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CONTAMINATION HARDENING OF SU-31 AND FS-85 COLUMBIUM ALLOYS

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Army Materials and Mechanics Research Center
Watertown, Massachusetts

April 1973

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13. ABSTRACT

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Technical Report by
ROBERT B. HERRING

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A study has been made of the contamination hardening of SU-31 and FS-85 columbium alloys which results when samples are exposed in air at temperatures of 1400 to 2600 F. Diffusion coefficients for the principal contaminant, calculated from the hardening profiles, are in good agreement with data previously reported for diffusion of oxygen in pure columbium. From that agreement it has been concluded that the hardening in the alloys is principally due to the absorption and diffusion of oxygen from the air. Activation energies measured were 22.5 kcal/mol for SU-31 and 20.3 kcal/mol for FS-85. Based on the measurements of this study, SU-31 has a higher resistance to contamination hardening than FS-85 by about a factor of two.

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INTRODUCTION

Columbium alloys are promising candidates for application in advanced gas turbine engines for service at metal temperatures up to 2600 F. However, columbium alloys, like other refractory metal alloys, are subject to rapid oxidation and to embrittlement by absorbed interstitial contamination. For those reasons coatings will be required where long service times are required. But in the event of an inherent coating defect or one produced by foreign object damage, oxidation at the coating damage site can be expected when the material is exposed to high temperature oxidizing service conditions. In addition to the metal lost through conversion to the oxide, material may be degraded by the interstitial diffusion of gaseous elements into the metal from the coating defect site. The rate of diffusion of oxygen generally will be the controlling factor in determining the size of the affected zone beneath a coating defect.

In this study the microhardness profile of specimens and the rate of advance of observable hardness changes were studied for SU-31* and FS-85† columbium-base alloys exposed at high temperatures in air. Diffusion coefficients for the principal contaminating species in the two alloys have been obtained from the hardness profiles and the rate of advance of the hardening. Those values are compared with data for diffusion of oxygen in pure columbium.[1-4] An analysis has also been made which compares the rate of contamination hardening in FS-85, SU-31, and pure columbium.

EXPERIMENTAL PROCEDURE

The SU-31 columbium-base material used in this study was obtained in the form of 1/2-inch-diameter rod. The material was in the recrystallized and precipitation-hardened condition. Specimens were prepared by cutting the rod into approximately 1/8-inch high cylinders and finishing the surfaces of the disks by grinding to a thickness of 0.125 inch. The FS-85 alloy was obtained in the form of 0.125-inch-thick sheet. Specimens 1/2-inch square were cut from the sheet. Prior to oxidation, each specimen was polished on metallographic papers through 2/0 grade and the surface cleaned with acetone and distilled water. The analyzed compositions of the two materials as supplied by the producers are shown in Table I.

Table I. COMPOSITION OF THE ALLOYS

	Elements							
	wt.%					ppm		
Alloy	Ta	W	Zr	Cb	Hf	C	O	N
SU-31	-	18.5	-	balance	3.6	1450	85	25
FS-85	27.6	10.6	0.94	balance	-	40	39	29

---

*Supplied by Kawacki-Berylco Industries, Inc., 220 E. 42nd Street, New York, New York 10017.

†Supplied by Fansteel Corp., 5101 Tantalum Place, Baltimore, Maryland 21226.

One set of specimens of SU-31 alloy was exposed in a tube furnace in still air at 1600 F for times of 1/2, 1, 2, 4, 8, 16, and 32 hours. Another series of specimens was oxidized in a Mettler thermogravimetric furnace in air at 760 torr at an air flow rate of 85 cm^3/min. For each such test, the specimen was equilibrated at temperature under an argon atmosphere and the time of the oxidation period was measured from the introduction of the flowing air atmosphere. The atmosphere was changed back to argon at the end of the test and the specimen cooled quickly at room temperature. Hardness profiles taken on polished cross-sections of the specimen are reported for oxidation carried out at temperatures of 1400 to 2600 F for measured periods of approximately one hour.

Following the elevated temperature exposure, the loose outer oxide was removed; the specimens were sectioned by spark cutting, mounted in bakelite, and polished by standard metallographic techniques. Microhardness versus depth profiles at the center of the sectioned disks were determined using a Leitz microhardness tester, a Vickers diamond pyramidal hardness (DPH) indenter, and a 200-gram load.

The thickness of the remaining metal was measured optically on the polished sections and compared with micrometer measurements of the thickness made prior to oxidation to determine the surface recession or metal lost through conversion to oxide. Since this study was concerned with the extent of penetration of the hardening which would be due to contamination entering early in the exposure, account was taken of the surface recession, and the depths reported are referred to the original position of the metal surface. In most of these tests the error involved in the neglect of surface recession would be small. However, surface recession would become important for longer time tests (greater than 10 hours).

As a measure of the penetration depth of the contamination, the depth to the point where the hardness was increased 25 DPH units over the unaffected interior was arbitrarily used.

RESULTS

Effect of Exposure Time

It was expected that the advance of the contamination hardening would be diffusion controlled and hence follow a depth proportional to the square root of time relation. That relation was verified by measurements on the set of samples exposed for times of 1/2, 1, 2, 4, 8, 16, and 32 hours in still air at atmospheric pressure at 1600 F. Upon cooling, parts of the outer oxide spalled from most of the specimens exposed at the longer times. After removal of the outer oxide, which was light yellow in color, the specimens were found to be covered with a dark adherent oxide layer which was 0.006 to 0.018 cm thick.

Microhardness versus depth profiles of the specimens exposed for times of 1/2 to 32 hours are shown in Figure 1. At times longer than about 12 hours, the hardening penetrated from both sides of the 1/8-inch-thick specimens as shown by the elevated hardness values at the centerline for the 16- and 32-hour specimens. Those specimens could not be considered infinite in extent and the penetration depth to a 25 DPH increase could not be measured on those as it could for the shorter time specimens.

The affected depths (at which the hardness was increased 25 DPH) are shown in Figure 2 plotted versus the exposure time. Within the error of the measurements, the hardening did follow the expected square root of time relationship given by the line in Figure 2 drawn for a slope of 1/2 on the log-log plot.

Also shown in Figure 2 are curves for the metal loss (surface recession) and the thickness of the inner adherent oxide. The metal loss followed approximately a power function relation in which the metal converted to oxide increased as $t^{0.38}$. The thickness of the inner oxide layer was proportional to the square root of exposure time for times up to 2 hours and then became constant at approximately 0.018 cm. Rapp and Goldberg[5] have also reported a constant inner oxide (or internal oxidation zone) thickness for Cb-Zr binary alloys and Cb-Zr-Re ternary alloys. The inner adherent oxide contained some of the suboxide phase CbO_2; however, the X-ray diffraction patterns obtained from the inner layer of the SU-31 oxides formed at 1600 F indicated small amounts of CbO_2 while the predominant phases present were Cb_2O_5 and $Cb_{12}WO_{33}$. Those were also the phases present in the outer oxide layers at that temperature. At higher temperatures for both SU-31 and FS-85 alloys the inner oxide layer, if present at all, was much thinner than the inner oxide formed on the SU-31 samples exposed at 1600 F. The appearance of the oxides formed at the surface and the X-ray diffraction identification of the phases present are discussed in detail in another report.[6]

Effect of Temperature

Microhardness profiles of the SU-31 and FS-85 alloy specimens following a one-hour exposure in air at temperature are shown in Figure 3. The maximum hardness, H_s, at the metal-oxide interface was estimated to be approximately 1400 DPH in the SU-31 alloy and 1000 DPH for the FS-85 alloy. The hardness of the interior region was 240 DPH for the SU-31 alloy and 205 DPH for the FS-85 alloys. The hardness of the uncontaminated material in the interior of the samples was unaffected by heating for the times and temperatures used in this study. The depth measurements indicated on Figure 3 are values referred to the original position of the specimen surface.

DISCUSSION

Hardness Profile

Klopp, Sims, and Jaffee[4] have studied the contamination hardening of pure columbium exposed in air, oxygen, and nitrogen. They concluded that for exposure in air, nitrogen has only a minor effect and that the contamination hardening in air is due almost exclusively to the diffusion of oxygen into the material. If the same holds true for the SU-31 and FS-85 columbium alloys, the motion of the contamination should reflect the diffusion of oxygen in the alloys.

The simplest model for calculating the expected hardness profiles is to assume that the surface recession is negligible and the absorption can be treated as a diffusion problem in which the specimen surface is maintained at a constant oxygen concentration. For that case, the solution to the diffusion equation is given by [7,8]

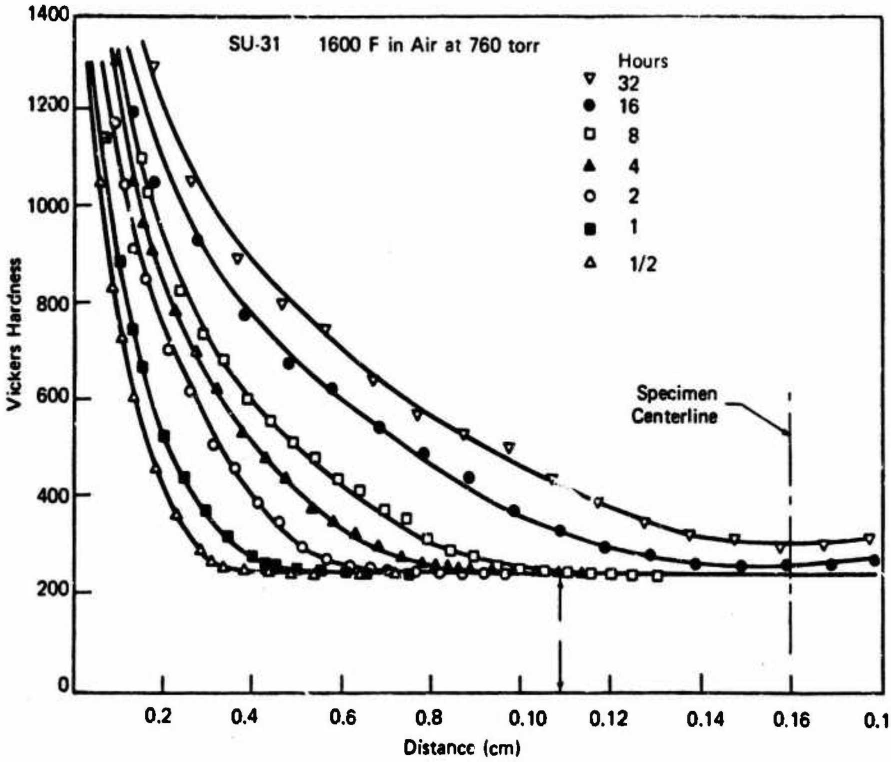

Figure 1. Hardness profiles of SU-31 specimens exposed for 1/2 to 32 hours in air at 1600 F

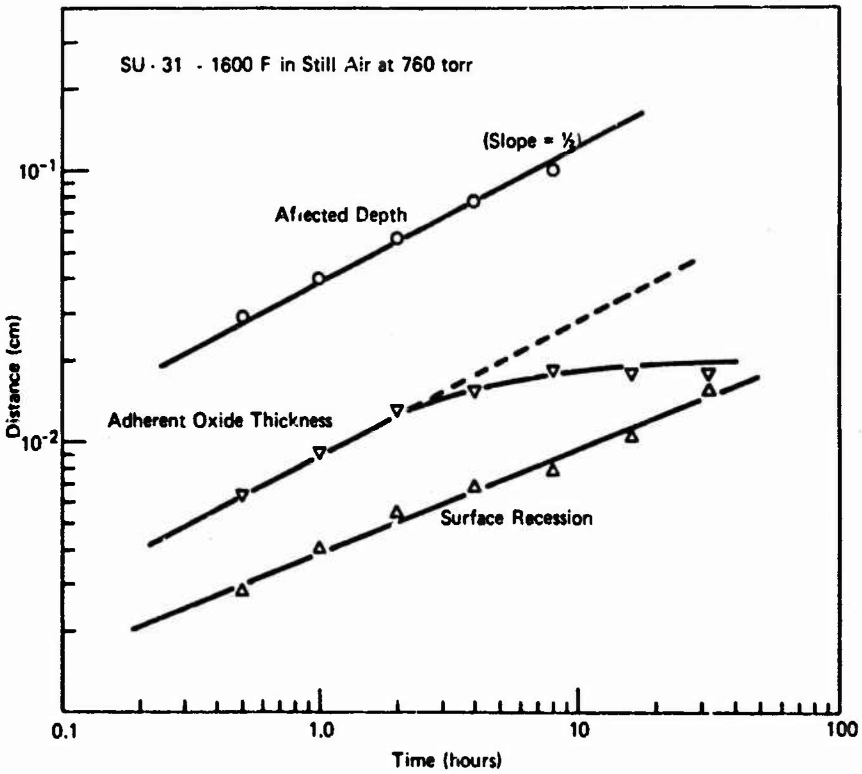

Figure 2. Oxidation and contamination of SU-31 exposed to air

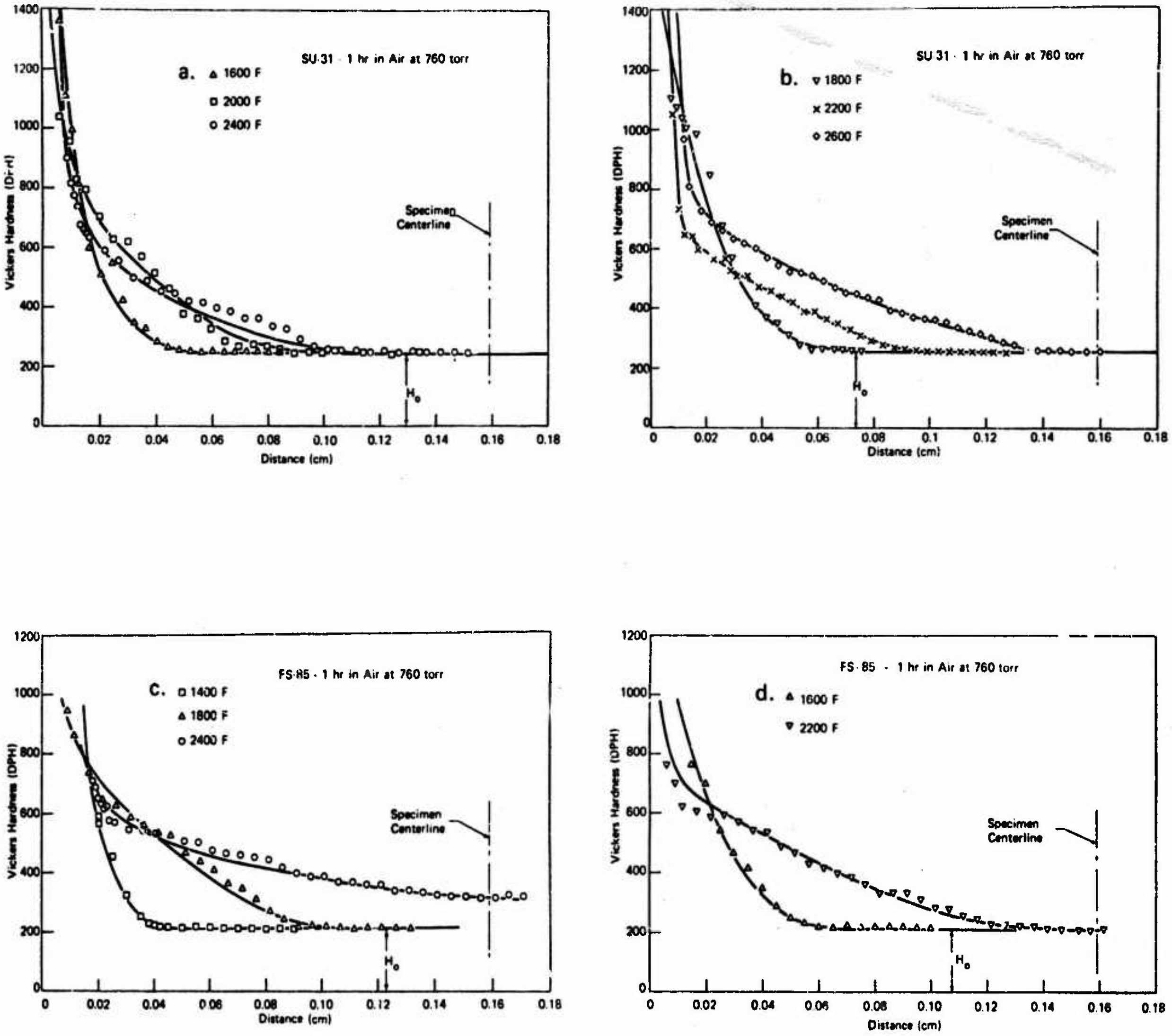

Figure 3. Hardness profiles of SU-31 and FS-85 specimens exposed in air for one hour at various temperatures

$$C - C_0 = (C_s - C_0)\ \mathrm{erfc}\left(\frac{X}{2\sqrt{Dt}}\right) \tag{1}$$

where C is the oxygen concentration, C_0 the initial oxygen concentration of the alloy, C_s the concentration at the surface, X the depth, D the diffusion coefficient (a function of temperature), and t the time of exposure.

Gebhardt and Rothenbacher[9] measured oxygen solubility in pure columbium and found it to increase from 1.1 at.% at 750 C to 5.5 at.% at 1540 C, in good agreement with the measurements by Bryant.[10] Microhardness measurements on the oxygen-saturated material by Gebhardt and Rothenbacher indicated a linear increase of hardness with oxygen concentration. Assuming a linear hardness-concentration relationship holds for the alloys SU-31 and FS-85, Equation 1 can be rewritten in terms of hardness as

$$(H-H_0)/(H_s-H_0) = \mathrm{erfc}\left(\frac{X}{2\sqrt{Dt}}\right) = 1-\mathrm{erf}\left(\frac{X}{2\sqrt{Dt}}\right) \tag{2}$$

or

$$\mathrm{erf}\left(\frac{X}{2\sqrt{Dt}}\right) = (H_s-H)/(H_s-H_0) \tag{2a}$$

where H_s is the hardness at the surface, H_0 the hardness of the unaffected interior, and H the hardness at the depth X.

To compare the observed hardness profiles with the predictions of Equation 2, the data were replotted using probability grid divisions. When plotted in this way, data following the error function relation given by Equation 2 will yield a straight line. Figure 4 shows data from Figure 1 plotted in this way. For clarity only four sets of data are shown. Closed circles indicate the position of the metal/oxide interface at the end of the test. The offset of those closed circles is equal to the amount of the metal converted to oxide during the test.

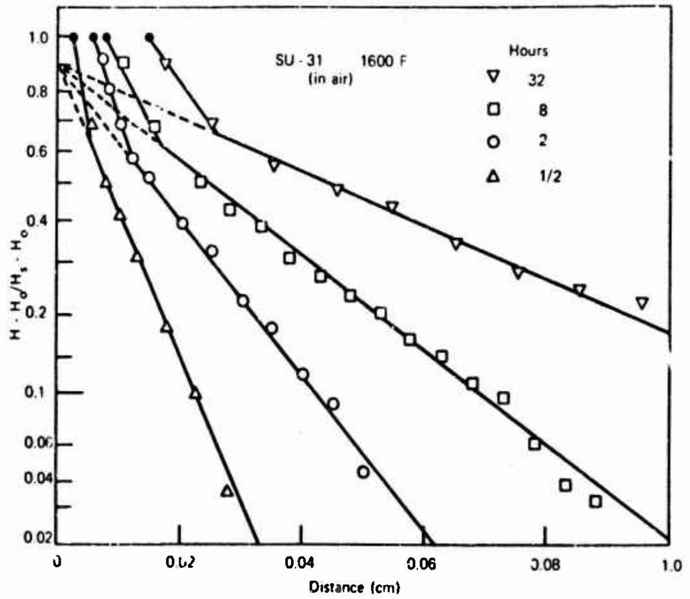

Figure 4. Profiles of hardness ratio versus distance for SU-31 exposed at 1600 F in air

The main portion of each set of relative hardness data is well fitted by a straight line. In all seven cases the line through the main portion of the data extrapolated to the distance origin to a value of $(H-H_0)/(H_s-H_0) = 0.90$. The main portion of the data is of interest because it reflects the presence of the most rapidly diffusing contaminant. The first few hardness values taken nearest the surface were elevated above values expected from the line through that main portion of the data. The elevation in hardness of those points near the surface is due to the effect of the advancing oxide/metal boundary and possibly to the presence of less rapidly diffusing species of contaminant. The elevation of the hardness very near the oxide/metal interface will be termed the "near surface effect".

To separate the contribution of that near surface effect from the major portion of the data, use was made of the fact that the lines through the major portion of all seven sets of data extrapolated to $(H'-H_0)/(H_s-H_0) = 0.90$ at the original position of the specimen surface. From that intercept, a value of H'_s = 1285 DPH was obtained. H'_s is the value of the surface hardness expected in the absence of the near surface effect. The data were normalized using that value, H'_s, and all seven sets are shown in Figure 5 with the elevated hardness points nearest the surface eliminated from the plot.

By use of Equation 2, and using the slopes of the best fit straight lines through the data shown in Figure 5, the diffusion coefficient at 1600 F for the principal contaminant was determined as 4.0×10^{-8} sq cm/sec.

The value of H_s obtained by graphical extrapolation of the hardness profiles shown in Figure 3 could be subject to some error. However, that error would not be transferred to the values of H'_s obtained from the intercept value of the best fit line through the major portion of the relative hardness data. Therefore, separation of the major portion of the data and normalization of the hardness increase using the value $H'_s - H_0$ should result in a more accurate value of the diffusion coefficient than could be obtained from the slopes of the lines in Figure 4.

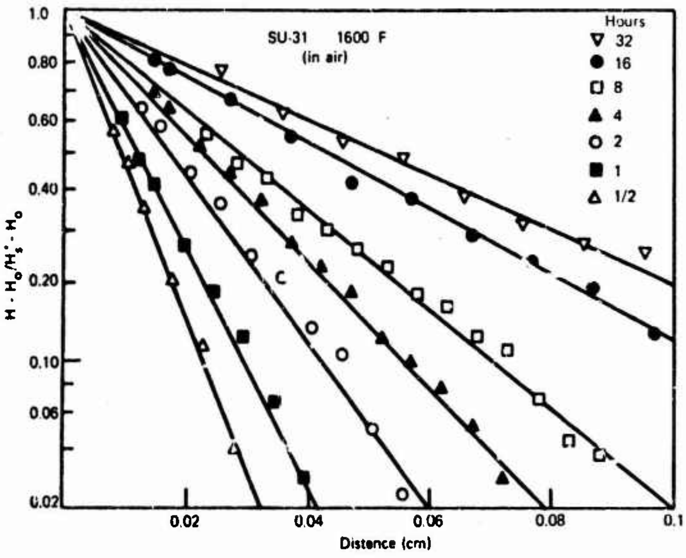

Figure 5. Contamination hardening profiles normalized to eliminate the surface effect.

The 2200 and 2600 F hardness profiles for SU-31 exposed in air for one hour are shown in Figure 6 replotted using probability grid divisions. Like the data for 1600 F, the data for the higher temperature tests deviated from the main line near the surface. Similar results were obtained at other temperatures and for the FS-85 alloy. The main portion of the data at 2200 F can be fitted by a line which extrapolates to the distance origin at a value of $(H-H_0)/(H_S-H_0) = 0.45$ and for 2600 F to a value of 0.49. Those intercept values were used to compute surface hardness values, $H_S^{'}$, appropriate for normalization of the main portion of the hardness data.

The values of the surface hardness increase, $H_S^{'} - H_0$, for SU-31 were found to decrease with temperature as shown in Figure 7. Also shown are the surface oxide phases identified by X-ray diffraction. A similar decrease in the surface hardness increase was found for FS-85 as shown in Figure 8. The decrease in the surface hardness shown in Figures 7 and 8 implies a decrease in the level of the contaminant at the oxide/metal interface.

In pure columbium, when the oxidation rate constant is plotted versus temperature, it has been found that for oxygen pressures above 10 torr the rate goes through a maximum around 1300 F, decreases to about 1500 F, after which it again increases with temperature.[11-13] In a study of that rate anomaly in binary Cb-Ta alloys[14] it was found that the oxidation rate maximum is shifted upward in temperature with increasing tantalum additions. The rate maximum was shifted to 1800 F by 30 at.% Ta with further additions having little effect on the temperature of the rate maximum. It has also been found by precision lattice parameter measurements[12] that the oxygen concentration in the pure columbium just below the oxide is smaller at temperatures above the rate maximum region than below it.

Two anomalies have been found in the oxidation rates of the alloys SU-31 and FS-85.[6] The first, a shift from linear to parabolic kinetics, occurred between 1200 and 1400 F in SU-31 and between 1600 and 1800 F in FS-85. That anomaly correlates with the appearance of CbO_2 at the metal/oxide interface. The second rate anomaly is a small peak in the parabolic rate constant at about 1800 F in SU-31 and 1600 F in FS-85. The rate drop just above those temperatures has been correlated with the appearance of the high temperature form of Cb_2O_5.

Kofstad[15] has suggested that below the maximum rate temperature, oxidation in pure columbium proceeds by the formation of CbO_Z, an ordered tetragonal suboxide and by the nucleation of Cb_2O_5 on or near the platelets of CbO_Z. Above a temperature of about 1200 F, the CbO_Z decomposes and is no longer an intermediate oxidation product. At the higher temperatures the phases CbO and CbO_2 have been observed at the metal surface.[16,17] In that range, Kofstad[15] suggests that the oxidation proceeds by the following steps:

$$Cb \rightarrow Cb - O \text{ (sol. soln.)} \rightarrow CbO \rightarrow CbO_2 \rightarrow Cb_2O_5. \qquad (3)$$

For pure columbium Kofstad ascribes the decrease in oxygen concentration at the oxide/metal surface around the rate anomaly region to an adjustment of the oxygen level to the solubility limit for oxygen in columbium in equilibrium with CbO.

Other explanations have been advanced to account for the rate anomalies in oxidation of pure columbium.[11,13,18-20] Sintering of the oxide, decrease in

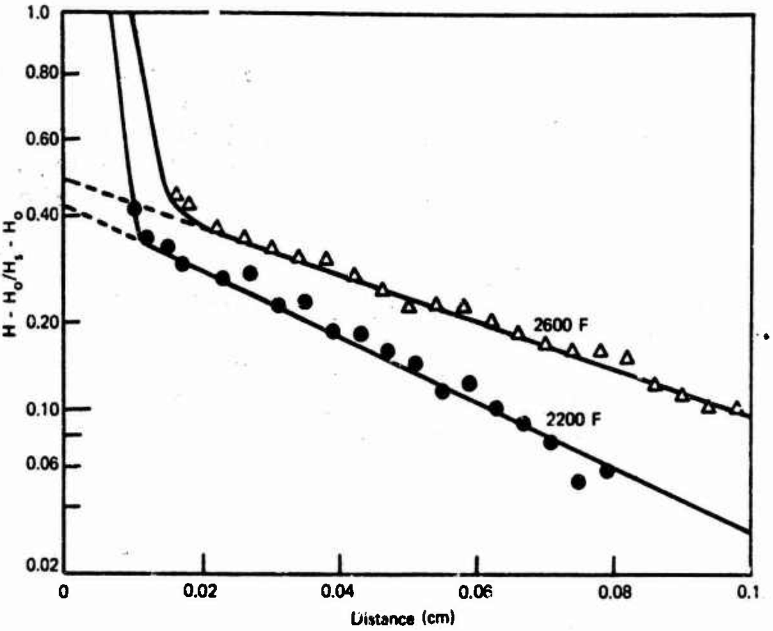

Figure 6. Contamination hardening profiles for SU-31 exposed at 2200 and 2600 F

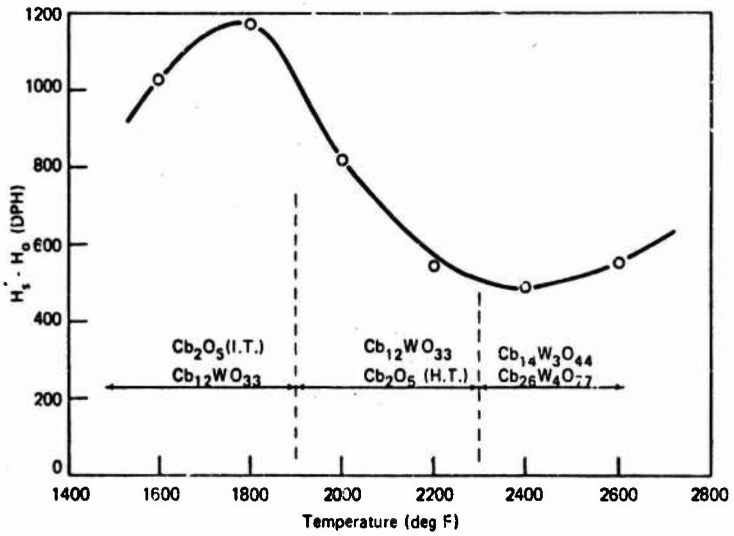

Figure 7. Surface hardness increase versus exposure temperature for SU-31. Also shown are the surface oxides identified by X-ray diffraction.

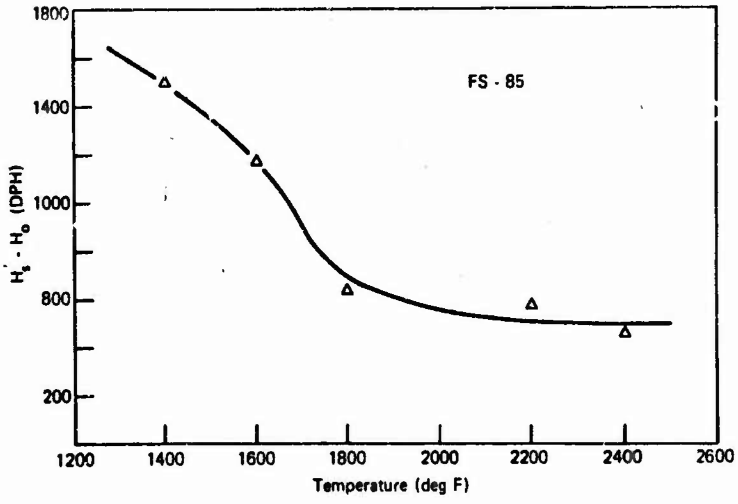

Figure 8. Surface hardness increase versus exposure temperature for FS-85

porosity of the oxide, change in the crystallographic form of the Cb_2O_5, and changes in the defect structure of the oxide have all been considered. The decrease in surface hardness shown in Figures 7 and 8 is not clearly related either to the appearance of the CbO_2 phase or to the change in the crystallographic form of the Cb_2O_5 in the alloys. The decrease may, however, be related to the presence of complex oxides such as $Cb_{12}WO_{33}$ which has been identified in the oxides on the SU-31 alloy.

Measurements of the diffusion coefficient for oxygen and nitrogen in pure columbium were first made by Ang[1] using torsional pendulum techniques. The values obtained were $D_0 = 0.0147$ sq cm/sec and $Q = 27.6$ kcal/mol for oxygen and $D_0 = 0.098$ sq cm/sec and $Q = 38.6$ kcal/mol for nitrogen. Marx et al.,[2] using ultrasonic damping techniques, obtained a value of $Q = 22.0$ kcal/mol for oxygen and $Q = 28.1$ kcal/mol for nitrogen in pure columbium.

Powers and Doyle[3] suggested that the difference between the earlier values[1,2] was due to concentration effects and to interactions between the oxygen and nitrogen which skew the relaxation peaks. Taking those effects into account, values of $D_0 = 0.0212$ sq cm/sec and $Q = 26.9$ kcal/mol for oxygen and $D_0 = 0.0086$ sq cm/sec and $Q = 34.9$ kcal/mol for nitrogen in pure columbium were obtained.[3] The relaxation measurements were all conducted in the temperature range below 650 C.

From the large difference in the activation energies for oxygen and nitrogen diffusion in pure columbium, it is easily shown that oxygen will diffuse much more rapidly than nitrogen in columbium and this supports the observations of Klopp, Sims, and Jaffee[4] that the contamination of pure columbium in air is due mostly to oxygen diffusion.

The diffusion coefficients for the principal contaminant in SU-31 and FS-85 calculated from Figure 9 are shown in Table II and also in Figure 10 plotted versus the reciprical of the absolute temperature. For comparison, the data of Powers and Doyle[3] for oxygen diffusion in pure columbium are shown and are extrapolated (dashed line) into the temperature range of the present results. Also shown are the data of Klopp, Sims, and Jaffee[4] for oxygen diffusion in pure columbium obtained by techniques similar to those used for this study.

Table II. DIFFUSION COEFFICIENT OF CONTAMINATING SPECIE IN THE ALLOYS

Temperature (°F)	SU-31		FS-85	
	D (sq cm/sec)	D (sq cm/hr)	D (sq cm/sec)	D (sq cm/hr)
1400	-	-	4.08×10^{-8}	1.47×10^{-4}
1600	4.67×10^{-8}	1.68×10^{-4}	1.09×10^{-7}	3.91×10^{-4}
1800	7.33×10^{-8}	2.64×10^{-4}	2.51×10^{-7}	9.05×10^{-4}
2000	1.39×10^{-7}	5.00×10^{-4}	-	-
2200	2.74×10^{-7}	9.85×10^{-4}	7.39×10^{-7}	2.66×10^{-3}
2400	4.78×10^{-7}	1.72×10^{-3}	1.19×10^{-6}	4.29×10^{-3}
2600	7.56×10^{-7}	2.72×10^{-3}	-	-

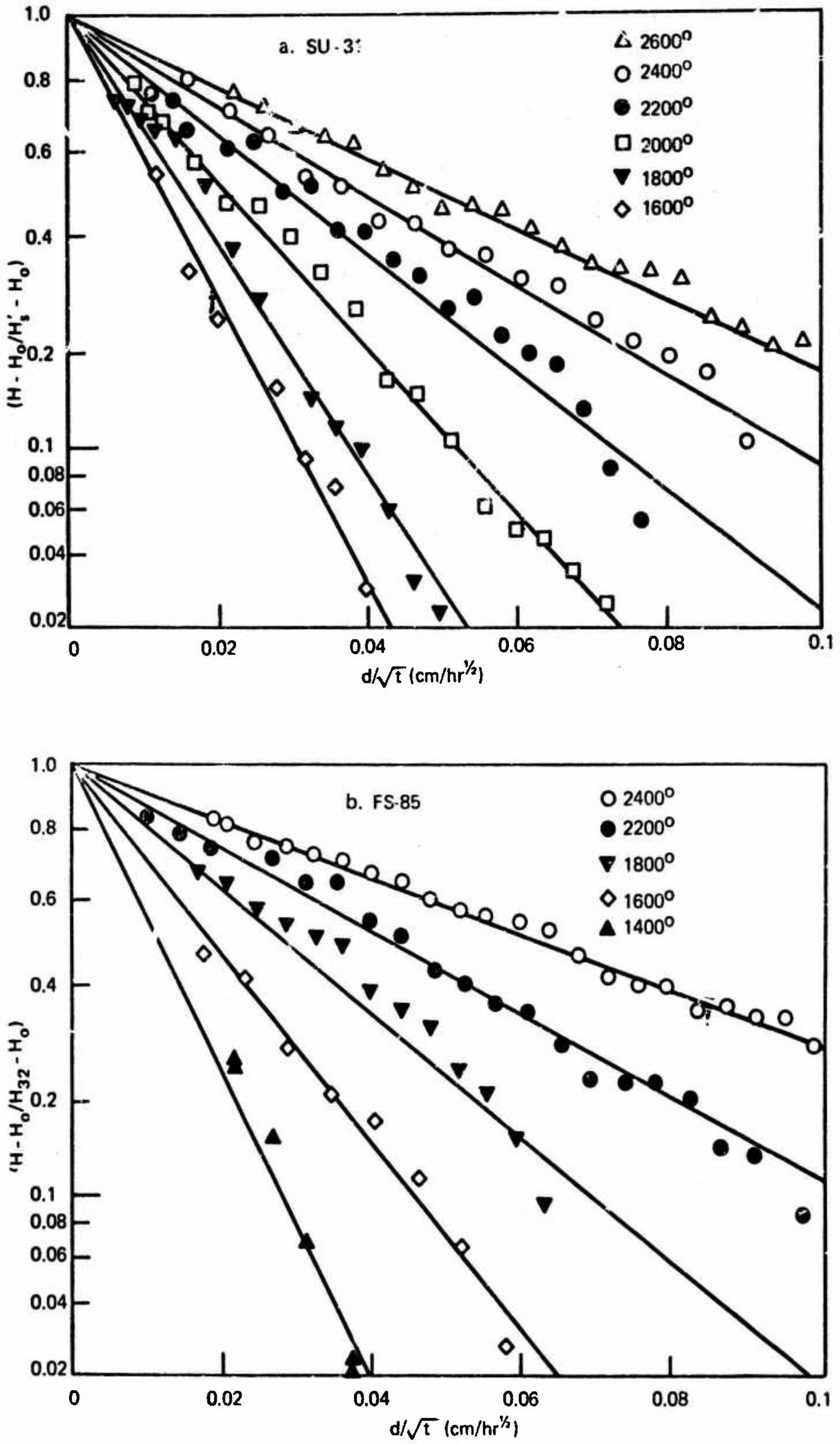

Figure 9. Contamination hardening profiles for SU-31 and FS-85 normalized to eliminate surface effect

Expressing the diffusion coefficient in the usual way as

$$D = D_0 \exp(-Q/RT), \tag{4}$$

the frequency factor D_0 and activation energy Q may be determined using the data shown in Figure 10. A least-squares fit to the present data yields a value of $D_0 = 3.31 \times 10^{-4}$ sq cm/sec and an activation energy of Q = 22.5 kcal/mol for the SU-31 alloy. For the FS-85 alloy the values obtained were $D_0 = 7.52 \times 10^{-4}$ sq cm/sec and an activation energy of Q = 20.3 kcal/mol. Those values are shown in Table III along with values previously reported[1-4] for oxygen diffusion in pure columbium.

Table III. FREQUENCY FACTOR AND ACTIVATION ENERGY FOR OXYGEN DIFFUSION

Material	D_0 (sq cm/sec)	Q (kcal/mol)	Reference
FS-85 alloy	7.52×10^{-4}	20.3	present work
SU-31 alloy	5.62×10^{-4}	22.3	present work
Pure Cb	1.47×10^{-2}	27.6	Ang[1]
Pure Cb	-	22.0	Marx et al[2]
Pure Cb	2.12×10^{-2}	26.9	Powers and Doyle[3]
Pure Cb	4.07×10^{-3}	24.9	Klopp et al[4]

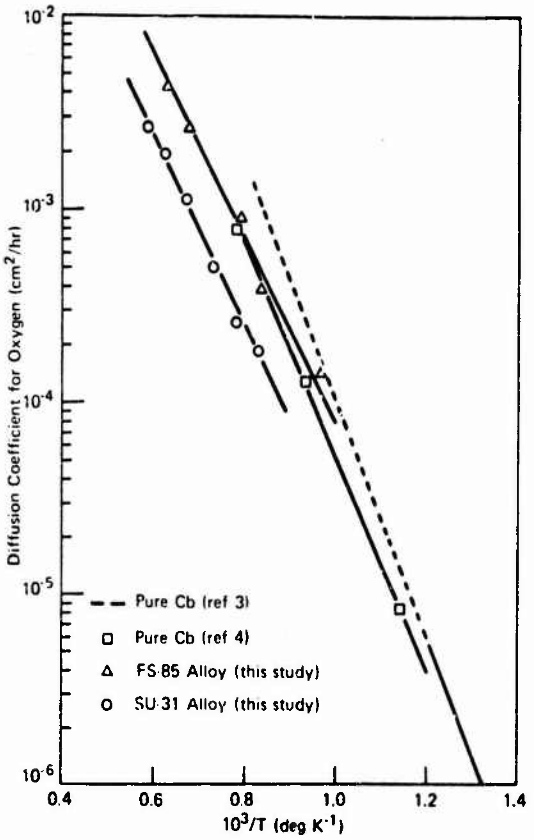

Figure 10. Diffusion coefficient of contaminating specie in SU-31 and FS-85 compared with reported data for diffusion coefficient of oxygen in pure columbium

From Figure 10 it can be seen that the measurements by Klopp, Sims, and Jaffee[4] for oxygen diffusion in pure columbium are in good agreement with the extrapolation of the values obtained at lower temperatures by relaxation techniques by Powers and Doyle.[3] The data shown in Figure 10 for the contaminant diffusion in FS-85 alloy is in good agreement with that for oxygen diffusion obtained by Klopp, Sims, and Jaffee[4] but with a slightly decreased slope reflecting the difference between the activation energy of 20.3 kcal/mol obtained for the FS-85 alloy and the value of 24.9 kcal/mol for pure columbium. The data for the diffusion coefficient of the principal contaminant for the SU-31 alloy lie almost parallel to that for FS-85 and that for oxygen in pure columbium in Figure 10 but are about a factor of two lower within the temperature range of the measurements (1600 to 2600 F). From this agreement it is concluded that the principal contaminant from exposure in air is oxygen.

Contamination Rate

Using Equation 3, the penetration of any arbitrary level of hardness increase could be calculated for a flat, thick specimen where the diffusion can be considered to occur in only one dimension. As an example, if X_{25} is the depth at which the hardness is increased 25 DPH units and t is the exposure time, $X_{25}/\sqrt{t}$ will be a constant for the material at any given temperature. Curves of $X_{25}/\sqrt{t}$ versus exposure temperature are shown in Figure 11 for SU-31, FS-85, and pure columbium. The contamination rates of FS-85 and pure columbium are very similar over this temperature range. The contamination depth for SU-31, however, is about a factor of two lower, mainly due to the lower value of the diffusion coefficient as shown in Figure 10.

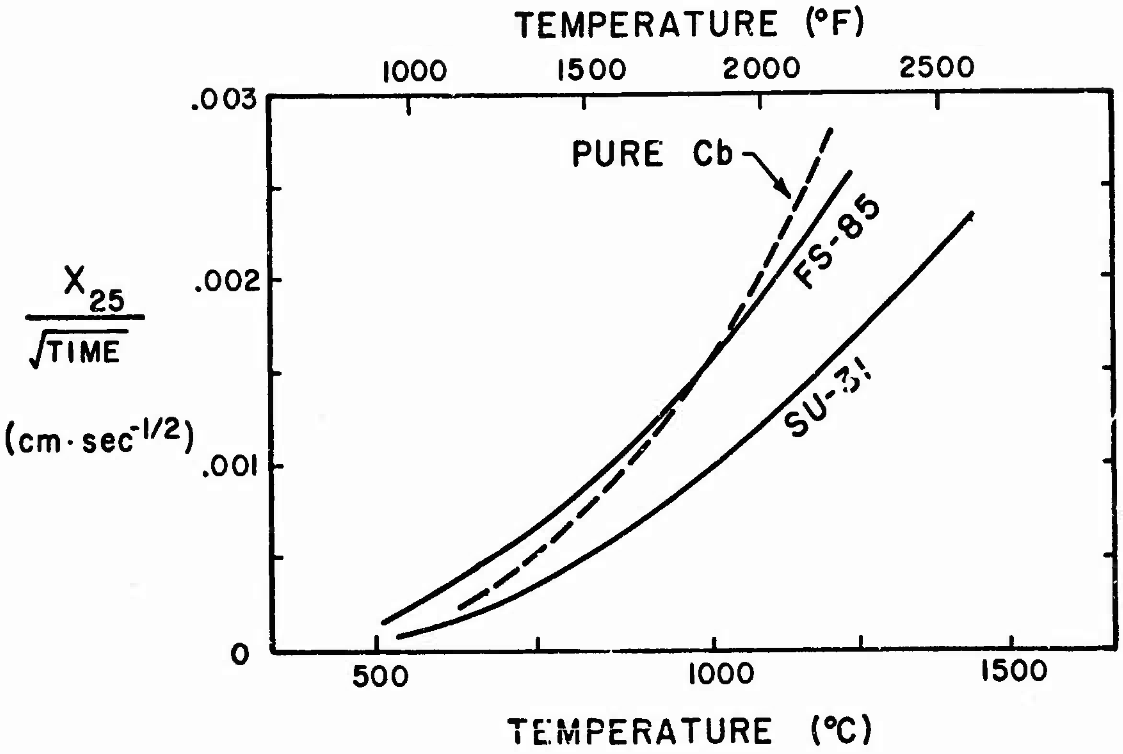

Figure 11. Contamination hardening (25 DPH increase) versus exposure temperature

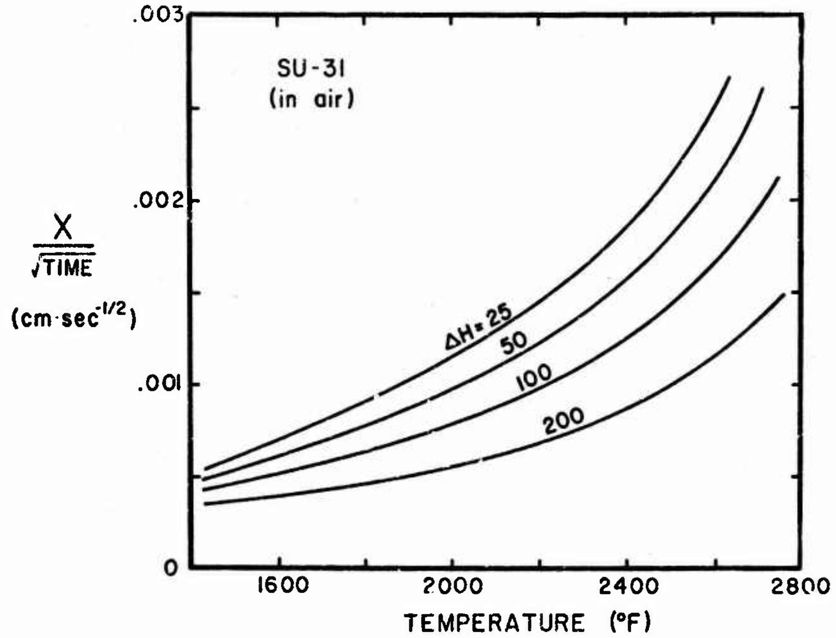

Figure 12. Expected contamination hardening to various levels for SU-31 versus exposure temperature

In a similar way, the diffusion coefficient data obtained in this study may be used to calculate a family of curves of $X/\sqrt{t}$ for various hardness levels. Such a set of curves is shown in Figure 12 for the SU-31 alloy.

The contamination data shown in Figure 11 indicate that contamination rates even in SU-31 are much too high to permit use of the material uncoated in long time applications without contamination and hence with embrittlement progressing far beneath the oxide. However, the type analysis developed above is useful because it readily allows comparison of the alloys in a manner more directly related to loss of mechanical properties than comparisons based on oxidation weight gain or surface recession measuremtnts. In addition, the availability of diffusion coefficient data permits prediction of the growth rate of embrittlement zones at coating defects and the assessment of the severity of coating defects of various geometries.

SUMMARY AND CONCLUSIONS

Data for the rate of contamination hardening of SU-31 and FS-85 columbium-base alloys were obtained for samples exposed in air at 1400 to 2600 F. Diffusion coefficients calculated from the hardening profiles have been shown to be in good agreement with the previously reported values for oxygen diffusion in pure columbium. From that agreement is is concluded that hardening is a result of the absorption and diffusion of oxygen from the air. The activation energies obtained in the present measurements are 22.5 kcal/mol in SU-31 and 20.3 kcal/mol in FS-85 with a diffusion frequency factor D_0, of 3.81×10^{-4} sq cm/sec in SU-31 and 7.52×10^{-4} sq cm/sec in FS-85. Based on these measurements, the contamination depth of SU-31 is found to be about a factor of two less than that of FS-85 over the temperature range of interest. Contamination rates in both alloys are too high to permit use of the material uncoated for long time applications at high temperatures in an oxidizing atmosphere.

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