O_3 and BeO , which have much smaller "Pilling-Bedworth Ratios" (i.e. the ratio of the volume associated with each metal atom in the scale to that in the metal) than the one of niobium (2.68). Nevertheless the preceding studies upon the oxidation behaviors of Nb-Al as well as Nb-Be alloys have been limited to several screening tests except some studies upon the relevant intermetallic compounds^{3),4)}. Accordingly the oxidation behaviors of niobium alloys containing less than 10% of Al or Be covered in this report have not been reported in details yet.

2 Experimental

2.1 Specimen preparation and surface treatment

The authors are interested in niobium based alloys and so samples containing less than 10 atomic % (later to be designated as a/o) of aluminum or beryllium were prepared. The alloys were prepared in an atmosphere of argon by using an arc-melting furnace. The niobium used was an electron-beam-melted one (99.9% up) with the following analytical quality; Ta: 500 ppm, W: 300 ppm, N, O, S and Fe: 100 ppm each, C and Cu: 40 ppm each. The aluminum was in the form of high purity block (99.99% up) and the beryllium was high purity rod (99.7%).

The melting of the specimens was repeated three times after inversion of the specimen each time, in order to ensure complete melting. Chemical analysis checks on the final compositions of some of these alloys showed that negligible loss of either aluminum or beryllium occurred during the preparation.

The castings of a series of Nb-Al alloys as well as Nb-Be alloys were cut into slabs about 2 mm thick, which were then rolled to 0.2 mm in thickness, all at room temperatures. Rectangular specimens 3 cm × 1 cm were machined from these sheets.

After polished with up to 1000 grit emery papers,

the rectangular specimens were thoroughly washed and degreased, then weighed by means of a chemical micro-balance.

2.2 Experimental method

The kinetic study was carried out by gravimetric determination of the weight gain of the sample on a quartz thermal balance in oxygen at a pressure of 0.2 atm. The finished specimen was contained in a quartz basket (to hold any fragments of oxide spalling from the metal) which was suspended in the reaction tube by means of a fine platinum wire attached to the calibrated quartz spring. The spring was suspended from a glass cock by means of a brass chain. The specimen was first introduced into the cool portion of the reaction tube above the furnace by means of the brass chain. After the atmosphere had become equilibrated at the test temperature, the specimen was lowered into the hot zone of the furnace by means of the glass cock and brass chain system. The lowering of the specimen into the hot zone was usually accomplished in less than 20 sec.

Temperature was controlled to limit deviation within $\pm 1^\circ\text{C}$ during the reaction measurement. The reactant gas was prepared by passing cylinder gas through magnesium perchlorate.

After oxidation all the specimens were examined metallographically by conventional techniques. X-ray diffraction patterns from the outer oxide scales *in situ* were obtained for identification purposes, using Ni-filtered Cu radiation. After the scales were abraded off, X-ray diffraction patterns from surfaces of the metal cores were also obtained.

3 Results

3.1 Kinetic studies

The results of the oxidation rate measurements are presented in Fig. 1~3. The weight gain curves for the reactions at lower temperatures in these figures generally start out in nearly parabolic form and then straighten out. At temperatures higher than 785°C for niobium and Nb-5.1 a/o Be alloy and than 835°C for Nb-4.0 a/o Al alloy, however, parabolic to linear transitions did not occur distinctly at least within the reaction periods investigated.

Most of parabolic to linear transitions occurred smoothly, but in the middle temperature range about 685°C to 735°C the transition occurred in a discontinuous fashion, usually with a transient region of a relatively slow oxidation rate between parabolic and linear portions of the curve. Such rate behaviors are rather similar to the ones previously observed by the authors in the study on the air oxidation of niobium and Nb-Zr alloys²³.

Curve no.	Temperature (°C)	Curve no.	Temperature (°C)
1	485	7	735
2	535	8	785
3	585	9	835
4	635	10	935
5	660	11	985
6	685	12	1035

Fig. 1 Weight gain curves for oxidation of niobium at oxygen pressure 0.2 atm

Curve no.	Temperature (°C)	Curve no.	Temperature (°C)
1	485	7	785
2	535	8	835
3	585	9	885
4	635	10	935
5	685	11	1035
6	735		

Fig. 2 Weight gain curves for oxidation of Nb-4.0 a/o Al alloy at oxygen pressure 0.2 atm

Curve no.	Temperature (°C)	Curve no.	Temperature (°C)
1	485	7	785
2	535	8	835
3	585	9	885
4	635	10	935
5	685	11	1035
6	735		

Fig. 3 Weight gain curves for oxidation of Nb-5.1 a/o Be alloy at oxygen pressure 0.2 atm

The "apparent" linear rate was calculated from the post-transition part of each parabolic type weight gain curve and its logarithmic value was plotted against the reciprocal absolute temperature in Fig. 4. At tempera-

○: Nb, ○: Nb-4.0 a/o Al alloy
 ⊙: Nb-1.0 a/o Al alloy
 ●: Nb-5.1 a/o Be alloy

Fig. 4 Dependence of linear oxidation rates of Nb, Nb-4.0 a/o Al alloy and Nb-5.1 a/o Be alloy on temperature

tures below 585°C the linear oxidation rates of Nb-1.0 and 4.0 a/o Al alloys were lower than the ones of niobium, but above 635°C the former became higher than the latter. An anomaly in the temperature dependence of the oxidation rate of the type observed by Bridges and Fassell⁹⁾ etc. in the oxidation of niobium was not observed in the oxidation of Nb-4.0 a/o Al alloy.

The linear rates of the Nb-Be alloys investigated were higher than the ones of niobium in a whole temperature range investigated and the anomalous temperature dependence observed in the oxidation of niobium was retained in the oxidation of Nb-5.1 a/o Be alloy.

Composition dependences of the linear rates of Nb-Al as well as Nb-Be alloys are illustrated in Fig. 5. It is apparent that the effect of adding aluminum or beryllium to niobium in relation to the linear oxidation rate becomes exaggerated with increasing the content of each alloying element in each alloy specimen.

○: Nb-Al alloy, 635°C, ●: Nb-Al alloy, 535°C
 △: Nb-Be alloy, 635°C, ▲: Nb-Be alloy, 535°C

Fig. 5 Dependence of linear oxidation rates of Nb-Al and Nb-Be alloys on alloy compositions

The parabolic rate constants k_p were also calculated and their logarithmic values were plotted against the reciprocal absolute temperatures in Fig. 8. The calculation methods of k_p will be described in the discussion section.

3.2 Identification of reaction products

As summarized in Fig. 6 for Nb-Al alloys and in Fig. 7 for Nb-Be alloys, respectively, identification of the scale by X-ray diffraction indicated that Nb_2O_5 formed most abundantly on both series of alloy specimens as well as pure niobium at all temperatures investigated. Nb_2O_5 has many polymorphs^{6),7)} and in this study the transitions $\delta \rightarrow \delta' \rightarrow \gamma^* \rightarrow \gamma \rightarrow \alpha'^* \rightarrow \alpha$ of the

*1 The δ - γ -modification means a less crystalline state of the γ -phase. The broad peak at 2θ equals 45° in the X-ray diffraction traces of δ - γ - Nb_2O_5 becomes resolved into two sharp peaks in the one of γ - Nb_2O_5 .

*2 The α' - α -modification means a less crystalline state of the α -phase.

Each broad peak at 2θ equals 25° , 31.5° and 54° in the X-ray diffractometer traces of α' - Nb_2O_5 becomes resolved into each two sharp peaks in the one of α - Nb_2O_5 .

Sign	Composition of oxide scale	
	Outer part	Inner part
○	δ -Nb ₂ O ₅	δ -Nb ₂ O ₅ , NbO _x
◐	δ - γ -Nb ₂ O ₅	δ - γ -Nb ₂ O ₅ , NbO ₂ , NbO
◑	γ -Nb ₂ O ₅	δ - γ -Nb ₂ O ₅ , NbO ₂ , NbO
●	γ -Nb ₂ O ₅	γ -Nb ₂ O ₅ , NbO ₂ , NbO
△	α' -Nb ₂ O ₅ , γ -Nb ₂ O ₅	γ -Nb ₂ O ₅ , NbO ₂ , NbO
▲	α' -Nb ₂ O ₅ , γ -Nb ₂ O ₅	α' -Nb ₂ O ₅ , γ -Nb ₂ O ₅ , NbO ₂ , NbO
△	α' -Nb ₂ O ₅	α' -Nb ₂ O ₅ , NbO ₂ , NbO
▼	α -Nb ₂ O ₅	α' -Nb ₂ O ₅ , NbO ₂ , NbO
▽	α -Nb ₂ O ₅	α -Nb ₂ O ₅ , NbO ₂ , NbO

Fig. 6 Variations in composition of oxide scale with reaction temperature and Al content

Sign	Composition of oxide scale	
	Outer part	Inner part
○	δ -Nb ₂ O ₅	δ -Nb ₂ O ₅ , NbO _x
◐	δ - γ -Nb ₂ O ₅	δ - γ -Nb ₂ O ₅ , NbO ₂ , NbO
◑	γ -Nb ₂ O ₅	δ - γ -Nb ₂ O ₅ , NbO ₂ , NbO
●	γ -Nb ₂ O ₅	γ -Nb ₂ O ₅ , NbO ₂ , NbO
△	α' -Nb ₂ O ₅ , γ -Nb ₂ O ₅	γ -Nb ₂ O ₅ , NbO ₂ , NbO
▲	α' -Nb ₂ O ₅ , γ -Nb ₂ O ₅	α' -Nb ₂ O ₅ , γ -Nb ₂ O ₅ , NbO ₂ , NbO
△	α' -Nb ₂ O ₅	α' -Nb ₂ O ₅ , NbO ₂ , NbO
▼	α -Nb ₂ O ₅	α' -Nb ₂ O ₅ , NbO ₂ , NbO
▽	α -Nb ₂ O ₅	α -Nb ₂ O ₅ , NbO ₂ , NbO

Fig. 7 Variations in composition of oxide scale with reaction temperature and Be content

structure of Nb₂O₅ were observed.

Dashed lines drawn in Fig. 6 and 7 show approximate composition dependences of the transition temperatures of the structure of Nb₂O₅ formed on Nb-Al and Nb-Be alloys, respectively. On Nb-Al alloys each transition temperature of Nb₂O₅ was raised gradually with increasing Al content in the alloy. On the other hand any transition temperature of Nb₂O₅ formed on Nb-Be alloys was hardly affected by changing Be content in the alloy.

The X-ray diffraction study of a region of metal-scale interface of each oxidized specimen indicated that layers of NbO and NbO_x formed beneath the outer scale of Nb₂O₅ other than δ -type one. Beneath the δ -Nb₂O₅ outer scale suboxide NbO_x platelets formed in the metal instead of NbO and NbO₂. Such behaviors are consistent with the results of the oxidation study of niobium by Sheasby in the temperature range 450–720°C¹³.

Any ternary oxide containing niobium as one component or any single oxides of aluminum as well as beryllium were not identified in the scales by means of an X-ray diffractometer.

3.3 Metallographic studies

Typical cross-sectional structures of reacted specimens are shown in Photo. 1 and 2 for Nb-4.0 a/o Al and Nb-5.1 a/o Be alloys, respectively. The composition range of the Nb-Be alloys investigated was in the

Photo. 1 Cross section of oxidized Nb-4.0 a/o Al alloy

(a) 1035°C, 31 min, (b) 785°C, 46 min
(c) 635°C, 105 min, (d) 485°C, 70 min
(e) The same part as (d) shows, but taken under polarized light

Photo. 2 Cross section of oxidized Nb-5.1 a/o Be alloy

two phase region of niobium and niobium beryllide (NbBe_2)⁹⁾. The beryllide phase was dispersed usually as spherical particles in the niobium matrix. The particles retained the metallic appearance after transferred into the scale within the innermost part of the scale several microns in thickness. The composition range of the Nb-Al alloys investigated was in the one phase region of Nb-Al solid solution¹⁰⁾, but many small precipitates were observed to exist in the substrate of the Nb-4.0 a/o Al alloy specimen reacted at all temperatures investigated, both along the grain boundaries and in the grains.

Observed cross-sectional structures of reacted niobium specimens were consistent with the results of observation by Sheasby⁹⁾ and Sheasby et al.¹¹⁾, which covered the temperature range below 825°C; that is, at δ - Nb_2O_5 -forming temperatures suboxide NbO_x platelets formed in the metal beneath the scale and the scale fracture was facilitated, with a chevron pattern of pores appearing in the scale. At δ - γ - or γ - Nb_2O_5 forming temperatures the scale formed consisted of a series of compact layers of δ - γ - or γ - Nb_2O_5 of about equal thickness which were separated by fractures. At about 800°C, in this experiment at 785° and 835°C, however, compact Nb_2O_5 scale formed.

At temperatures at which α' - and α - Nb_2O_5 form, which were not covered in the studies by Sheasby et al.^{9),11)}, the scales formed contained numerous pores very irregular in shape and size as reported in the

preceding paper²⁾.

Cross-sectional structures of reacted Nb-4.0 a/o Al alloy were considerably similar to the ones of niobium reacted at the temperatures at which the same type of Nb_2O_5 formed as on the alloy specimen. At temperatures below 585°C, however, suboxide NbO_x platelets formed in the substrate of the reacted Nb-4.0 a/o Al alloy specimen were much smaller in both size and number than the ones formed in the substrate of the reacted niobium specimen. This resulted in a much smaller number of pores appearing in the scale formed on Nb-4.0 a/o Al alloy specimen than in the one on niobium specimen.

It was frequently observed in the scale formed on Nb-5.1 a/o Be alloy that crevices existed between the nearly spherical oxide regions originated from the beryllide particles and the remaining region of the scale.

Compact scales formed at 785° and 835°C on niobium as well as Nb-5.1 a/o Be alloy and at 835° and 885°C on Nb-4.0 a/o Al alloy. It was a common striking feature of the compact oxide scales on these specimens that Nb_2O_5 composing the scales were mixtures of γ - Nb_2O_5 and α' - Nb_2O_5 .

The δ - γ - or γ - Nb_2O_5 scale consisted of a series of compact layers of Nb_2O_5 as described above. The width of laminations in the Nb_2O_5 scale was measured at several points on every specimen. At lower temperatures at which δ - Nb_2O_5 forms the scale layers are not clearly defined making it extremely difficult to measure the mean layer depth X_c with any accuracy. Observation of cross-sections of the specimens reacted at the lower temperatures under polarized light exhibited, however, the existence of dark, optically inactive material in the innermost part of the scale adjacent to the substrate boundary, as seen in Photo. 2 (e). The observed dark part of the scale was believed to be a compact layer that had been in the process of growing at the stopping time of reaction. Accordingly the mean compact layer width X_c was determined to be twice the mean thickness of the dark part of the scale at the lower temperatures. Determinations of X_c are given in Table 1 for niobium, Nb-4.0 a/o Al alloy and Nb-

Table 1 Thickness of compact layer, X_c

Temperature (°C)	X_c (μ)		
	Nb	Nb-4.0 a/o Al alloy	Nb-5.1 a/o Be alloy
485	2.2	2.4	0.5
535	1.1	2.4	0.6
585	1.1	2.4	0.8
635	17	2.4	7.2
685	19	3.9	10
735	15	8.7	15
785		50	

5.1 a/o Be alloy. At temperatures higher than the ones at which γ -Nb₂O₅ formed values corresponding to X_c could not be obtained.

The values of X_c of the reacted Nb-4.0 a/o Al alloy were greater below 585°C, but smaller above 635°C than the ones of the reacted niobium specimen. On the other hand the values of X_c of the reacted Nb-5.1 a/o Be alloy were smaller than the ones of the reacted niobium at almost all temperatures investigated.

4 Discussion

The kinetic study of the oxidation of Nb-Al and Nb-Be alloys as well as pure Nb at low temperatures showed transitions from parabolic to linear behavior, suggesting the scaling of the oxide. Sheasby interpreted the parabolic type reaction observed in the oxidation of niobium to emanate from the formation of the effective barrier of a virtually constant thickness between the reactants after ceasing of oxide accumulation as a protective layer. The metallographic results presented in this report appeared to support this mechanism. The dark layer observed in the scale should be the compact layer in which the lattice diffusion of defects proceeds.

The linear oxidation rate k_l should be related by the mean layer width X_c to the underlying parabolic rate constant k_p for the reaction¹², according to the equation

$$k_p = k_l \times X_c$$

This parabolic rate constant should have the same value as that of the parabolic oxidation at the start of the reaction, and this was confirmed by Sheasby² at temperatures between 600° and 750°C.

The derived parabolic rate constants of the specimens reacted at the lower temperatures were shown as functions of $1/T$ (°K) in Fig. 8. The parabolic rate constants derived for niobium fitted comparatively well with the values obtained by Sheasby in the study of oxidation of Nb at oxygen pressure 380 torr.

When the dimension of X_c was converted from (μ) to (g/cm^2) in order to calculate the parabolic rate constant k_p , an assumption was made that the density of a compact part of the scale would be equal to the density of Nb₂O₅, whether the specimen be pure niobium or not. The error in k_p to be introduced in this unit conversion process was estimated to be less than 5% for each alloy specimen investigated. For the density of Nb₂O₅ the value of 4.99 g/cm^3 was adopted, which had been derived from the X-ray diffraction data of γ -Nb₂O₅¹³.

At 785° and 835°C for both niobium and Nb-5.1 a/o Be alloy and at 835° and 885°C for Nb-4.0 a/o Al alloy compact scales were observed to grow according to a parabolic rate law and so parabolic rate constants

Circle : Nb,
Triangle : Nb-4.0 a/o Al alloy
Square : Nb-5.1a/o Be alloy
○ △ □ : k_p calculated from k_l and X_c
● ▲ ■ : k_p calculated directly from weight-gain curve

Fig. 8 Dependence of parabolic oxidation rates of Nb, Nb-4.0 a/o Al alloy and Nb-5.1 a/o Be alloy on temperature

were calculated directly from the weight-gain curves at these temperatures. The parabolic rate constants calculated in this way were shown as functions of $1/T$ (°K) in Fig. 8 in addition to the values calculated from k_l and X_c . It is immediately apparent that the points calculated from weight gain curves in Fig. 8 are distributed with continuous connection with the points calculated from k_l and X_c . This result was interpreted to prove the appropriateness of the parabolic type oxidation model proposed by Sheasby.

Fig. 8 exhibits that the parabolic rate constant k_p , or the lattice diffusion rate of defects in the scale was hardly influenced by alloying niobium with either aluminum (4%) or beryllium (5%). In the case of Nb-5.1 a/o Be alloy it is believed that this behavior is explained from the fact that the bulk beryllium in the scale did not make solid solution with the bulk niobium oxide. In fact the beryllide precipitates formed an oxide phase apparently different from the bulk niobium oxide in the scale.

On the other hand it was believed that a considerable part of aluminum in the scale should make solid solution with the bulk niobium oxide, taking the elevation of transition temperature of Nb₂O₅ in the scale

caused by aluminum addition to niobium into consideration. Nevertheless the value of k_p was hardly influenced by alloying niobium with aluminum. This may indicate that Nb_2O_5 can be an example of the anion-deficit n -type semiconductor in which the diffusion rate of defects is hardly affected by adding other cations of lower valency, as observed in the case of aluminum addition to TiO_2 ¹²⁾.

The kinetic results presented showed that the linear rate constant k_l was affected by alloying niobium with aluminum as well as beryllium. The parabolic rate constant k_p was, however, hardly affected by such alloying as described above. Accordingly the variation in k_l should be explained to be caused by the change in the thickness of the diffusion barrier. In fact on Nb-5.1 a/o Be alloy the value of X_c was generally smaller than the one on niobium. This fact was considered to be caused by the crack-facilitating effect of the beryllide precipitates, which to be explained as follows: The beryllide precipitates retained the metallic appearance in the innermost part of the scale several microns in thickness, even though the niobium matrix was converted to the voluminous oxide. The large difference in the volume changes suffered by the two phases during the process of crossing over the metal-scale interface should facilitate the crack and cavity formation in the scale. The metallographic results apparently proved the appropriateness of this estimation.

On Nb-4.0 a/o Al alloy the value of X_c was larger than the one of niobium at the lower temperatures. This fact resulted in the slower linear oxidation of Nb-4.0 a/o Al alloy at the lower temperatures. The metallographic observation exhibited that suboxide platelets formed were rather smaller in both size and number on Nb-4.0 a/o Al alloy than on niobium. This was considered to be a cause of the great value of the thickness of the compact layer formed on Nb-Al alloy, taking the crack-facilitating effect of the suboxide into consideration.

5 Conclusion

(1) Para-linear type reaction has been observed to occur at relatively low temperatures in the oxidation of Nb-Al as well as Nb-Be alloys. The mechanism of the reaction has been shown to be in accordance with Sheasby's model which explains this type reaction to emanate from the formation of the effective diffusion barrier of a virtually constant thickness between the reactants.

(2) The mean compact layer width of the reacted Nb-4.0 a/o Al alloy is greater below 585°C, even though smaller above 635°C, than the one of the

reacted niobium. The cause of the smaller compact layer width of the Nb-4.0 a/o Al alloy has been attributed to the formation of the suboxide platelets smaller in both size and number than on niobium.

The mean compact layer width of the reacted Nb-5.1 a/o Be alloy is smaller than the one of the reacted niobium at almost all temperatures from 485° to 735°C. The cause of this has been attributed to the crack-facilitating effect of the beryllide precipitates.

(3) The parabolic oxidation rate constant of niobium has been shown to be hardly affected by alloying niobium with 4.0 a/o of aluminum as well as 5.1 a/o of beryllium.

The linear oxidation rates of Nb-1.0 to 4.0 a/o Al alloys are lower than the ones of niobium below 585°C, even though the former are higher than the latter above 635°C. On the other hand the linear rates of the Nb-0.8 to 9.8 a/o Be alloys are higher than the ones of niobium at temperatures 485° to 735°C. The variations in the linear rate constants caused by alloying niobium with aluminum as well as beryllium have been shown to emanate from the change in the thickness of the effective diffusion barrier.

(4) The transition temperature of the structure of each modification of the dominant product Nb_2O_5 is gradually raised with increasing Al content in the substrate of Nb-Al alloys. On the other hand it is hardly influenced with increasing Be content in the substrate of Nb-Be alloys.

(5) The results of this study are suggesting that among the most important factors on which improvement of the oxidation resistance of niobium alloys should depend appear to be:

1. The uniformity of the substrate of the alloy.
2. The diminution or disappearance of the NbO_x platelets beneath the outer scale at relatively low temperatures.
3. The retarding effect of added elements on the diffusion of oxygen through the Nb_2O_5 scale, or the formation of complex oxides which decrease the rate of oxygen diffusion through the scales.

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Literature:

- 1) T. Mukaibo, M. Kanno, M. Yamawaki, *J. Nucl. Sci. Technol.* **2**, 516 (1965).
- 2) M. Yamawaki, T. Mukaibo, M. Kanno, *This Journal* **36**, 671 (1968), (in Japanese).
- 3) R.F. Voitovich, *Zh. Fiz. Khim.* **38**, 2954 (1964).
- 4) J.F. Nuchmann, AEC report DRI 20888 (1963).
- 5) D.W. Bridges, W.M. Fassel, *J. Electrochem. Soc.* **103**, 326 (1956).
- 6) F. Holtzberg, A. Reisman, M. Berry, M. Berkenblit, *J. Am. Chem. Soc.* **79**, 2039 (1957).
- 7) N. Terao, *Jap. J. Appl. Phys.* **2**, 156 (1963).
- 8) J.S. Sheasby, *J. Electrochem. Soc.* **115**, 695 (1968).

- 9) G.V. Samsonov, "Beryllides", Clearinghouse for Federal Scientific and Technical Information (CESTI), U.S. Department of Commerce, Springfield (1966).
- 10) C.E. Lundin, A. Yamamoto, *Trans. Met. Soc. AIME* **238**, 864 (1966).
- 11) J.S. Sheasby, G.R. Wallwork, W.W. Smeltzer, *J. Electrochem. Soc.* **113**, 1255 (1966).
- 12) J. Stringer, *Met. Rev.* **11**, 113 (1966).
- 13) N. Terao, *J. Japan Inst. Metals* **8**, 509 (1966).

Research Paper

Effects of Oxygen Concentration and pH on Corrosion Behavior of Iron and Steel in Oxygen Dissolved Solution of Potassium Chloride*

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Corrosion of iron and steel in aerated solutions of KCl under various conditions of the pH and the partial pressure of oxygen was determined. Since the corrosion under such conditions was controlled by diffusion of oxygen from the bulk of solution toward the metal surface, the rotating disk was used as the test specimen. In an acidic solution (pH 1-4), the corrosion rate was proportional to the partial pressure of oxygen and the square root of the rotating speed, and was independent of metal. In neutral solution (pH 6-10), the metal surface is still thermodynamically active, but the oxide film covers and protects the metal surface from its corrosion, and the rate becomes zero practically. In a concentrated alkali solution such as 1 N KOH, the surface was bright after 70 hours. Variation of the pH and the corrosion potential during experiment was recorded as reference. Some polarization curves, mostly the cathodic behavior of oxygen dissolved, were determined with iron and platinum electrodes. The corrosion rate agreed sufficiently with the limiting current density of oxygen under the same conditions.

Corrosion of metals in aqueous solution can be classified by three factors :

- (1) Thermodynamically active or passive,
- (2) How high is the pH? and
- (3) How much is the concentration of oxygen dissolved?

Factor (1) is the most basic condition because it defines possibility of corrosion. A special behavior of metal immersed in a certain solution is "Passivation". It is essentially different phenomenon from so-called "Immunity", because very thin oxide film or the passive film protects the metal surface from corrosion environment. Study on passivation is an attractive field in corrosion science and many researchers continue to make efforts today. It is well-known that some anions, particularly chloride ions, destroy the

passive film on iron and steel, and the metal surface dissolves into solution with a simple way. Relatively high concentrated KCl solution, mostly 1 M KCl, was, therefore, employed in this work to avoid passivation. The pH of the solution moved toward alkaline with proceeding of corrosion, but no change of the conductivity of solution was confirmed.

Factor (2) should be considered in connection with the solubility product of the corrosion products deposited on the metal surface, because most of the corrosion products consist of hyd. oxide and/or oxy-hydroxide which requires a large amount of OH⁻ and/or H₂O for its formation from the ions.

The cathodic reaction of the local cell established on the metal surface is provided by Factor (3). The cathodic reduction of oxygen is the main reaction in an oxygen-dissolved solution, whereas the hydrogen formation may take priority in overall cathode reaction

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