CENTRAL RESEARCH LIBRARY
DOCUMENT COLLECTION

MARTIN MARIETTA ENERGY SYSTEMS LIBRARIES
3 4456 0349502 8

ORNL-1565
Metallurgy and Ceramics
4a

SCALING OF COLUMBIUM IN AIR

H. Inouye

CENTRAL RESEARCH LIBRARY
DOCUMENT COLLECTION

LIBRARY LOAN COPY

DO NOT TRANSFER TO ANOTHER PERSON

If you wish someone else to see this document, send in name with document and the library will arrange a loan.

OAK RIDGE NATIONAL LABORATORY
OPERATED BY
CARBIDE AND CARBON CHEMICALS COMPANY
A DIVISION OF UNION CARBIDE AND CARBON CORPORATION
UCC
POST OFFICE BOX P
OAK RIDGE, TENNESSEE

ORNL-1565

This document consists of 20 pages

Copy 4 of 294 copies Series A

Contract No W-7405-eng-26

METALLURGY DIVISION

SCALING OF COLUMBIUM IN AIR

H. Inouye

DATE ISSUED

SEP 1 1953

OAK RIDGE NATIONAL LABORATORY
operated by
CARBIDE AND CARBON CHEMICALS COMPANY
A Division of Union Carbide and Carbon Corporation
Post Office Box P
Oak Ridge, Tennessee

MARTIN MARIETTA ENERGY SYSTEMS LIBRARIES

3 4456 0349502 8

INTERNAL DISTRIBUTION

1. C. E. Center
2. Biology Library
3. Health Physics Library
4-5. Central Research Library
6. Metallurgy Library
7. Reactor Experimental Engineering Library
8-12. Laboratory Records Dept.
13. Laboratory Records, ORNL R.C.
14. C. E. Larson
15. W. B. Humes (K-25)
16. L. B. Emlet (Y-12)
17. A. M. Weinberg
18. E. H. Taylor
19. E. D. Shipley
20. F. C. VonderLage
21. R. C. Briant
22. J. A. Swartout
23. S. C. Lind
24. F. L. Culler
25. A. H. Snell
26. A. Hollaender
27. M. T. Kelley
28. K. Z. Morgan
29. W. D. Manly
30. T. A. Lincoln
31. A. S. Householder
32. C. S. Harrill
33. C. E. Winters
34. D. S. Billington
35. D. W. Cardwell
36. E. M. King
37. A. J. Miller
38. D. D. Cowen
39. P. M. Reyling
40. G. C. Williams
41. E. J. Boyle
42. L. K. Jetter
43. H. Inouye
44. W. H. Bridges
45. G. P. Smith
46. J. V. Cathcart
47. J. E. Cunningham
48. T. K. Roche
49. W. J. Fretague
50. J. M. Warde
51. W. O. Harms
52. R. J. Gray
53. E. C. Miller
54. P. Patriarca
55. D. C. Vreeland
56. J. A. Milko
57. E. S. Bomar
58. J. H. Coobs
59. R. B. Oliver
60. G. M. Adamson
61. H. W. Savage
62. G. M. Slaughter
63. E. E. Hoffman
64. W. B. Cottrell
65. R. H. Thielemann
66. M. J. Skinner
67. J. H. Frye, Jr.
68. ANP Reports Office

EXTERNAL DISTRIBUTION

69. D. B. Bendict, C&CCC, South Charleston
70. R. F. Bacher, California Institute of Technology
71. A. Levy, Pratt and Whitney Aircraft Division
72. A. E. Focke, General Electric Company (ANPP)
73. D. E. Deutsch, Atomic Energy Commission, Washington
74. M. J. Whitman, Materials Laboratory (WADC)
75. S. L. Simon, National Advisory Committee for Aeronautics, Cleveland

76-294. Given distribution as shown in TID-4500 under Metallurgy and Ceramics Category

DISTRIBUTION PAGE TO BE REMOVED IF REPORT IS GIVEN PUBLIC DISTRIBUTION

SCALING OF COLUMBIUM IN AIR

H. Inouye

ABSTRACT

The scaling of columbium in dry air and in air containing 18 6 mm of water vapor was determined between 400 and 1200°C

In dry air at 400°C, the oxidation proceeds by short periods of rapid oxidation followed by longer periods of slower oxidation, but after an interval of 21 hr, the rate becomes linear The presence of water vapor greatly accelerates the linear oxidation rate

In dry air at 600°C, the oxidation rate is linear The presence of moisture in the air reduces the oxidation rate and causes a deviation from linearity. The explanation of this is that an increased surface area results from uneven oxidation when the runs are made in dry air Above 600°C, the presence of water vapor does not affect the oxidation, the rate is linear

Both black and white oxides were formed at these temperatures and have been identified as Cb_2O_5 Three modifications of the pentoxide were found, the temperatures at which they are stable are not necessarily those found by Brauer

Rate constants were calculated for each temperature investigated, and an Arrhenius plot was made A straight line was obtained when the logarithm of the rate constant was plotted vs $1/T$ An inflection of the curve occurs at 900°C, which corresponds to the temperature at which the scale undergoes a modification of its form Energies of activation were calculated to be 13,400 cal/mole between 600 and 900°C and 4350 cal/mole between 900 and 1200°C

INTRODUCTION

The investigation of the scaling of columbium was undertaken to determine the high-temperature properties of this metal The basis for the consideration of columbium as a constructional material is its high melting point (2415°C), its comparatively low neutron cross section, and its relative ease of cold fabrication. The ultimate use of this material is justified only when its high-temperature properties permit its use at temperatures greater than those for which conventional materials are now considered.

Unlike molybdenum which is characterized by brittleness at low temperatures, columbium is ductile to the extent that it is always fabricated at room temperatures Furthermore, joining of the metal produces no brittleness in the heat-affected zone as it does in the case of molybdenum For these reasons, the metal offers attractive properties as a high-temperature structural material A disadvantage of the metal is its reactivity with gases at elevated temperatures.

The scaling of columbium was determined in order to clearly define the conditions of operation in its ultimate use. It was especially desired to determine its reaction rate, for information of this kind leads to a clearer understanding of the nature of the scale formed.

Thus, the formation of a dense adherent scale retards the reaction rate between the metal and the gases because the process is governed by the diffusion of the reactants through this scale. The reaction rates characteristic of this type of scale are parabolic, logarithmic, and, less frequently, cubic Such scales are said to be protective In contrast, when the growth of scale or the amount of material reacting is proportional to the time of exposure, a linear oxidation rate is observed, and the

scale formed offers no protection to the underlying metal This is called a phase-boundary reaction in which diffusion processes occur instantaneously [1] In alloys containing molybdenum and vanadium, an acceleration of the oxidation rate was observed.[2] This is attributed to the formation of volatile oxides with low melting points

CONCLUSIONS

The use of columbium in air at high temperatures will, of necessity, include the application of a protective coating or the development of oxidation-resistant alloys Unlike molybdenum, which is also being considered for high-temperature applications, the columbium oxide formed is not volatile up to the temperatures investigated. The amount of metal which reacts with air in 15 min at 800°C is 0.2500 g/cm^2 for molybdenum and 0 0125 g/cm^2 for columbium.

PREVIOUS WORK

Gulbransen and Andrew[3] determined the reactions of columbium in vacuum and in oxygen, nitrogen, and hydrogen in the temperature range of 250 to 375°C A parabolic oxidation rate was found for the reaction between oxygen (at a pressure of 76 mm) and columbium, and the energy of activation was calculated to be 22,800 cal/mole The amount of oxide formed during a period of 2 hr was negligible (80 μg/cm^2)

Three oxides of columbium with a small range of homogeneity have been found by Brauer [4] The lower oxide, CbO, is face-centered cubic, has a lattice constant of 4.203 Å, and can be prepared by the reduction of Cb_2O_5 with hydrogen

The three modifications in which Cb_2O_5 exists have been named "T", "M", and "H" according to the temperature range in which they are stable Brauer found that the low or "T" form is stable between 500 and 900°C, that the middle or "M" form is stable between 1000 and 1100°C, and that the high or "H" form exists above 1100°C. This oxide was found by Zachariasen[5] to be isomorphous with Ta_2O_5. The structure of Cb_2O_5 is pseudohexagonal orthorhombic, and the cell dimensions are as follows

$$a_1 = 6.16 \pm 0\ 03\ \text{Å},$$
$$a_2 = 3\ 65 \pm 0.02\ \text{Å},$$
$$a_3 = 3\ 94 \pm 0.02\ \text{Å}$$

The metal atoms are at (0, 0, 0) and (1/2, 1/2, 0). A calculated density for Cb_2O_5 is 4.95 g/cc.

The structure of CbO_2 is similar to that of rutile, and the lattice constants are as follows a = 4.84 Å, c = 2.99 Å, c/a = 0.618.

EXPERIMENTAL

Several methods of investigation are possible and are described by Wagner.[1] The advantages and limitations of the several methods indicated that it was desirable to determine the course of oxidation by following the weight change as a function of time The incorporation of an analytical balance with the sample suspended into the furnace from one arm eliminates the number of samples required, sample variations, and errors resulting from handling This method requires that the oxides formed adhere to the sample and that such oxides not be volatile at the temperatures employed in the investigation.

It has been reported[6] that the oxides of columbium are volatile near the melting point of columbium,

---

(1) C Wagner, "Methods of High Temperature Oxidation Testing and Evaluation of Observations," *High Temperature Properties of Metals*, p 93, American Society for Metals, Cleveland, 1951

(2) A deS Brasunas and N J Grant, *Trans Am Soc Metals* **44**, 1117 (1952)

(3) E A Gulbransen and K F Andrew, *Trans Am Inst Mining Met Engrs* **188**, 586 (1950)

(4) G Brauer, *Z anorg u allgem Chem* **248**, 1 (1941)

(5) W H Zachariasen, p 11 in *Physics Division Report for Month Ending April 15, 1945*, CF-2926 (classified)

(6) *Fansteel Columbium*, p 5, Fansteel Metallurgical Corp , 1946

1440°C [7] In order to ascertain the the degree of volatility of the oxide, 0 5-g samples were heated in air for 18 hr, the results are given in Table 1. These results indicate that the method of investigation described above would not lead to any serious error, since it was expected that the oxidation rate of columbium would be rapid and that the amount of oxide vaporized would be below the accuracy of the method

TABLE 1 STABILITY OF Cb_2O_5 IN STATIC AIR

(0.5-g sample heated for 18 hr)

TEMPERATURE (°C)	WEIGHT CHANGE (g)	REMARKS
1000	+0 0001	Starting material contained a few black specks
1100	+0 0001	Oxide completely white
1200	None	Oxide yellow
1250	None	Oxide yellow
1300	-0 0006	Oxide yellow
1375	-0 0009	Oxide yellow

Test Specimens

The material tested was Fansteel sheet of the following approximate dimensions 5/16 by 2 by 0 024 in. and 5/16 by 2 by 0.048 inch. The columbium strips were polished successively on 2/0, 3/0, and 4/0 metallographic paper and were then given an alcohol wash. Spectrographic analysis showed that the major impurities were titanium and copper, however, it is known that tantalum is not detected by this method below a concentration of about 0 2%. The oxygen content of the samples was approximately 0.25%

Equipment and Test Procedure

The sample of columbium was suspended from a weighted 0 005-in platinum wire attached to one arm of an analytical balance and was lowered into a vertical silica tube, 1 in ID, which was heated by a platinum wound furnace. The lower end of the silica tube was stoppered, and air was admitted through a 1/4-in. hole. Two platinum (10% rhodium-platinum) thermocouples were incorporated into the stopper, one was wired to a Micromax controller and the other was wired to a potentiometer About 6 in of Al_2O_3 insulating bubbles was placed in the silica tube for stopper insulation and for preheating the air This left approximately 3 in of thermocouple exposed The air was taken from a compressed-air line at a flow rate of 2 liters/min and was then dried by means of Anhydrone and a mixture of acetone and dry ice The runs designated as "wet air" were made by passing the dried air through two bubblers containing a saturated solution of NH_4Cl at 25°C When the moisture content was checked by absorbing the air in Anhydrone, the value agreed within 0 5% of that calculated. The dew point of the dried air was -70°F Saturated NH_4Cl at 25°C has a vapor pressure of 18 6 mm H_2O at STP.

The samples were lowered into the furnace at temperature, and the weight measurement was made while the air supply was momentarily turned off so as to avoid the buoyancy of the flowing air.

TEST RESULTS AND DISCUSSION

Oxidation of Columbium at 400°C

Columbium oxidizes slowly in dry air at 400°C for a period of about 21 hours. The course of oxidation during this time proceeds by short periods of rapid oxidation followed by longer periods of slower oxidation, as is shown in Fig. 1. After the 21-hr interval, the oxidation rate becomes linear. The oxide scale after a period of 47 hr is adherent and is shown in the photomicrograph in Fig. 2. The scale consists of a black oxide surrounded by a white oxide matrix. The oxide can be identified as the "T" form

[7] E A Durbin, H E Wagner, and C G Harman, *Properties of Some Columbium Oxide-Basis Ceramics*, BMI-792 (Dec 15, 1952)

of Cb_2O_5 by means of x-ray data (see Appendix).

The data agree in magnitude with those of Gulbransen and Andrew[3] who made their measurements in oxygen. Undoubtedly, they might have observed breaks in the curve, such as those reported here, had they prolonged their test beyond a period of 2 hours. The phenomena are ascribed to a periodic rupture of a protective oxide.[8]

[8] D. Caplan and M. Cohen, *J. Metals* **4**, 1057 (1952).

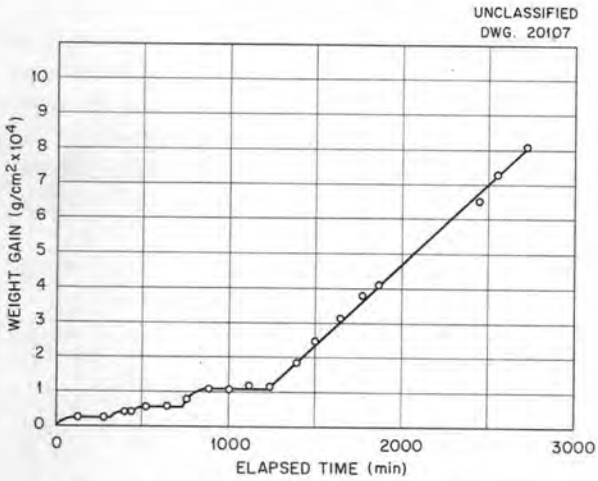

Fig. 1. Oxidation of Columbium Sheet at 400°C (Dry Air).

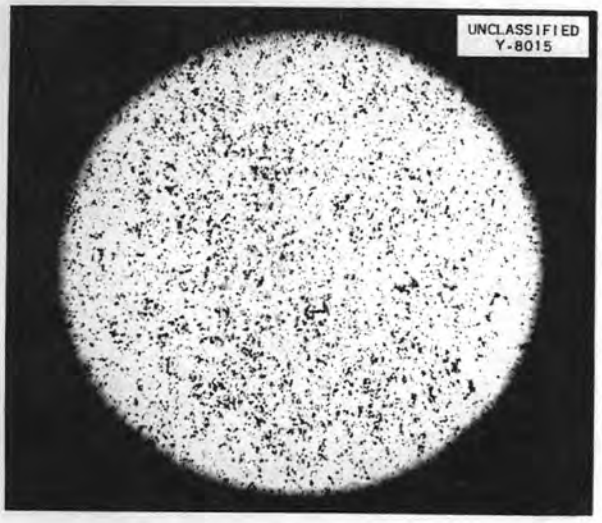

Fig. 2. Columbium Sheet Exposed for 47 hr in Dry Air at 400°C. Scale on metal is "T" Cb_2O_5. 10X. Reduced 24%.

The reason for a change to a linear oxidation rate beyond the duration of 21 hr is less apparent. It is postulated that the mechanism by which this occurs is as follows: The initial oxide produced is black and dense and in this form, offers protection. As the time of exposure increases, the black oxide is converted to the rather porous white oxide and consequently offers no protection to the underlying metal.

When tests were made in air containing water vapor, the oxidation of the columbium was accelerated by several factors, as shown in Fig. 3. The oxide was entirely white - the "T" form of Cb_2O_5 - and was freely scaling. A photomicrograph of the transverse section is shown in Fig. 4. The increased oxidation rate cannot be accounted for by the formation of a hydrated Cb_2O_5 (the oxide formed at 400°C was subjected to temperatures of 600 and 800°C and showed no weight decrease) or by the increased area caused by internal rupture (see

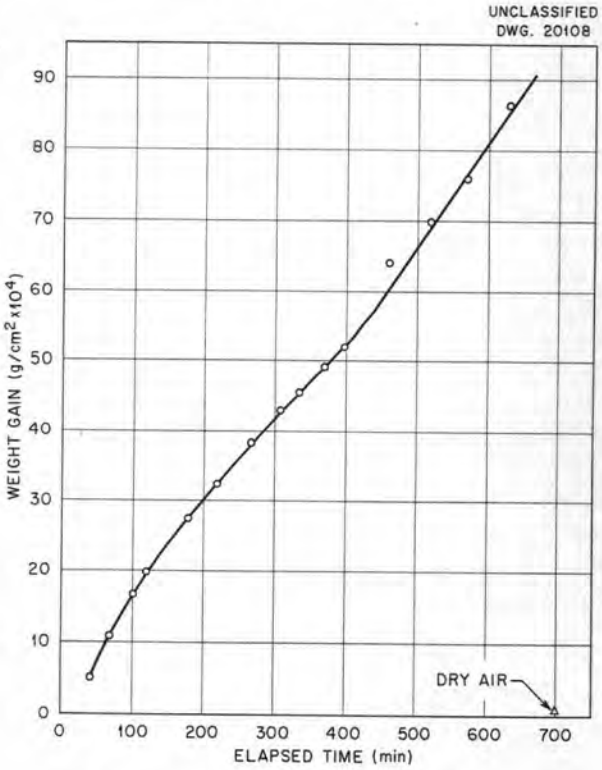

Fig. 3. Oxidation of Columbium Sheet at 400°C in Wet Air.

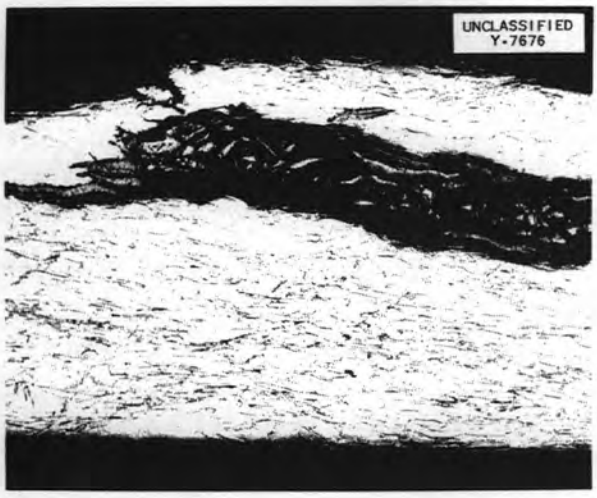

Fig. 4. Columbium Sheet Exposed for 12 hr in Wet Air at 400°C. Fractured area shows the formation of oxide below the surface. 150X. Reduced 24%.

Fig. 4), for only one such area was found. Therefore, since the slopes of the linear portion of the curves vary by a factor of 90 and since no appreciable difference is noted in the x-ray patterns, it can be concluded that water vapor acts only as a catalyst.

Oxidation of Columbium at 600°C

The oxidation rate of columbium in dry air at 600°C is linear. Duplicate runs made in air containing water vapor showed a slower oxidation rate that was not linear until after a period of 2 1/2 hr; the results are shown in Fig. 5. An x-ray diffraction pattern was used to identify the oxide as the "T" form of Cb_2O_5. No apparent difference was noted in the diffraction patterns of tests made either in dry or wet air (the oxide in both cases was "T" Cb_2O_5).

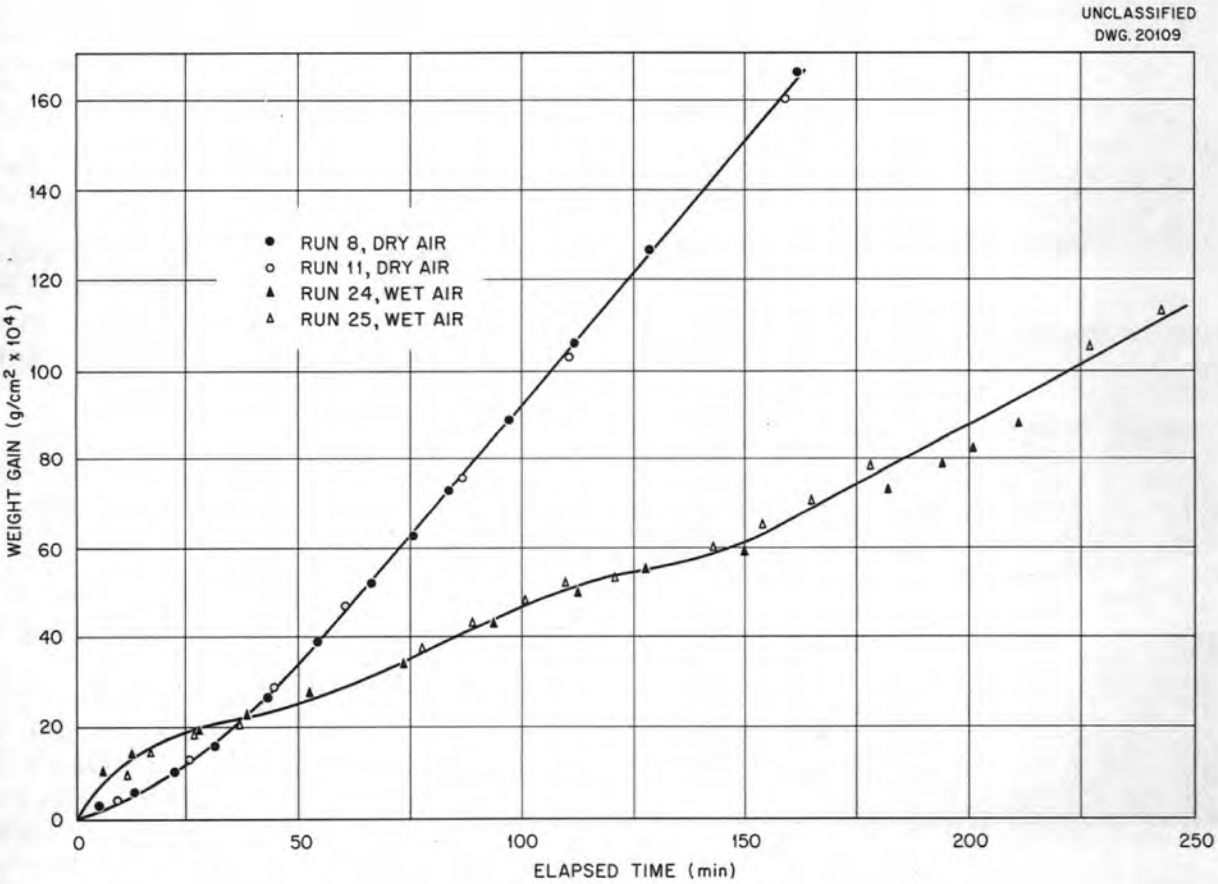

Fig. 5. Oxidation of Columbium Sheet at 600°C.

The oxide was entirely white, and the amount formed in a period of 2 hr spalled immediately upon removal from the furnace, as shown in Fig. 6. Exposure of the sample for 4 hr produced an oxide which was quite thick. A transverse section of this sample (Fig. 7) shows lamellar structure of the oxide.

It will be noted that the effect of moisture on the oxidation rate at 600°C is reversed to that found at 400°C, but to a lesser degree. This is explained by the fact that in dry air the reacting surface area is materially increased because of its uneven oxidation, as compared with the relatively smooth oxidation surfaces of the tests made in wet air (see Figs. 8 and 9). In several instances, the samples tested in dry air broke as a result of the penetration of the oxide throughout the sample cross section. Thus, it was found that although the oxidation rate was linear, checks could not be obtained from sample to sample. The result reported in Fig. 5 for dry air approaches the median value of six runs.

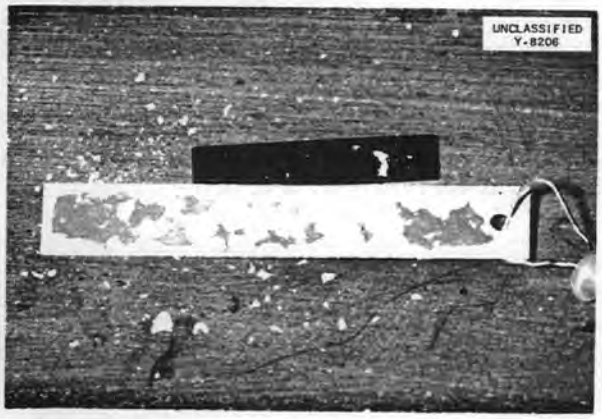

Fig. 6. Columbium Sheet Exposed for 2 hr in Dry Air at 600°C. 2X. Reduced 39%.

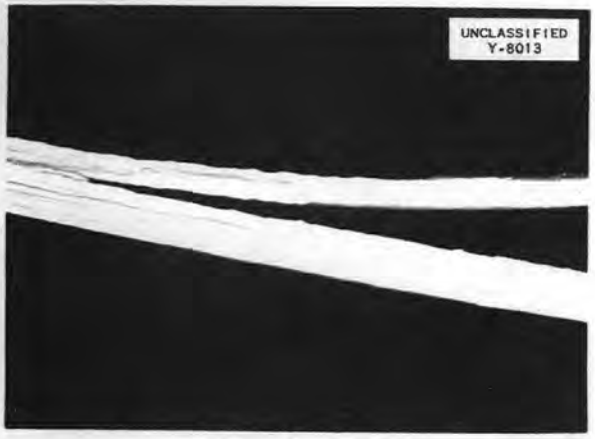

Fig. 7. Columbium Sheet Exposed for 4 hr in Dry Air at 600°C. Transverse section. 10X. Reduced 26.5%.

Oxidation of Columbium at 800°C

No appreciable difference is noted in the oxidation rates of columbium at 800°C between tests made in dry air and those made in wet air (see Fig. 10). The oxidation rate at 800°C is linear.

Tests made of sheet material showed that the faces were covered with a black oxide, whereas the edges were white (see Fig. 11). Both the white and the black oxides are mixtures of "T" Cb_2O_5 and "H" Cb_2O_5. A cross section of the oxidized sheet material is shown in Fig. 12; Fig. 13 shows the same sample at a higher magnification. A 0.040-in. wire forms an oxide that is entirely white and which is the "T" Cb_2O_5 (see Fig. 14).

It is not known why a black Cb_2O_5 forms on the flat faces of sheet material at 800°C, whereas at any other temperature, the surface oxide is white. Deviations from linearity occurred in several different runs until the sample thickness was increased; these deviations were all characterized by a decreased oxidation rate. The formation of the black oxide undoubtedly depends on the geometry of the sample, as evidenced by the oxidized wire.

Oxidation of Columbium at 1000°C

The oxidation rate of columbium is linear at 1000°C. Sheet material deviates from linearity, but it was later established that this is due to the reduced area of the test sample as oxidation proceeded and not to any protective nature of the overlying oxide. Linearity of the oxidation rate was determined by swaging Inconel tubing onto a rod of columbium and by exposing a section of this composite

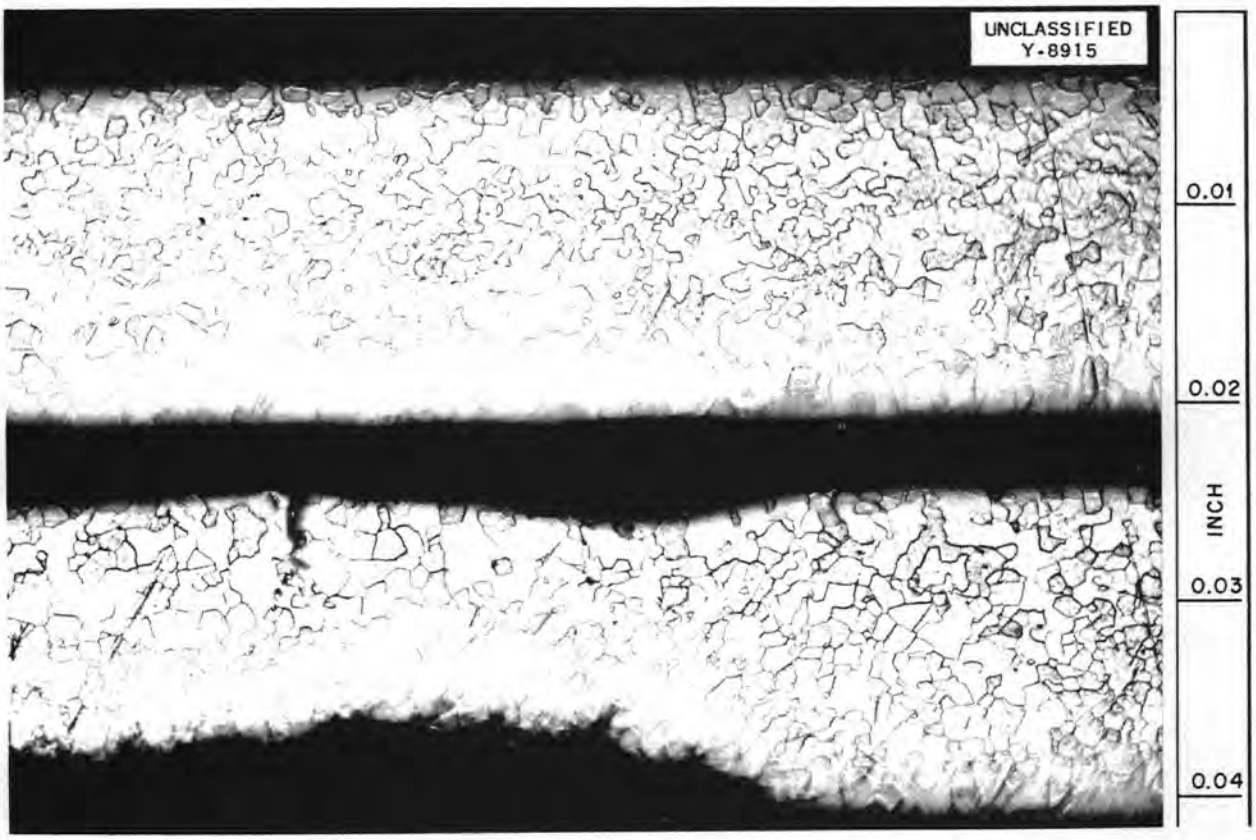

Fig. 8. Columbium Sheet Exposed in Dry Air at 600°C. 100X

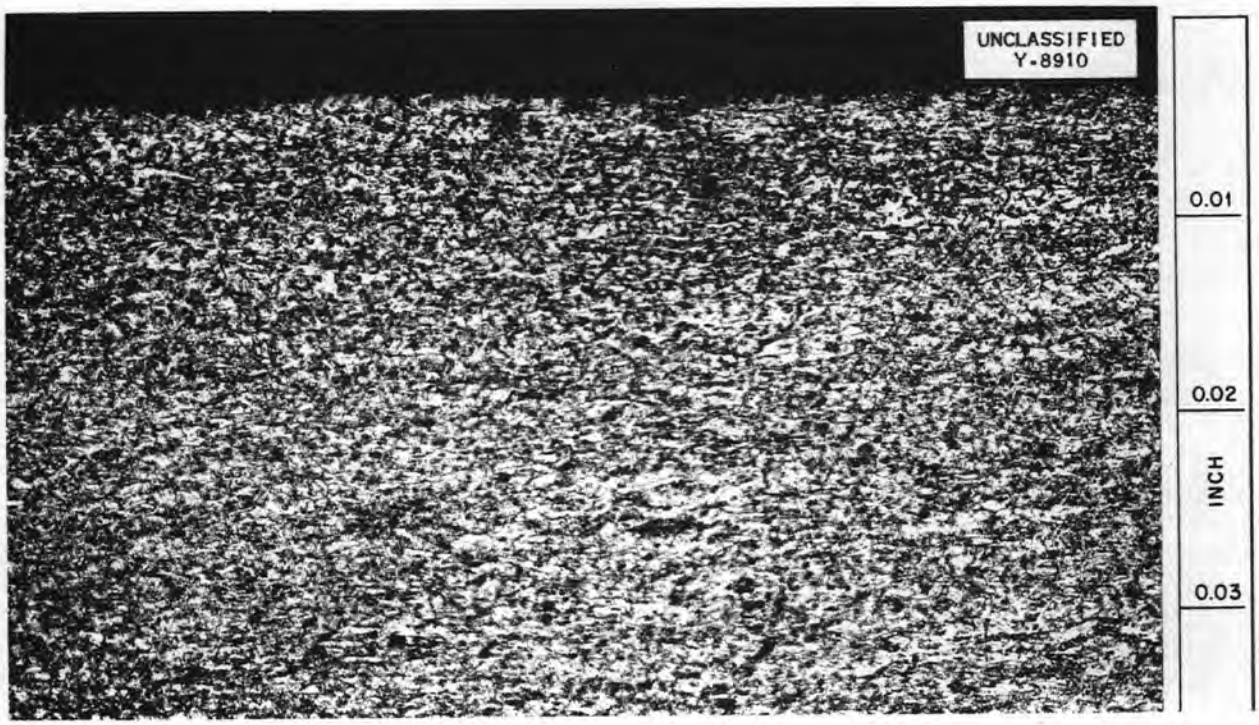

Fig. 9. Columbium Sheet Exposed in Wet Air at 600°C. 100X

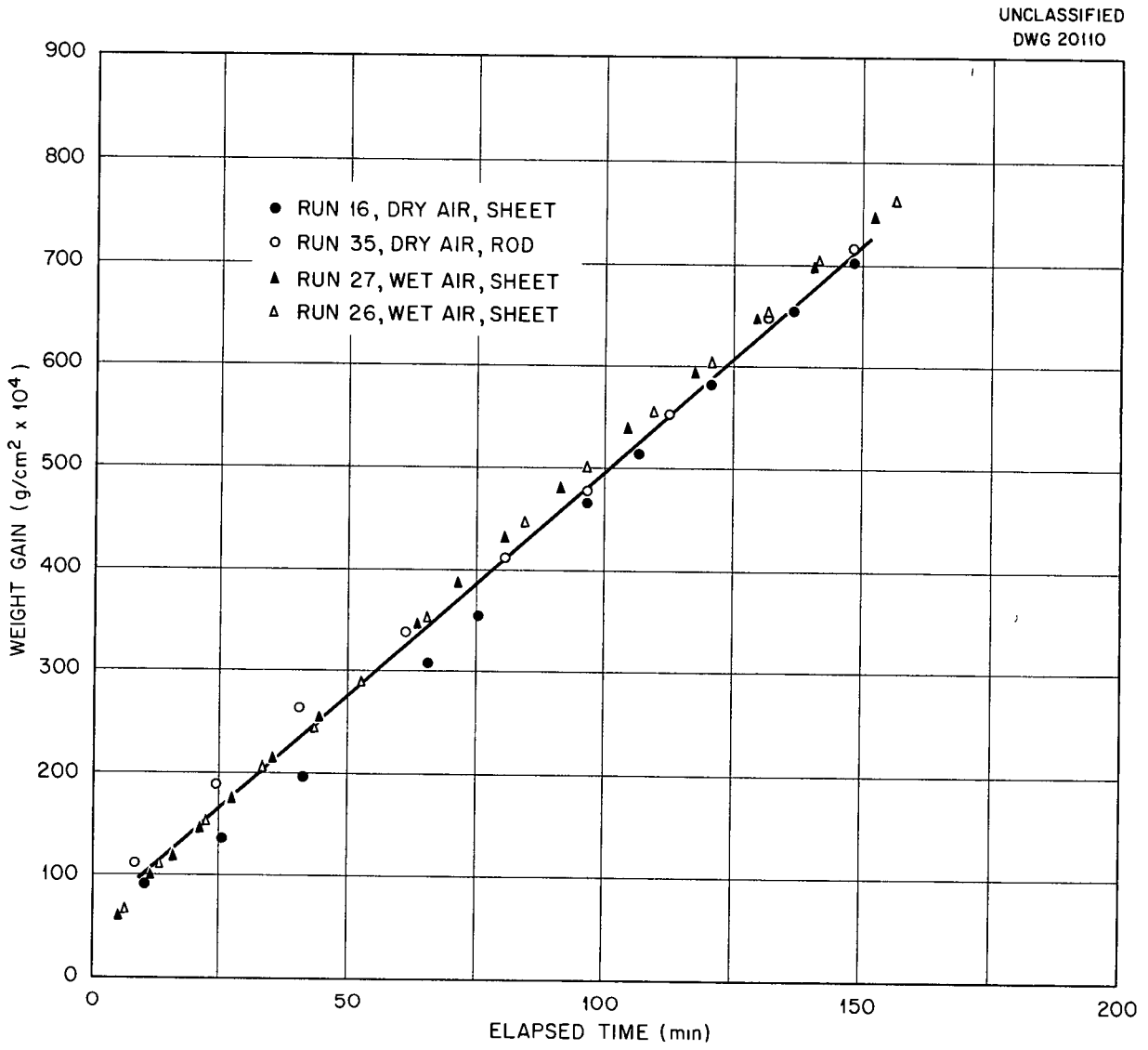

Fig. 10. Oxidation of Columbium in Air at 800°C.

at temperature. Thus, only the ends of the rod were exposed because the cylindrical surface was protected by the Inconel. The oxide is voluminous and has been identified as "H" Cb_2O_5 (see Fig. 15). The presence of water vapor did not affect the test results, as is shown in Fig. 16. The metal surface remains relatively smooth (see Fig. 17).

Oxidation of Columbium at 1200°C

Within the limits of accuracy, the oxidation rate of columbium is linear at 1200°C. A deviation from linearity similar to that mentioned in the previous paragraph was noted when sheet material was tested. The constant-area sample also described above showed a linear oxidation rate after a period of 1/2 hr, as shown in Fig. 18.

The white oxide is dense and consists of the "H" form of Cb_2O_5. Figure 19 shows the test piece immediately upon its removal from the furnace, and Fig. 20 shows the test piece a few seconds later.

A clue to the mechanism of oxidation is shown in Figs. 14 and 19. It will be noted that the raised surfaces of oxide shown in Fig. 19 are approximately of the same dimensions as those of the original test piece. In order that this may occur, the oxygen must migrate to the metal-oxide interface and must react with the metal. The resulting oxide then forces the overlying oxide outward. On a flat surface, this would appear as raised surfaces, whereas on a rounded surface, it will result in "pie-shaped" oxide segments (Fig. 14). This mechanism of oxidation is further established as being possible, for the platinum hook holding the sample was expanded during the test instead of being buried in the oxide, as was found by Brasunas and Grant.[2]

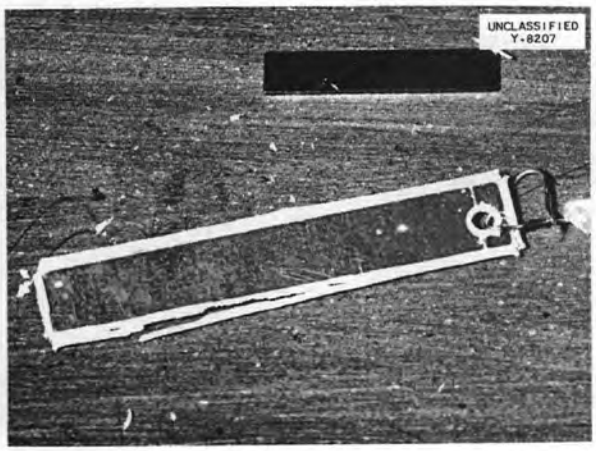

Fig. 11. Columbium Sheet Exposed for 2 hr in Dry Air at 800°C. 2X. Reduced 37.5%.

The vigorous spalling of the oxide is due to the relatively dense Cb_2O_5 which has a negative temperature coefficient of expansion.[7]

Temperature Dependence of the Oxidation Rate

Tests were made at 700 and 900°C in order to establish the temperature at which Cb_2O_5 undergoes a modification of its structure from its low-temperature form to its high-temperature form and also to determine the temperature dependence of the oxidation rate. The

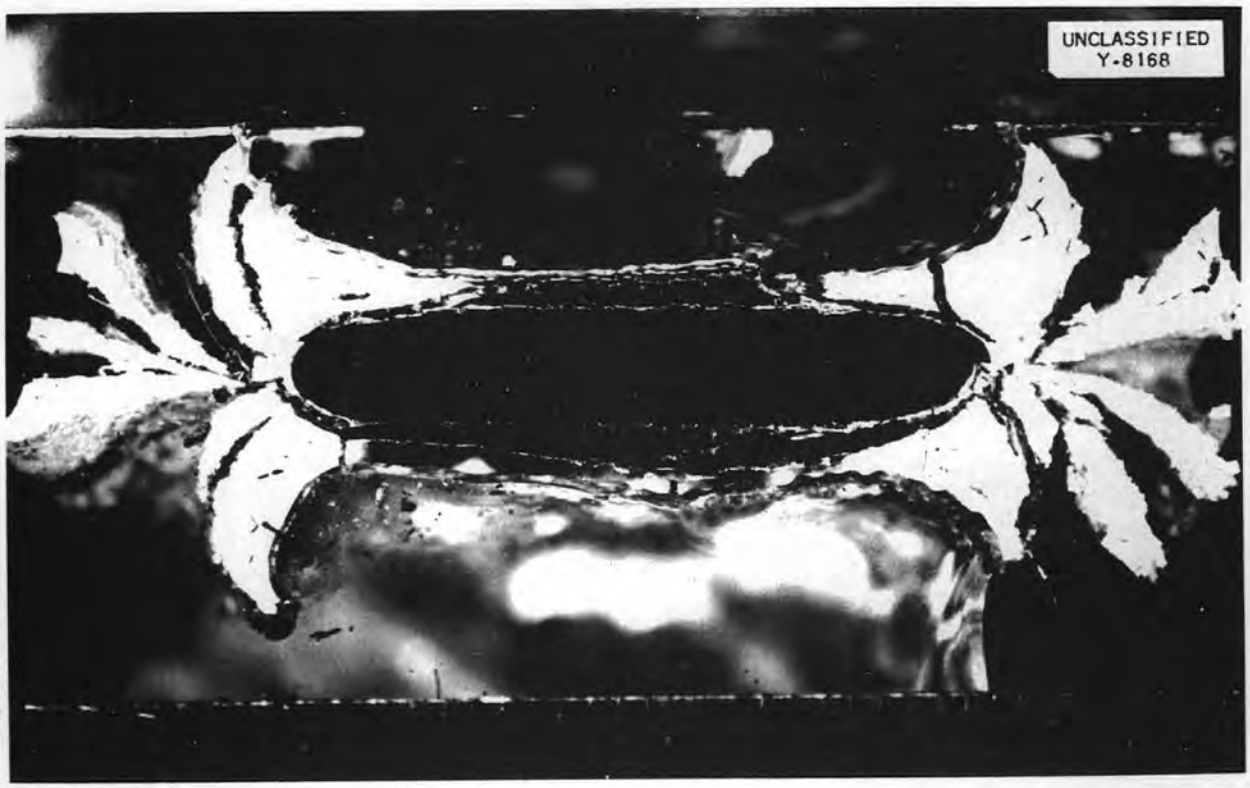

Fig. 12. Cross Section of Columbium Sheet Exposed for 2 hr at 800°C. 15X

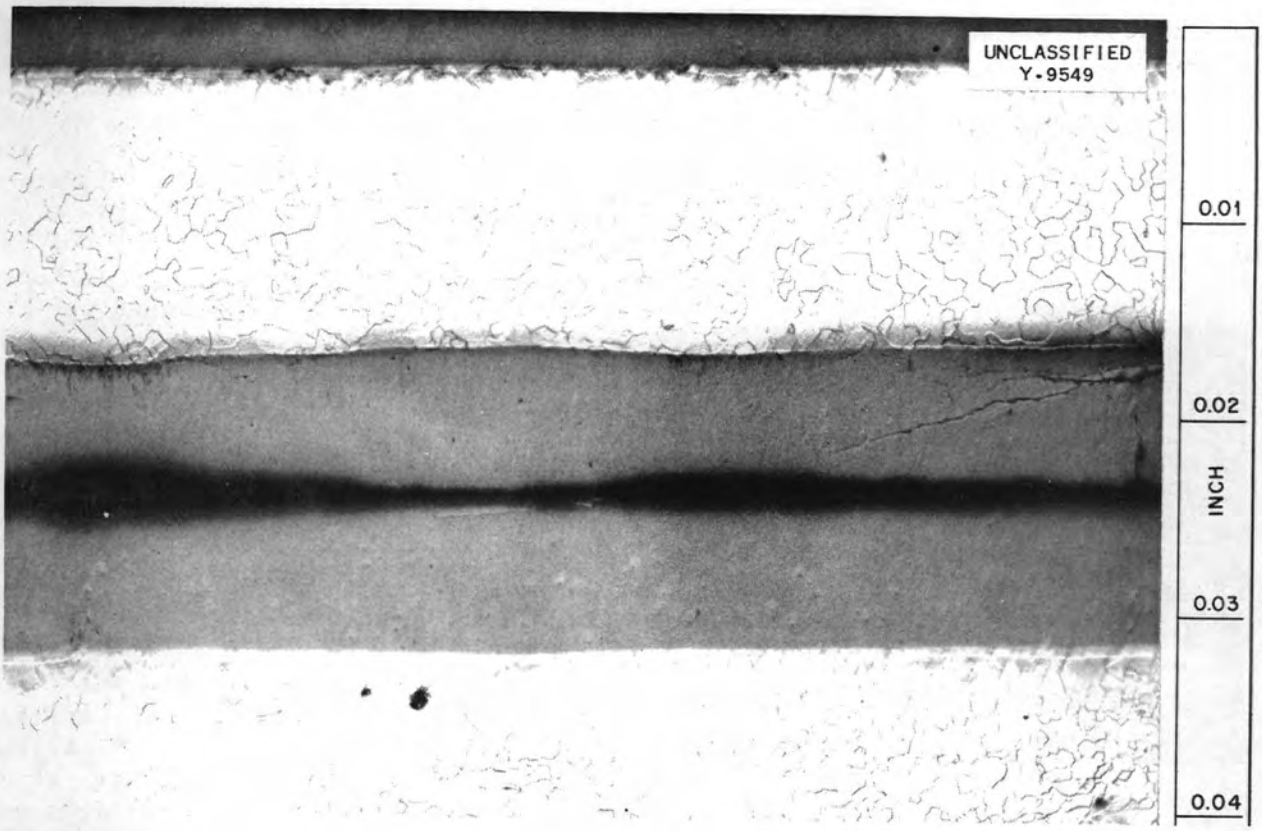

Fig. 13. Longitudinal Section of Columbium Sheet Exposed for 2 hr in Dry Air at 800°C. The adhering scale is black. 100X

Fig. 14. Cross Section of 0.040-in. Columbium Wire Exposed for 1 hr in Dry Air at 800°C. 40X

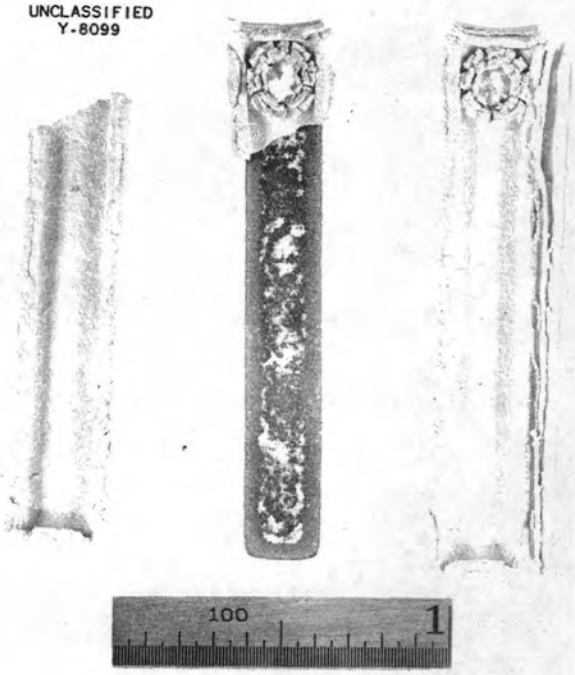

Fig. 15. Columbium Sheet Exposed for 2 hr in Dry Air at 1000°C. 2X. Reduced 14%.

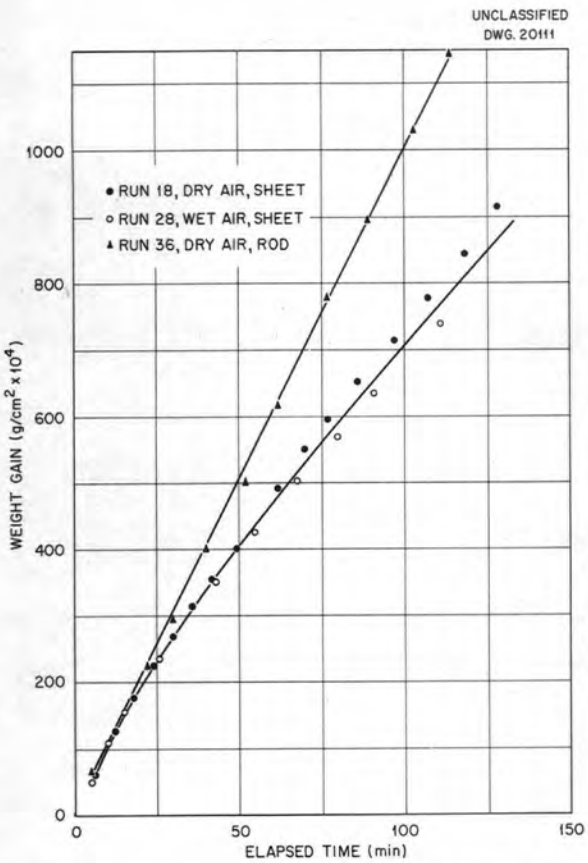

Fig. 16. Oxidation of Columbium at 1000°C.

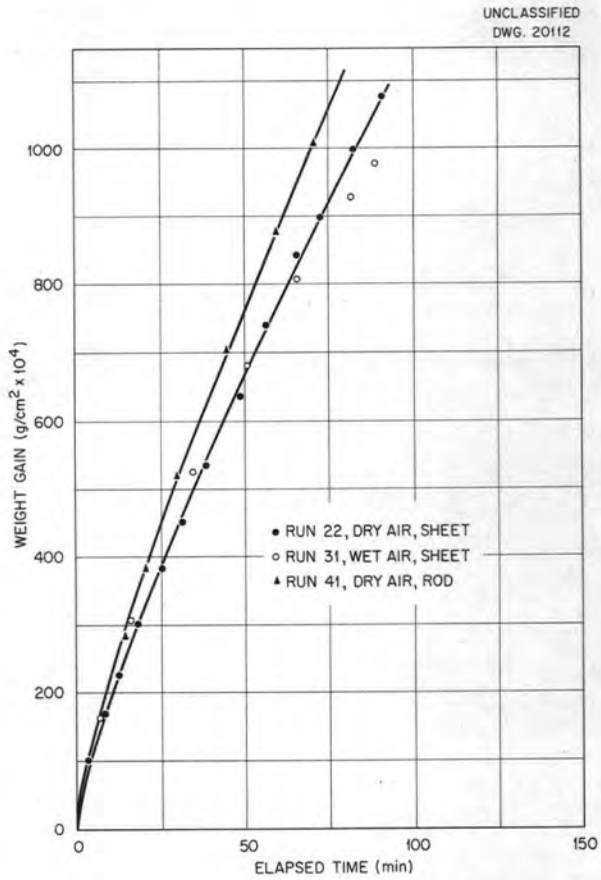

Fig. 18. Oxidation of Columbium at 1200°C.

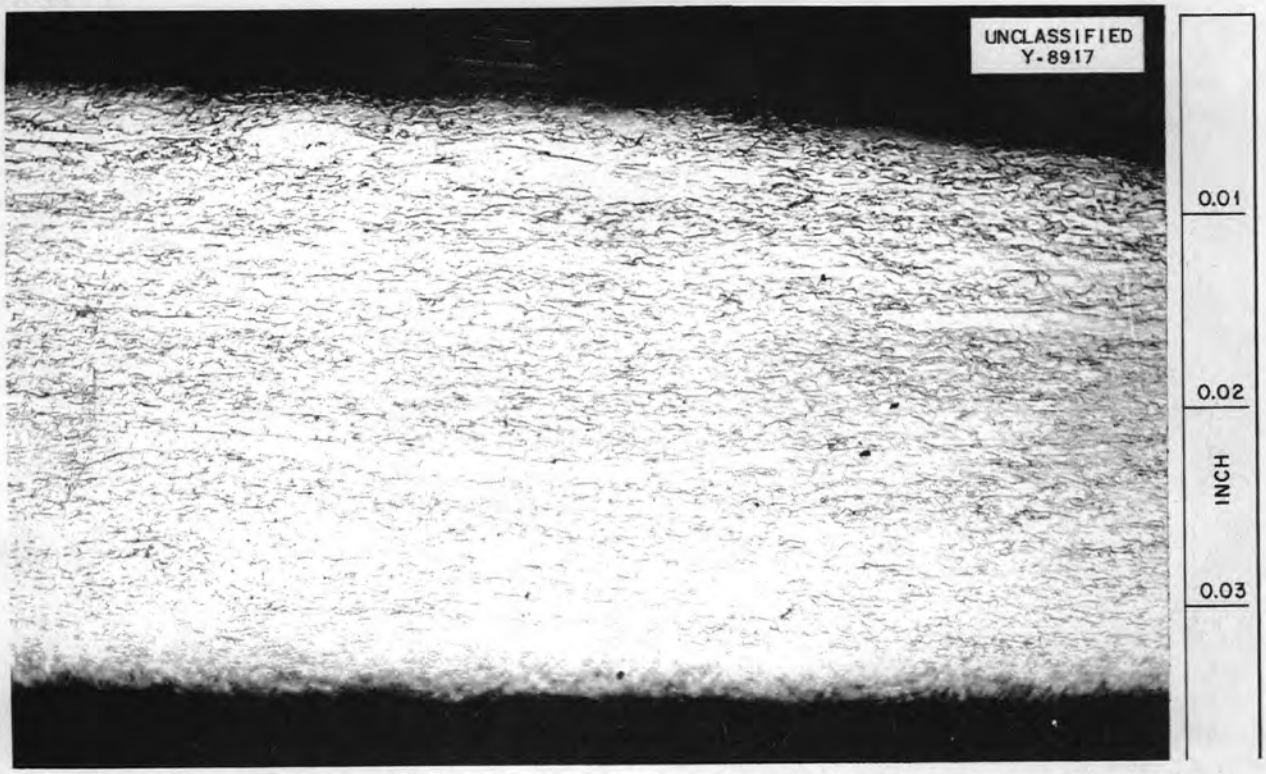

Fig. 17. Columbium Sheet Exposed for 2 hr in Dry Air at 1000°C. 100X

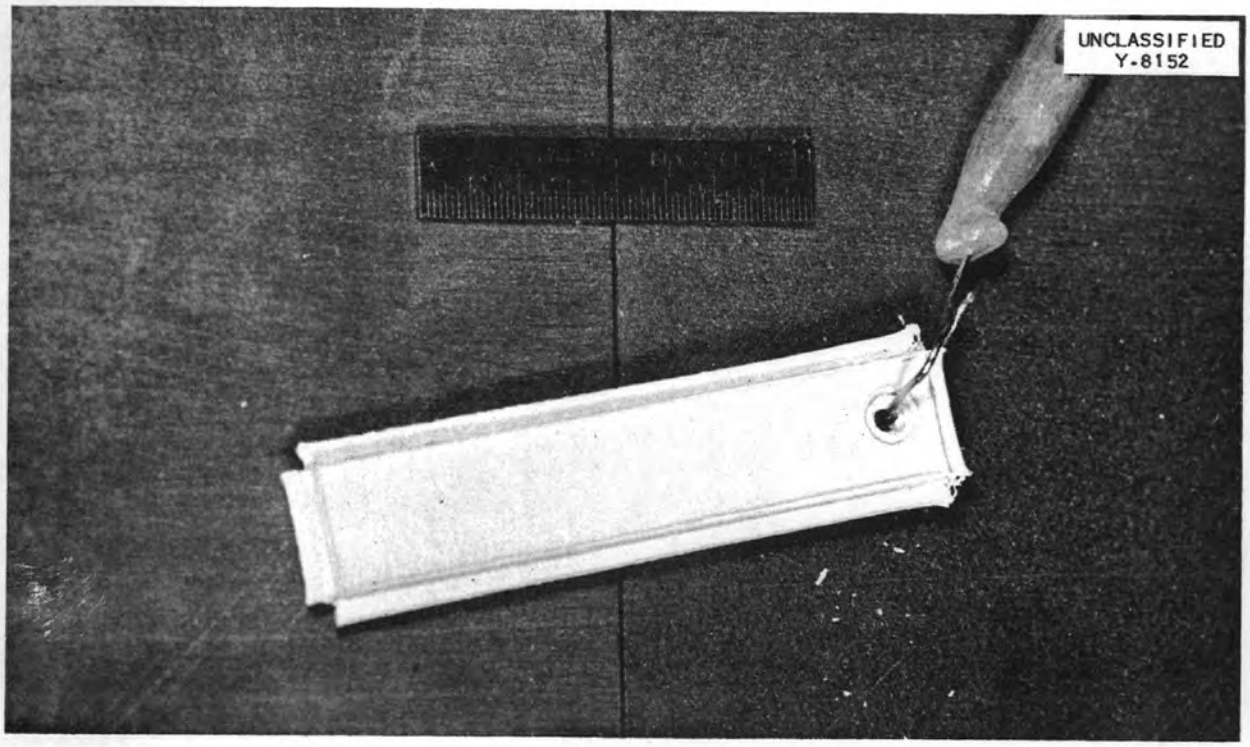

Fig. 19. Columbium Sheet Exposed for 1 1/2 hr in Dry Air at 1200°C. About 5 sec after removal from furnace. 2X

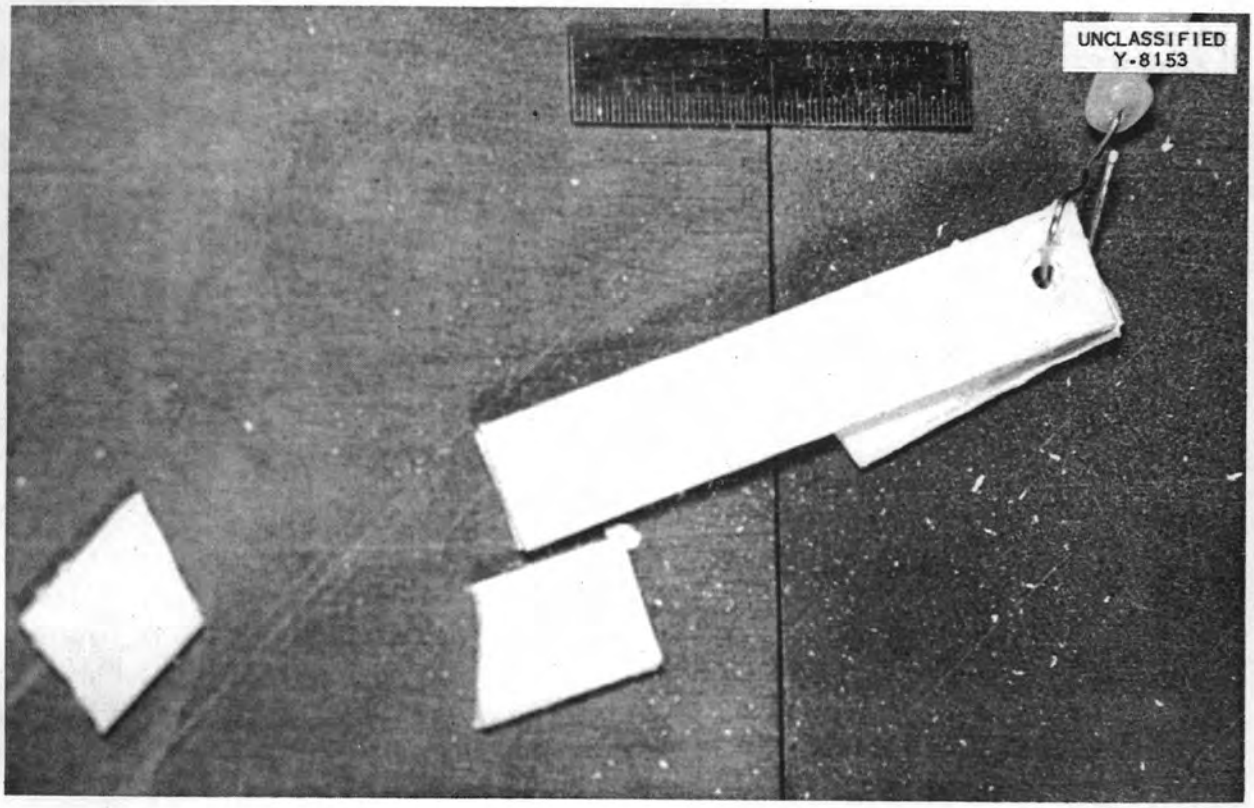

Fig. 20. Columbium Sheet Exposed for 1 1/2 hr in Dry Air at 1200°C. About 60 sec after removal from furnace. 2X

data at 700°C were determined on a sheet specimen and those at 900°C on a constant-area rod described previously.

X-ray diffraction patterns show that the oxide formed at 700°C is "T" Cb_2O_5 and that formed at 900°C is a mixture of the "H" and "M" modifications.

The data at all temperatures investigated are summarized in Fig. 21. From the slopes of the lines, a rate constant was calculated and an Arrhenius plot was made. A straight-line relationship was obtained with an inflection in the curve occurring at 900°C (see Fig. 22). It is of interest to note that the temperature at which "T" Cb_2O_5 disappears corresponds to the break in the curve in the Arrhenius plot. The energy of activation for the oxidation process was calculated to be 13,400 cal/mole between 600 and 900°C and 4350 cal/mole between 900 and 1200°C.

The oxidized specimens were also tested for ductility, Fig. 23 shows that brittleness occurs in the samples heated at 800°C and above.

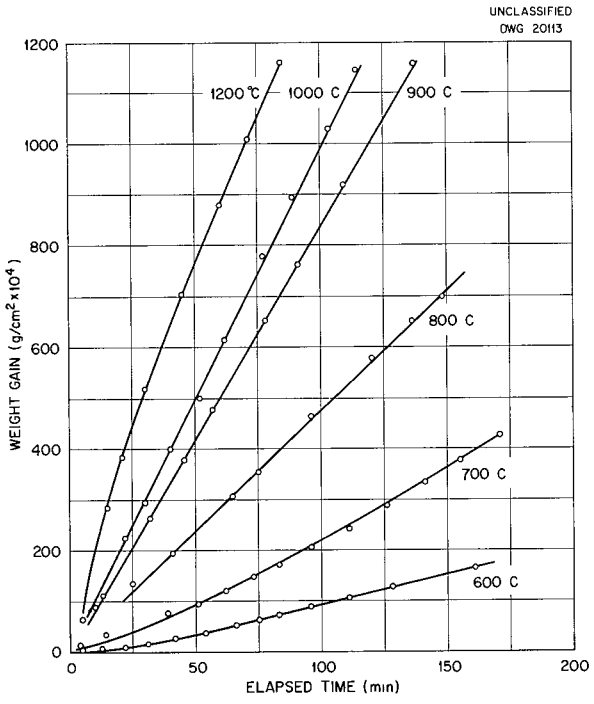

Fig. 21. Air Oxidation of Columbium at Various Temperatures.

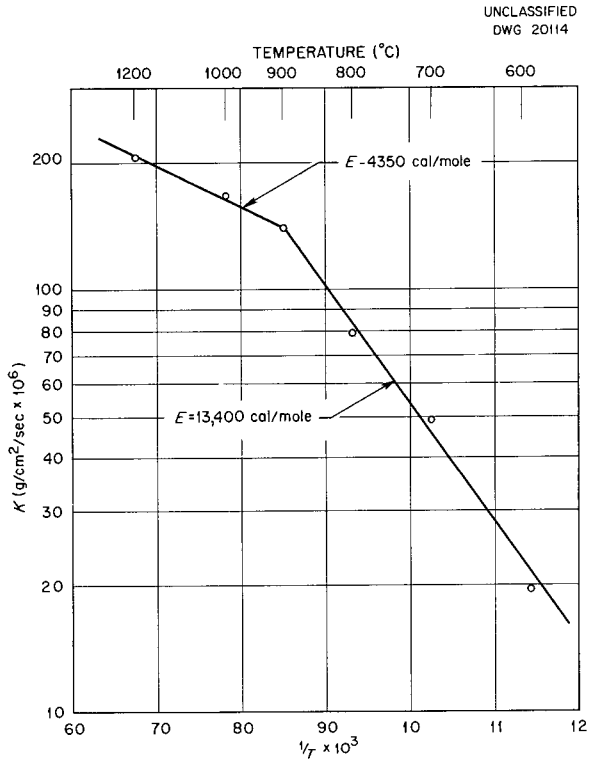

Fig. 22. Dependence of Oxidation Rate on Absolute Temperature.

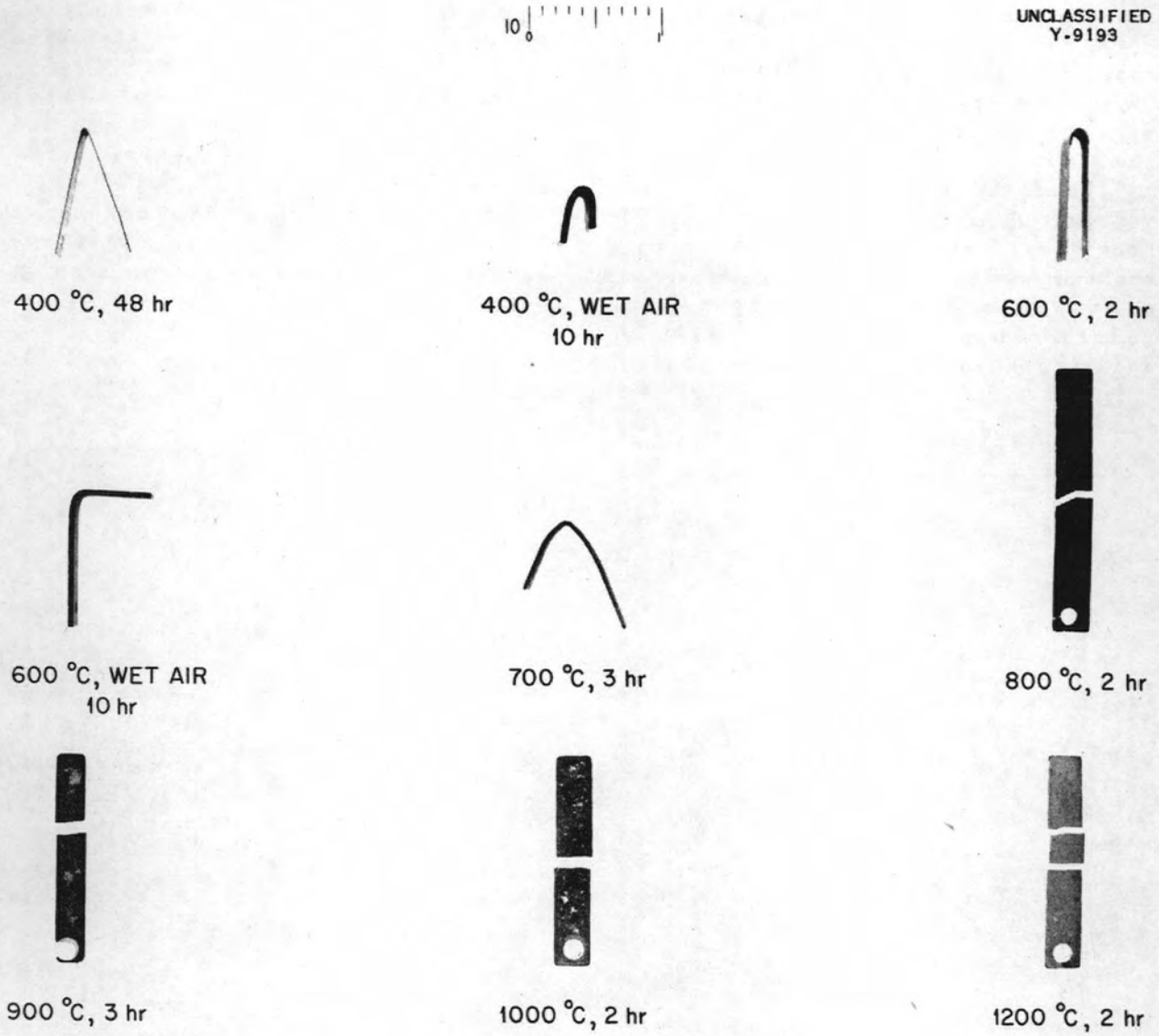

Fig. 23. Ductility of Columbium Exposed to Air at Various Temperatures (Dry Air Except Where Noted.) 3/4X

Appendix

X-RAY DATA OF Cb_2O_5

Radiation Cu K_α

400°C DRY AIR

"T" Cb_2O_5

Intensity	d
60	3.943
50	3.132
15	2.452
15	1 973
25	1.817
70	1.675
40	1.363

400°C WET AIR

"T" Cb_2O_5

Intensity	d
55	3.917
68	3.164
38	3.100
20	2 442
10	1 961
10	1.831

600°C DRY AIR

"T" Cb_2O_5

Intensity	d
55	3.934
82	3.148
28	3.089
20	2 455
12	2.436
10	1.969
14	1.831
8	1.794
12	1.661
5	1 573

600°C WET AIR

"T" Cb_2O_5

Intensity	d
50	3.917
86	3.170
21	3.079
23	2 452
8	2.420
8	1.961
14	1.828
9	1.787
10	1.657
5	1.573

700°C DRY AIR

"T" Cb_2O_5

Intensity	d
66	3.917
90	3.148
30	3.089
24	2.455
14	2.423
12	1.965
15	1.828
10	1 794
13	1.661
10	1.573

800°C DRY AIR, WIRE

"T" Cb_2O_5

Intensity	d
70	3.926
37	3.143
24	3.079
15	2.455
11	2 426
15	1.965
3	1.828
8	1 791
8	1.661
6	1.630

800°C DRY AIR, SHEET

Intensity	d	Modification
83	3.663	"H", "M"
85	3.339	"H"
19	3.175	"T"
13	3.094	"T"
37	2.988	"H"
75	2.694	"H"
28	2.515	"H", "M"
20	2.449	"T"
15	1.916	"H", "M"
65	1.810	"H", "T"
18	1.710	"H"

900°C DRY AIR, SHEET

Intensity	d	Modification
60	3.738	"H"
40	3.633	"H"
45	3.576	"M"
40	3.548	"M"
37	3.493	"H"
10	3.351	"H"
13	2.823	"H"
18	2.543	"H"
7	2.495	"H"
11	2.315	"H"

1000°C DRY AIR, SHEET

"H" Cb_2O_5

Intensity	d
20	5.140
21	4.646
80	3.746
80	3.648
80	3.493
24	3.363
9	3.164
30	2.831
25	2.780
20	2.706

1100°C DRY AIR, SHEET

"H" Cb_2O_5

Intensity	d
12	5.111
16	4.622
80	3.721
80	3.633
80	3.480
18	3.351
5	3.153
35	2.827
20	2.772
25	2.706

1200°C DRY AIR, SHEET

"H" Cb_2O_5

Intensity	d
16	5.111
13	4.599
48	3.723
73	3.633
64	3.480
15	3.345
6	3.153
25	2.822
16	2.767
14	2.698