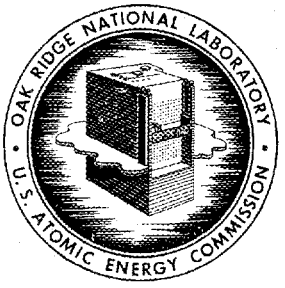

OAK RIDGE NATIONAL LABORATORY
operated by
UNION CARBIDE CORPORATION
for the
U.S. ATOMIC ENERGY COMMISSION

UNION CARBIDE

ORNL-TM-481

INFLUENCE OF CO-CO_2 ENVIRONMENTS OF THE CALIBRATION OF CHROMEL-P-ALUMEL THERMOCOUPLES

H. E. McCoy, Jr.

ORNL-TM-481

Copy

Contract No. W-7405-eng-26

METALS AND CERAMICS DIVISION

INFLUENCE OF CO-CO_2 ENVIRONMENTS OF THE CALIBRATION OF CHROMEL-P–ALUMEL THERMOCOUPLES

H. E. McCoy, Jr.

Date Issued

MAR 28 1963

OAK RIDGE NATIONAL LABORATORY
Oak Ridge, Tennessee
operated by
UNION CARBIDE CORPORATION
for the
U. S. ATOMIC ENERGY COMMISSION

INFLUENCE OF CO-CO_2 ENVIRONMENTS OF THE CALIBRATION OF CHROMEL-P–ALUMEL THERMOCOUPLES

H. E. McCoy, Jr.

ABSTRACT

It is shown that the thermal output of Chromel-P–Alumel thermocouples decreases as a result of exposure to CO-CO_2 mixtures at elevated temperatures. These calibration changes are significantly greater than those observed for these thermocouple materials in air. In CO_2-rich mixtures the negative drift is felt to be due primarily to the loss of chromium from solution in the Chromel-P wire as a result of oxidation. In CO-rich mixtures carburization in addition to oxidation removes chromium from solution thus causing the thermal electromotive force of the thermocouple to decrease.

INFLUENCE OF CO-CO_2 ENVIRONMENTS OF THE CALIBRATION OF CHROMEL-P–ALUMEL THERMOCOUPLES

H. E. McCoy, Jr.

INTRODUCTION

Probably no single problem has hindered the work of the metallurgist as has his inability to measure temperatures accurately. Although several basic systems are used for making temperature measurements over the range of 200 to 1300°C, measurements are made principally with thermocouples. For a dissimilar metal element to comprise a good thermocouple, it must (a) have a thermal electromotive force large enough to measure with reasonable accuracy, (b) have a thermal electromotive force which increases continuously with increasing temperature, (c) be available in lots having reproducible properties and at a reasonable cost, and (d) have a calibration which is not altered appreciably by use at desired service temperatures and atmospheric conditions. Several dissimilar metal combinations have been found which satisfy the first three requirements, but the requirement of calibration stability imposes severe restrictions upon the service conditions under which these thermocouples can be used. The demands for materials technology at elevated temperatures and in a variety of environments have shown that calibration instabilities in thermocouples pose a serious problem in making temperature measurements. These changes in calibration are usually brought about by changes in the chemistry of the thermocouple which occur as a result of chemical reactions between the metals composing the thermocouple and the service environment.

One of the most widely used thermocouples over the temperature range of 500 to 1000°C is the Chromel-P–Alumel couple consisting of a Chromel-P wire (90% Ni–10% Cr) and an Alumel wire (95% Ni–2% Al–2% Mn–1% Si). The materials for this couple are produced by the Hoskins Manufacturing Company. As operating experience has been obtained with this thermocouple, it has been found that certain environmental conditions lead to significant

changes in the thermocouple calibration. McElroy[1] and Potts[2] have defined several such deleterious environments and have evaluated the resultant changes in calibration.

It is the purpose of this memorandum to report observations made of the behavior of Chromel-P–Alumel thermocouples in carbon monoxide and carbon dioxide environments. These tests were run to determine satisfactory techniques for measuring temperatures in these environments rather than as a basic thermocouple study. All thermocouples were prepared by normal techniques with the hot junction being prepared by fusing the two wires with a Heliarc torch.

RESULTS

Carbon Monoxide Environment

A test was run in which the drift rate of a 20-gage (0.032-in. diam) Chromel-P–Alumel thermocouple in a carbon monoxide environment was measured. A stainless steel thermocouple well was sealed inside a refractory tube through which carbon monoxide was passed. A standard thermocouple was attached to the outside of the thermocouple well so that it was exposed to the carbon monoxide environment. The furnace temperature was controlled on the basis of the thermal output of the exposed thermocouple. The results of this test are shown in Fig. 1. The thermal output of the thermocouple exposed to carbon monoxide decreased such that after 650 hr the furnace temperature was actually at 1000°C in order to supply the controller with a 34.1-mv signal.

The exposed thermocouple was analyzed for carbon after the test and both wires contained greater than 5 wt % C near the hot junction. The as-received carbon analyses of the Chromel-P and Alumel wires were 0.024 and 0.033 wt %, respectively.

Small pieces of the thermocouple wires near the hot junction were examined metallographically. Representative photomicrographs of the as-received wires are shown in Fig. 2 and those of the test wires are shown

---

[1]D. L. McElroy, Progress Report I, Thermocouple Research Report for the Period Nov. 1, 1956 to Oct. 31, 1957, ORNL-2467 (March 5, 1958).

[2]J. F. Potts, Jr., and D. L. McElroy, Thermocouple Research to 1000°C – Final Report, Nov. 1, 1957 through June 30, 1959, ORNL-2773 (Jan. 16, 1961).

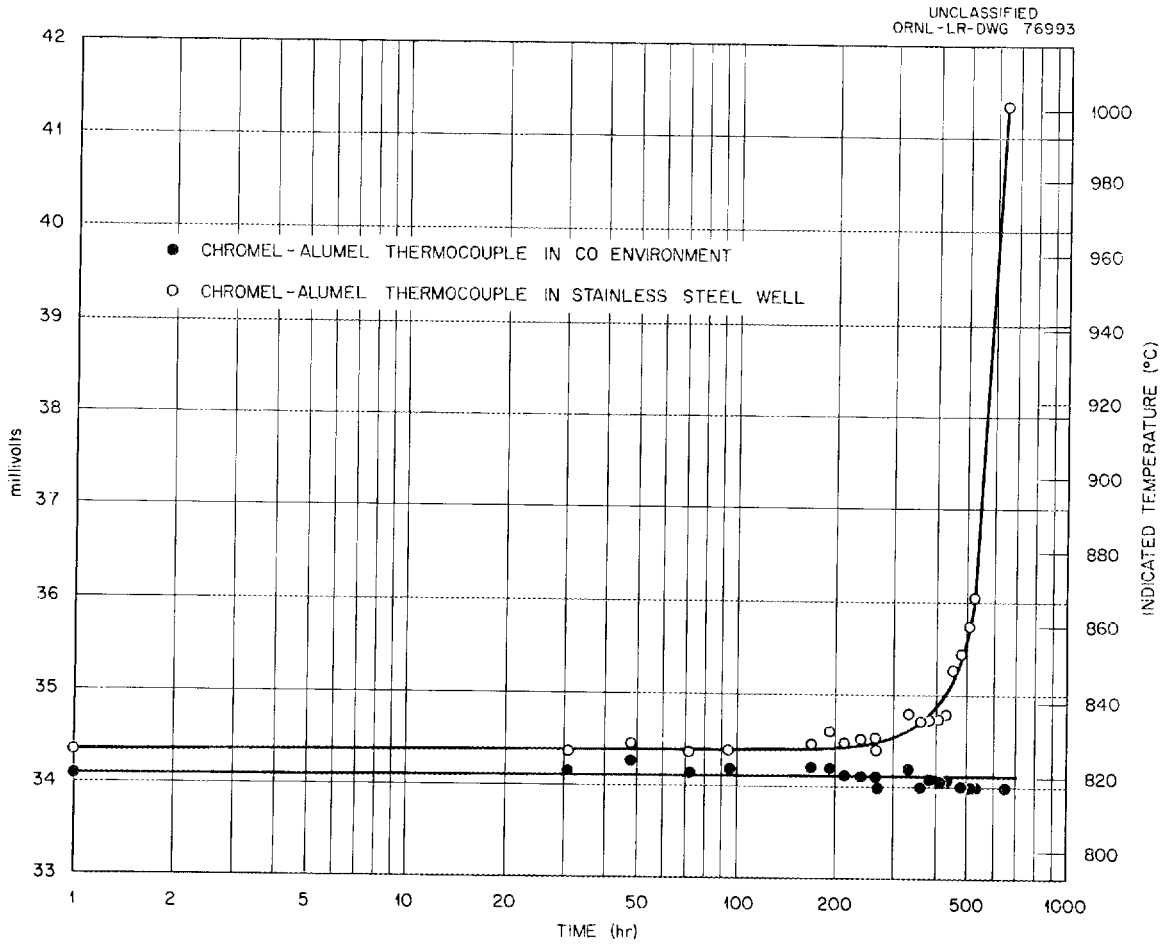

Fig. 1. Effect of a Carbon Monoxide Environment on the Calibration of Chromel-P–Alumel Thermocouples.

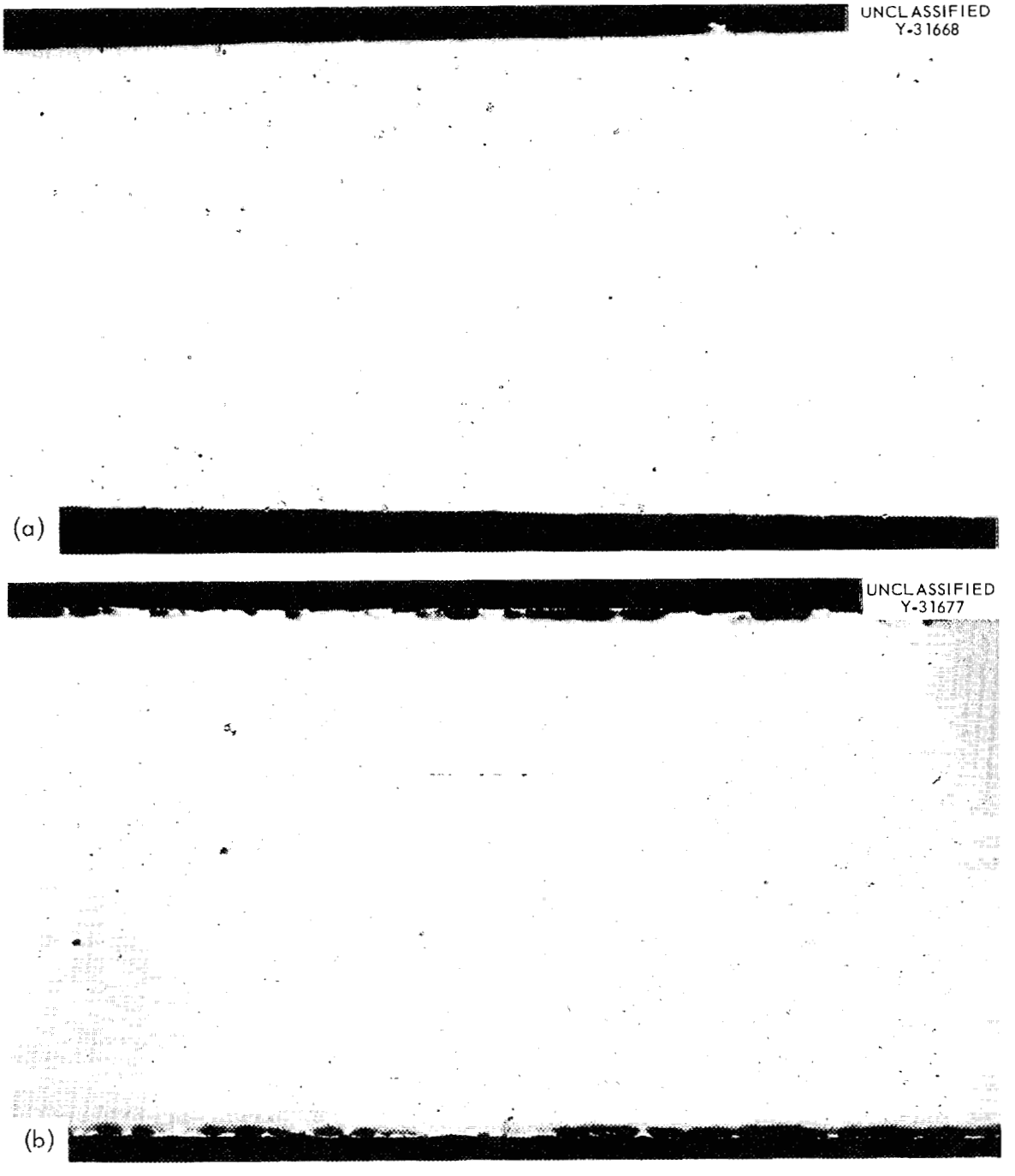

Fig. 2. Photomicrographs of As-Received (a) Chromel-P and (b) Alumel Thermocouple Wire in the As-Polished Condition. 100X.

in Figs. 3 and 4. The Alumel wire was internally oxidized throughout the entire cross section. The Chromel wire was heavily oxidized and a grain-boundary precipitate, probably a chromium carbide, was formed.

95% CO_2–5 vol % CO Environment

Three 24-gage (0.020-in. diam) Chromel-P–Alumel thermocouples were tested at approximately 650, 750, and 850°C in flowing 95 vol % CO_2–5 vol % CO. The hot junction of each of these thermocouples was mechanically fastened to the hot junction of a calibrated 24-gage (0.020-in. diam) Pt vs Pt–10% Rh thermocouple. The thermocouples were inserted different distances into a furnace to obtain the different hot-junction temperatures. All of the thermocouples were contained in a 2-in. diam refractory tube through which the gas mixture flowed. The furnace temperature was controlled by a thermocouple placed near the furnace windings. Comparative thermal electromotive force readings were made of the test Chromel-P–Alumel and the noble metal thermocouples as a function of time. The results of the tests are shown graphically in Figs. 5, 6, and 7. Much of the scatter obtained in these measurements resulted from the furnace tube being moved and thus causing the hot-junction temperatures to change slightly. The thermocouple at 650°C showed an initial positive calibration shift of about 7°C. The thermal electromotive force output continued to drift positive and reached a value of 10°C after 2500 hr. At 750°C an initial positive calibration shift equivalent to about 16°C was observed. The positive drift continued to a maximum value of 19°C in 80 hr. The thermocouple then began to drift negative and indicated a temperature too low by 50°C after 2500 hr. At 850°C the initial positive shift was not noted, but rather the thermocouple drifted negatively throughout the test. After 2500 hr the indicated temperature was low by about 120°C. At the end of the 2500-hr test, all thermocouples were extremely brittle.

Samples were cut from the thermocouples for carbon analyses. The samples were physically located over the distance from 1 to 2 in. from the hot junction. The carbon analyses of these specimens are given in Table 1. Since the samples were small and were severely oxidized, it is felt that the small apparent changes in carbon content are not significant.

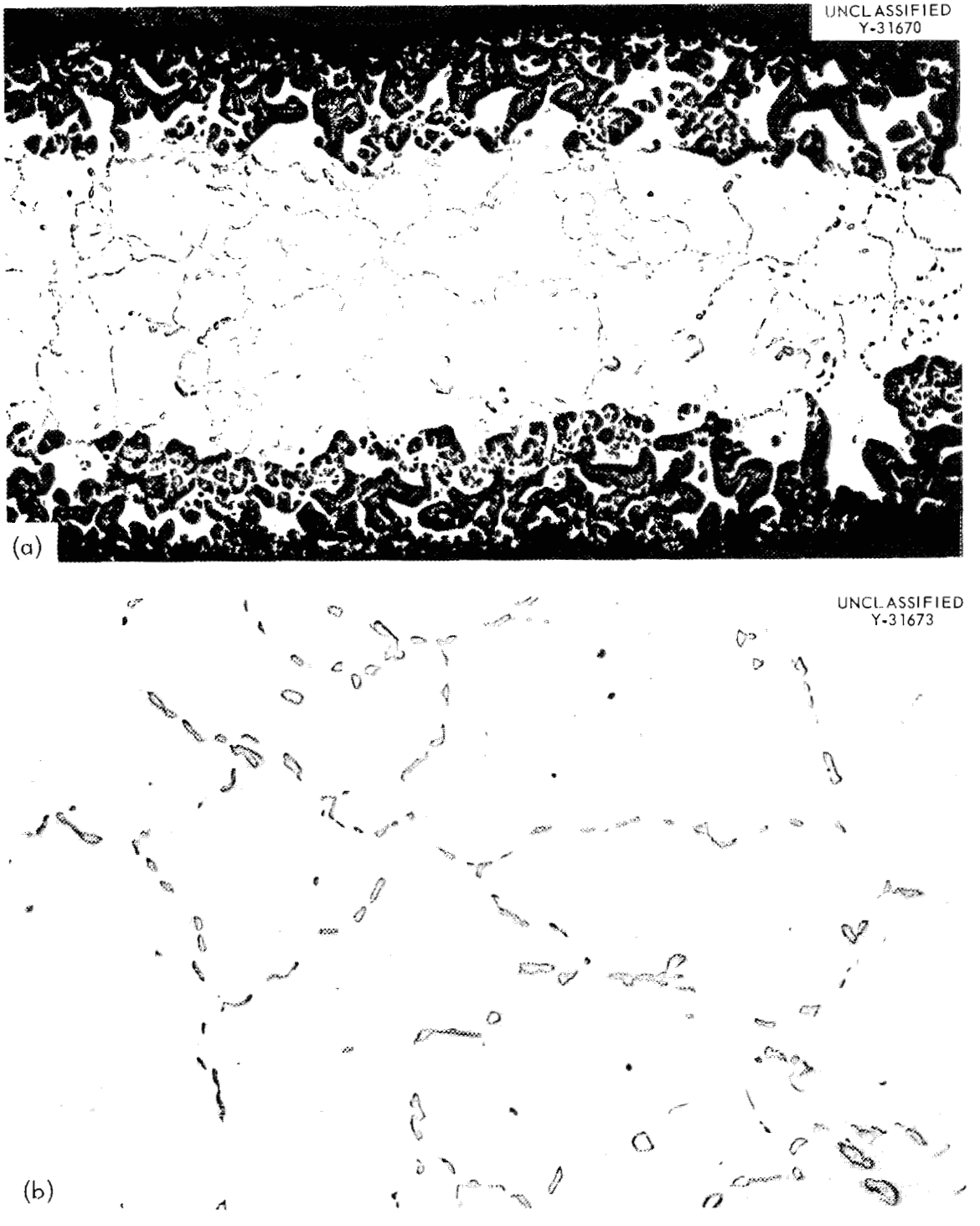

Fig. 3. Photomicrographs of Chromel-P Thermocouple Wire Tested in CO. Photographed in the as-polished condition. (a) 100X, (b) 500X.

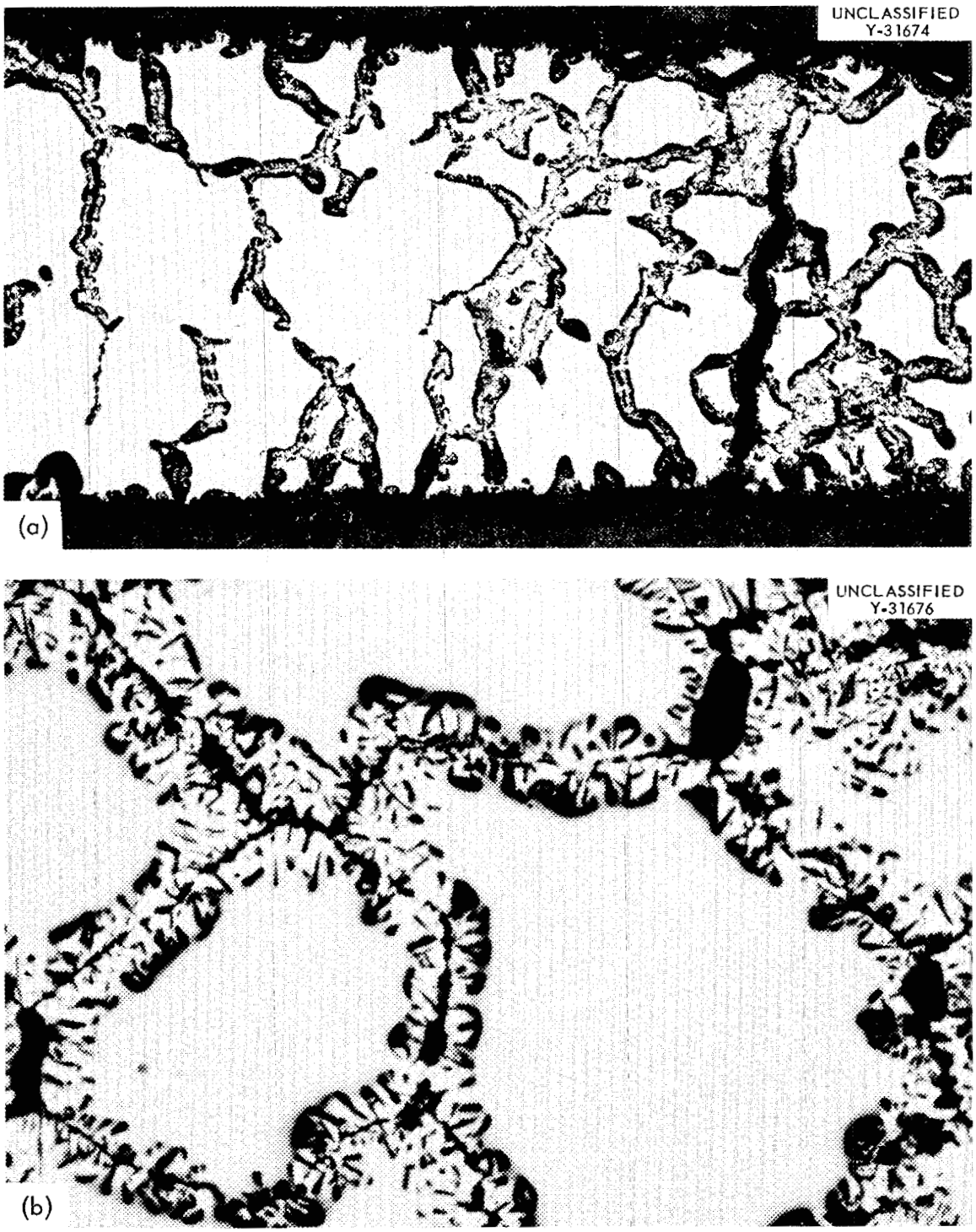

Fig. 4. Photomicrographs of Alumel Thermocouple Wire Tested in CO. Photographed in the as-polished condition. (a) 100X, (b) 500X.

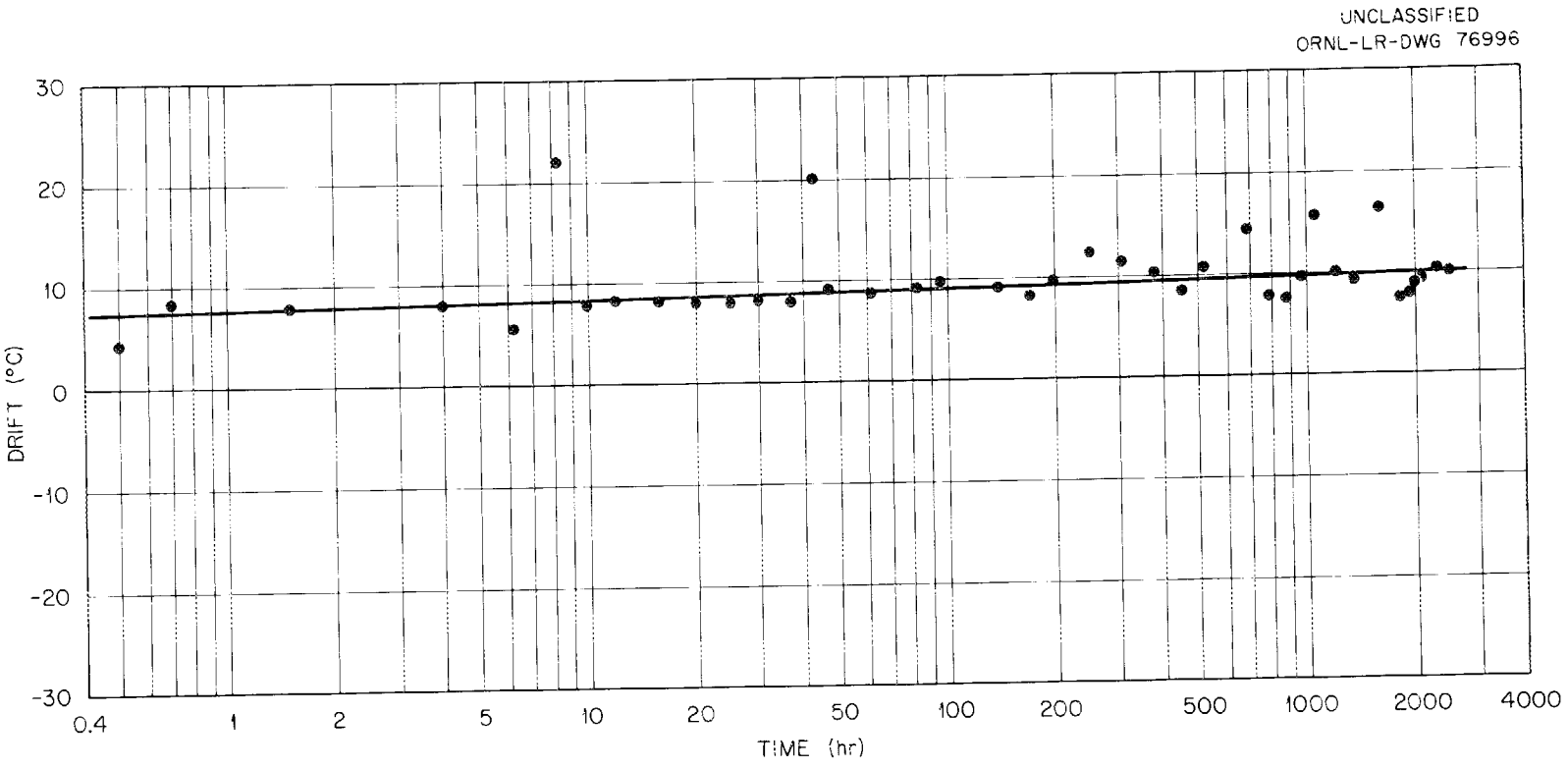

Fig. 5. Behavior of Chromel-P–Alumel Thermocouples in CO_2–5 vol % CO at 650°C.

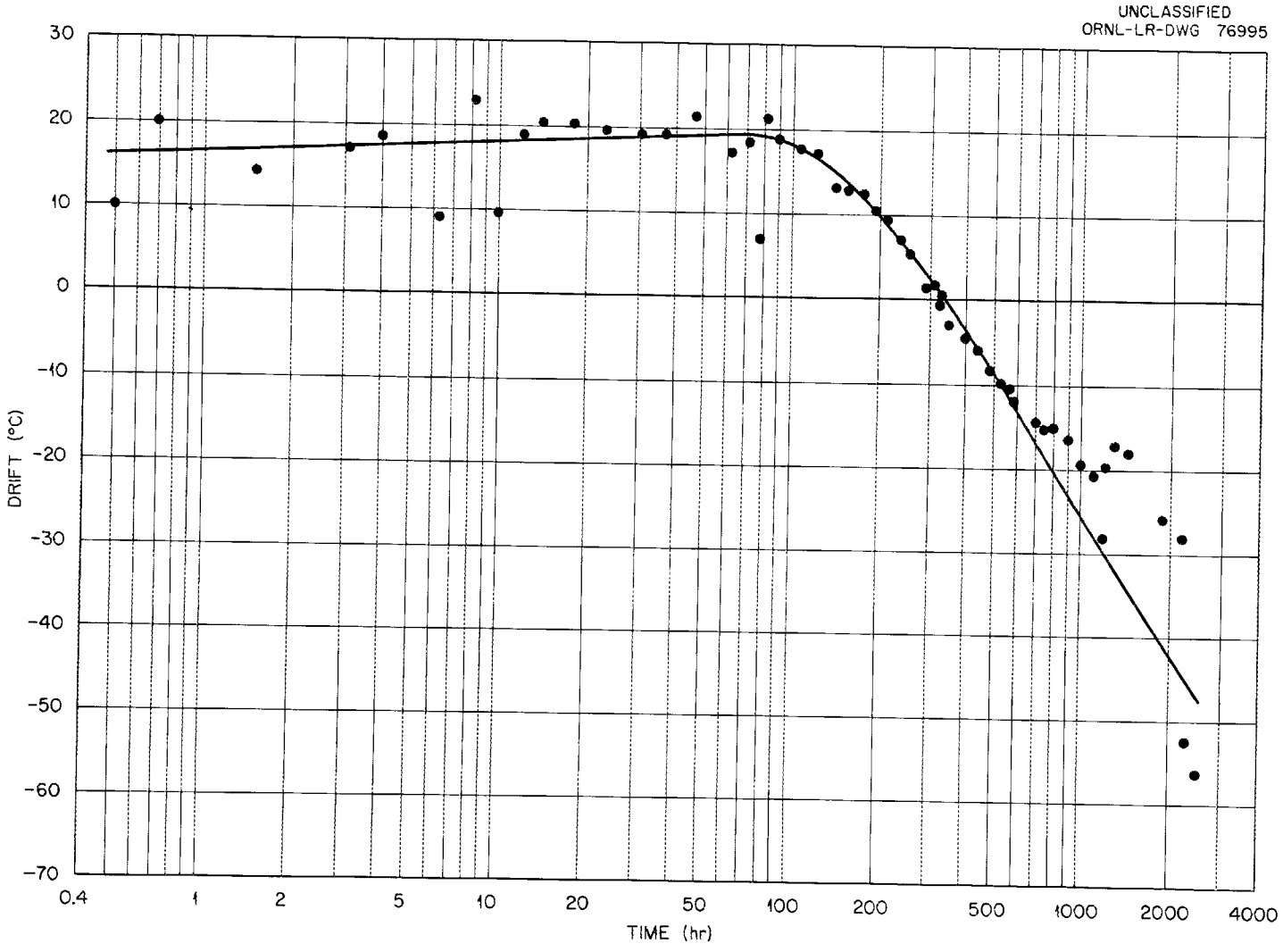

Fig. 6. Behavior of Chromel-P–Alumel Thermocouples in CO_2–5 vol % CO at 750°C.

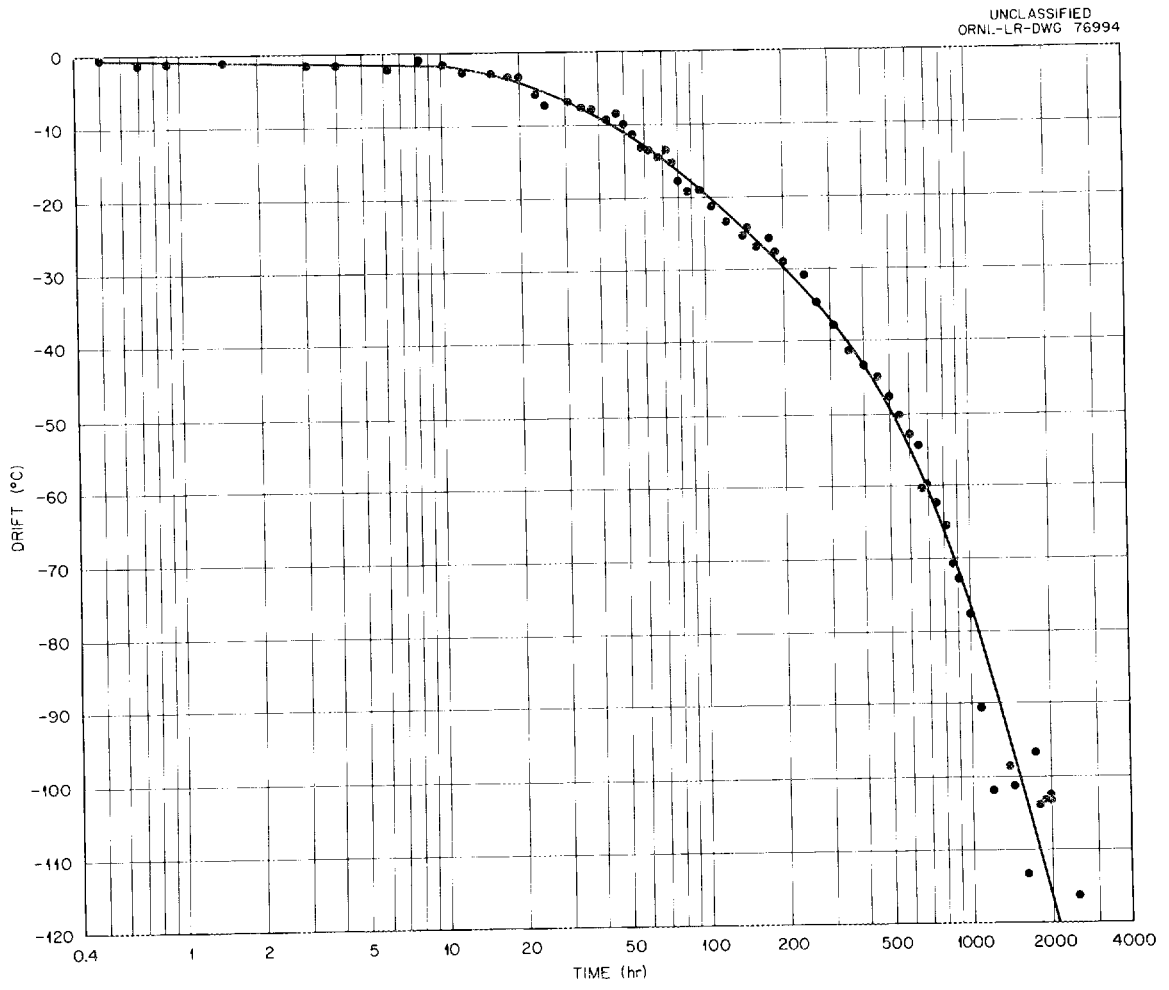

Fig. 7. Behavior of Chromel-P–Alumel Thermocouples in CO_2–5 vol % CO at 850°C

Table 1. Carbon Analyses of Chromel-P and Alumel Thermocouple Wires Exposed to 95 CO_2–5 CO Mixture for 2500 hr

Temperature of Exposure	Wire Designation	Carbon Content (wt %)
As-received	Chromel-P	0.022
As-received	Alumel	0.015
650°C	Chromel-P	0.009
650°C	Alumel	0.017
750°C	Chromel-P	0.017
750°C	Alumel	0.012
850°C	Chromel-P	0.009
850°C	Alumel	0.016

Metallographic samples were taken from the thermocouples which included the hot junction and about 1 in. of each wire. Representative photomicrographs are shown in Figs. 8 through 13. At 650°C both wires were oxidized appreciably. The Alumel wire was uniformly oxidized internally to a depth of about 3.5 mils (Fig. 9). The Chromel-P wire in general looked quite good except for oxidation in isolated areas such as that shown in Fig. 8. The depth of this attack extended to 5 mils. At 750°C the Chromel-P wire was internally oxidized throughout (Fig. 10). The Alumel wire was uniformly oxidized to a depth of 1.5 mils (Fig. 11). At 850°C both the Chromel-P and the Alumel wires were internally oxidized throughout (Figs. 12 and 13).

CO_2 Environment

Three 20-gage (0.032-in. diam) Chromel-P–Alumel thermocouples were run 1000 hr in a carbon dioxide environment. The thermocouples were attached to small stainless steel tabs which were the intended test pieces. Although electromotive force readings were not made as a function of time, the electromotive force output of each thermocouple was checked at the initiation and at the end of the 1000-hr exposure. The thermocouples were brittle after test. Small specimens were cut near the hot junction for carbon analyses. The available data on these thermocouples are given in Table 2.

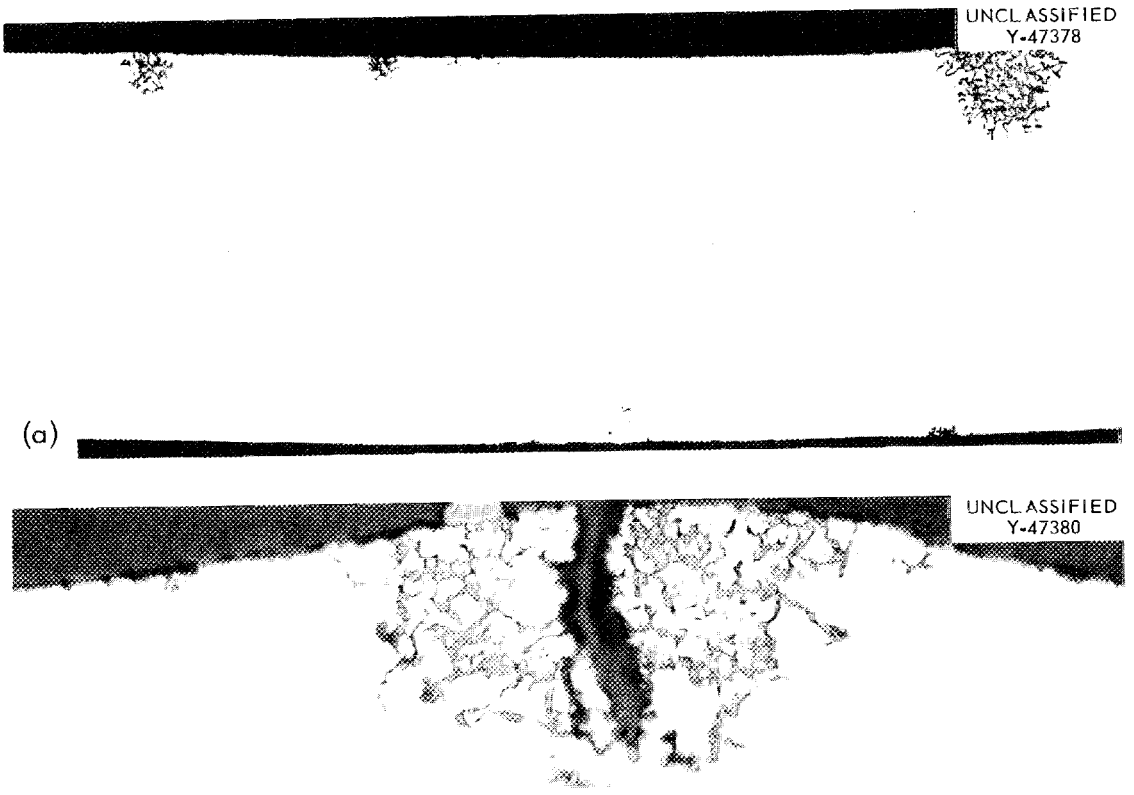

Fig. 8. Chromel-P Thermocouple Wire Exposed to Flowing CO_2–5 vol % CO at 650°C for 2500 hr. As-polished. (a) 100X, (b) 500X.

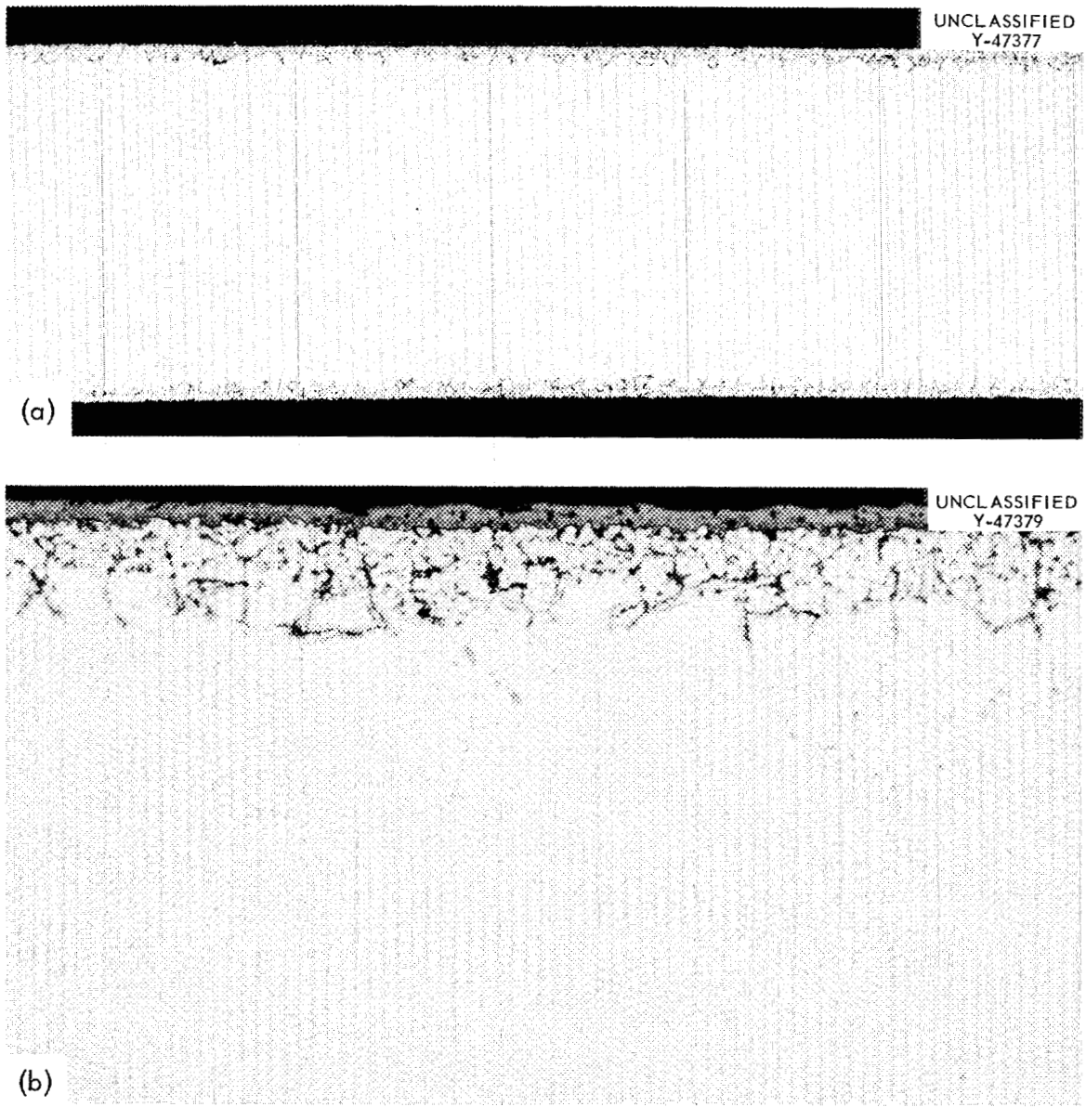

Fig. 9. Alumel Thermocouple Wire Exposed to Flowing CO_2–5 vol % CO at 650°C for 2500 hr. As-polished. (a) 100X, (b) 500X.

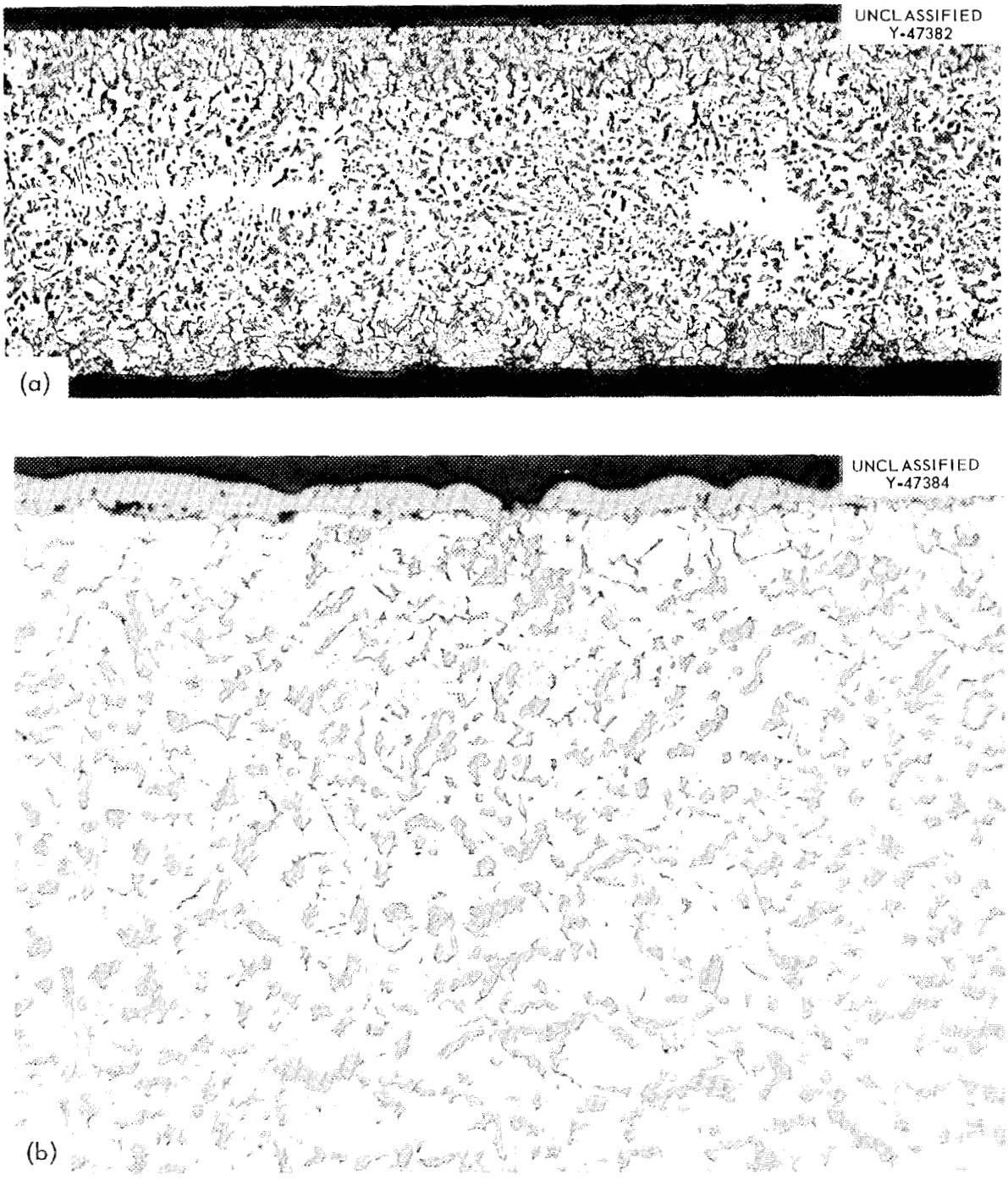

Fig. 10. Chromel-P Thermocouple Wire Exposed to Flowing CO_2–5 vol % CO at 750°C for 2500 hr. As-polished. (a) 100X, (b) 500X.

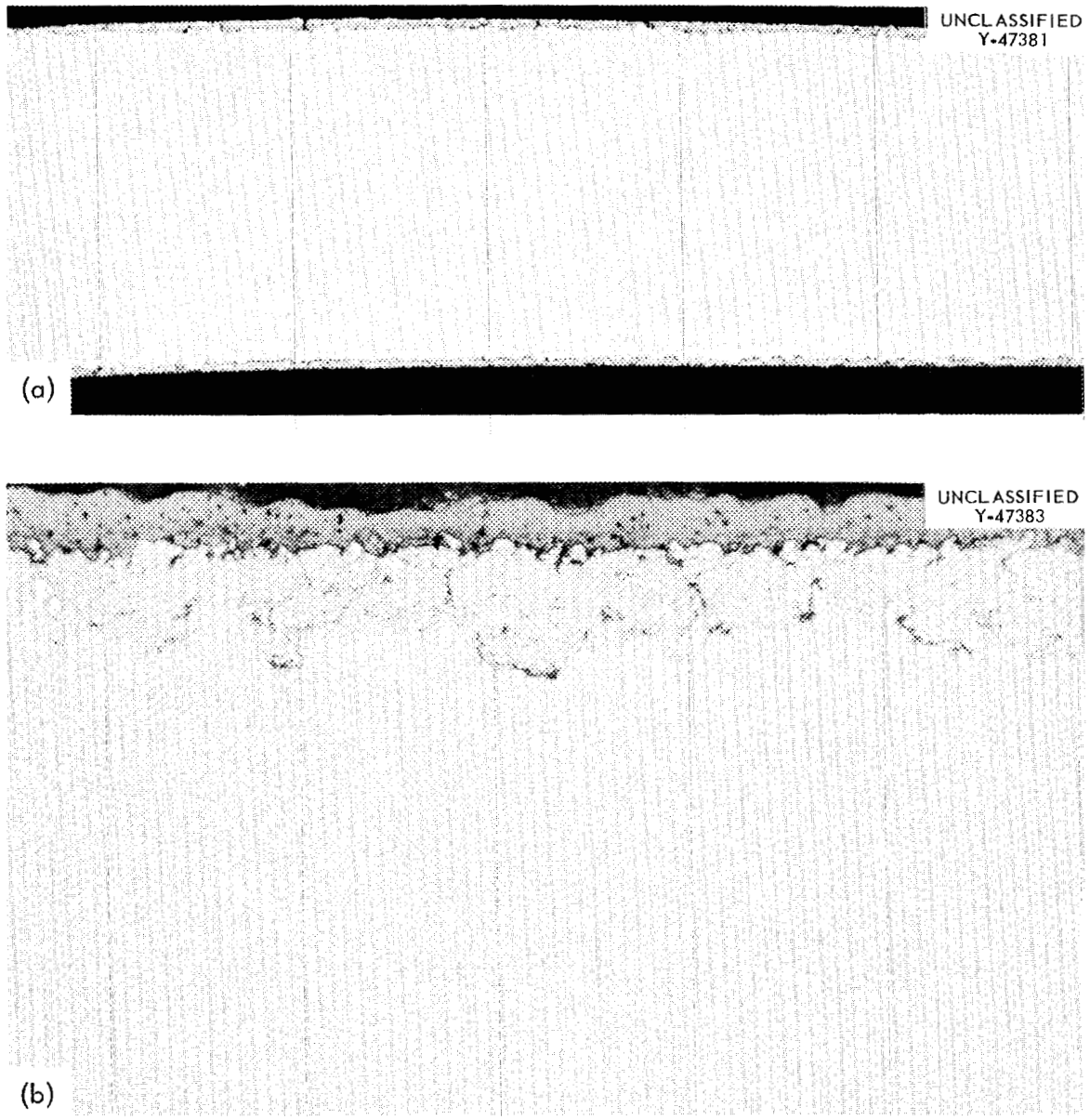

Fig. 11. Alumel Thermocouple Wire Exposed to Flowing CO_2–5 vol % CO at 750°C for 2500 hr. As-polished. (a) 100X, (b) 500X.

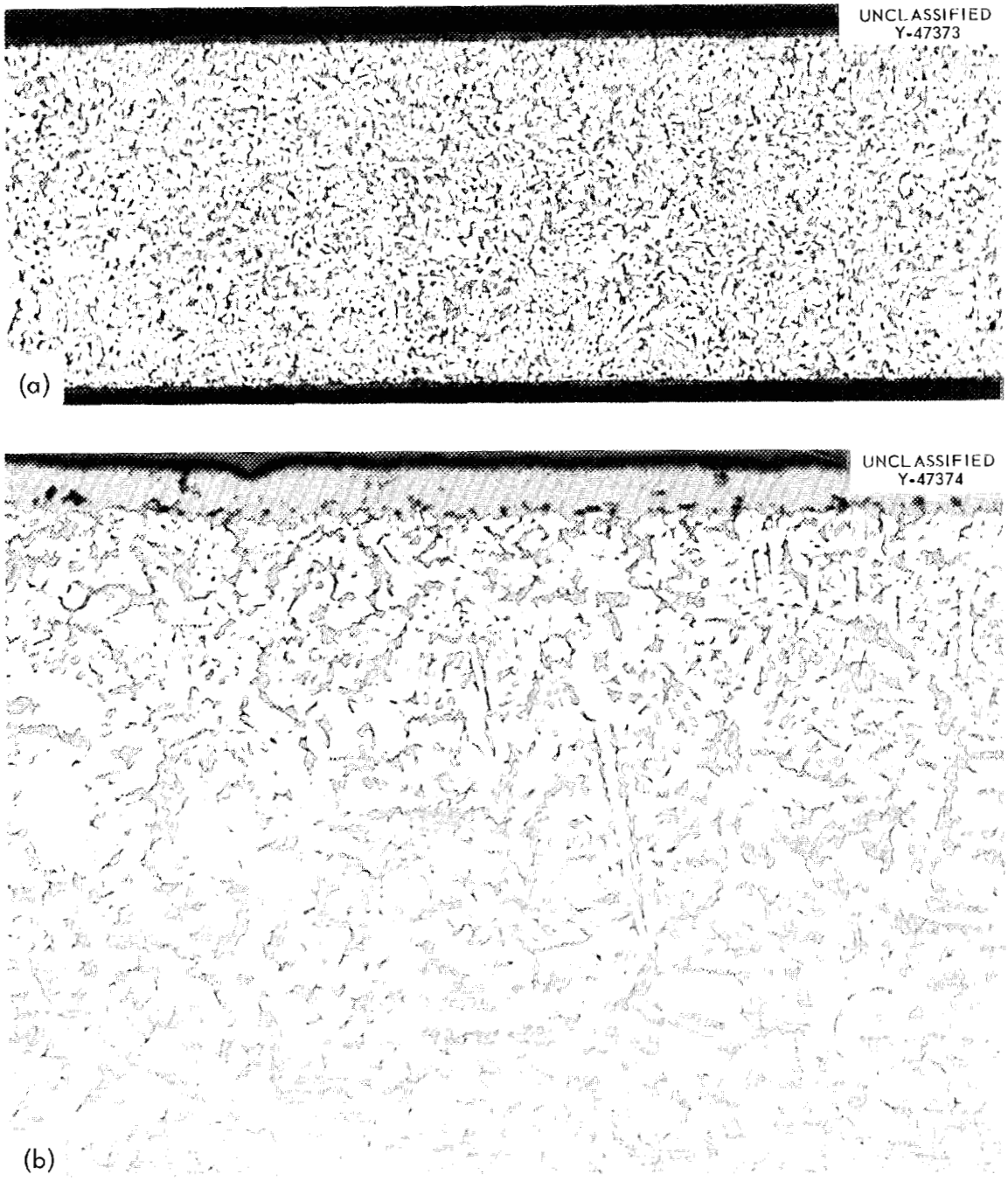

Fig. 12. Chromel-P Thermocouple Wire Exposed to Flowing CO_2–5 vol % CO at 850°C for 2500 hr. As-polished. (a) 100X, (b) 500X.

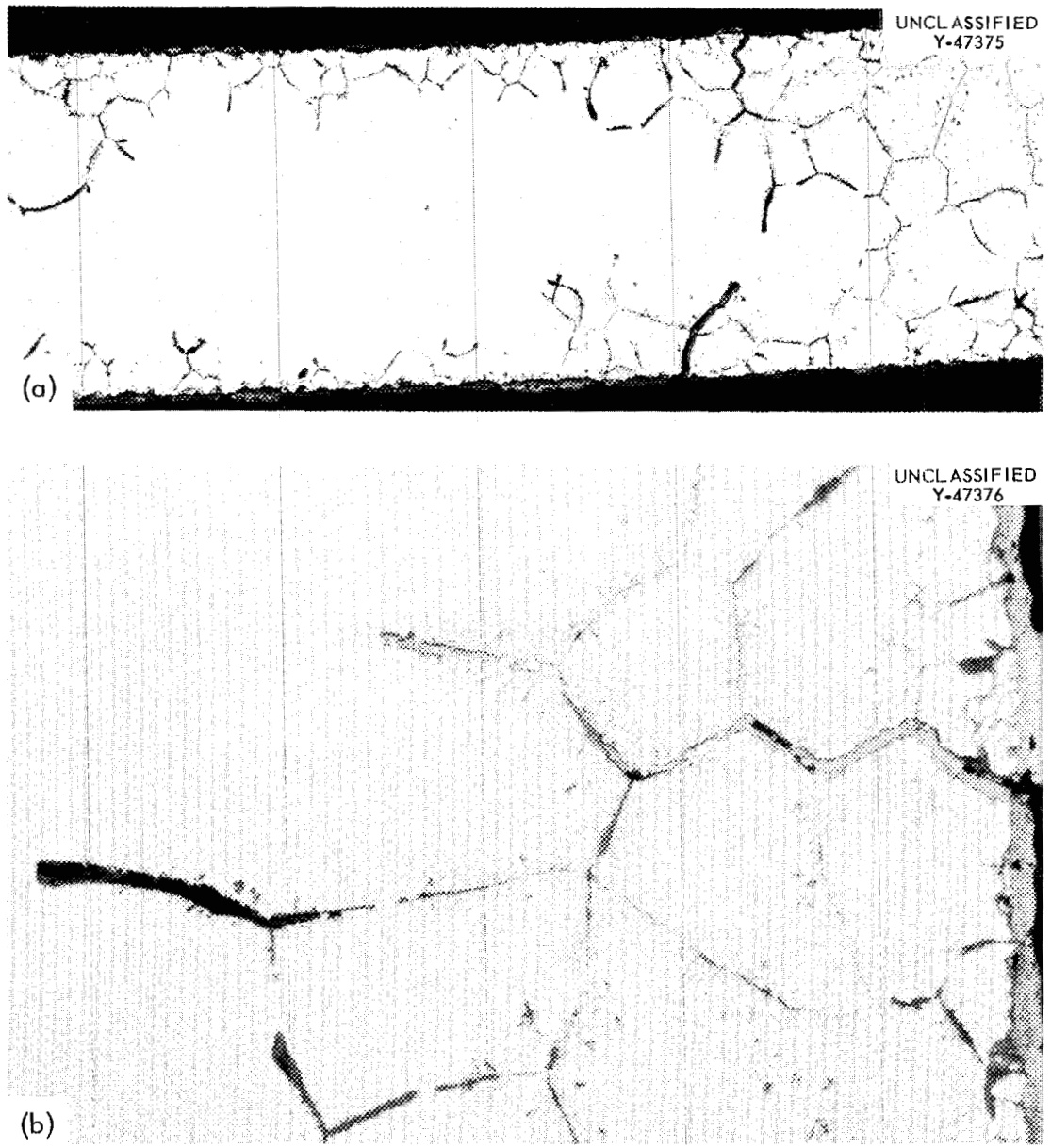

Fig. 13. Alumel Thermocouple Wire Exposed to Flowing CO_2–5 vol % CO at 850°C for 2500 hr. As-polished. (a) 100X, (b) 500X.

Table 2. Data on Chromel-P–Alumel Thermocouples Exposed to Flowing CO_2 for 1000 hr

Original Temperature	Indicated Temperature after 1000 hr	Wire Designation	Carbon Content (wt %)
As-received		Chromel-P	0.006
As-received		Alumel	0.008
704°C	698°C	Chromel-P	0.013
704°C	698°C	Alumel	0.014
815°C	723°C	Chromel-P	0.020
815°C	723°C	Alumel	0.018
927°C	804°C	Chromel-P	0.003
927°C	804°C	Alumel	0.011

In a test similar to the above it was found that in 257 hr the output of three thermocouples drifted such that the indicated temperatures changed from 833 to 753°C, from 722 to 714°C, and from 620 to 611°C. No further examination of these thermocouples was made.

DISCUSSION OF RESULTS

Appreciable negative drifts have been observed for Chromel-P–Alumel thermocouples in various CO-CO_2 environments. These drifts are considerably larger than those observed by Potts and McElroy[2] for Chromel-P–Alumel thermocouples in air. It is felt that the behavior of these thermocouples in CO-CO_2 environments can be explained in terms of chemical reactions which tend to carburize and oxidize the components of the thermocouple. As discussed by McElroy[1] the thermal electromotive force of a Chromel-P–Alumel thermocouple goes through a maximum with respect to chromium content. Since the composition of Chromel-P has been chosen to give the maximum thermal electromotive force, any change in the chromium in solution in the alloy decreases the thermocouple output. Carburization and oxidation would both remove chromium from solid solution and cause the thermocouple to drift negative. Pure carbon monoxide will not oxidize nickel at elevated temperatures but would readily oxidize the alloying elements present in Chromel-P and Alumel such as chromium, aluminum,

manganese, and silicon.[3] Carbon dioxide would be oxidizing to all elements present.[3] The oxidization studies by Potts and McElroy[2] showed that the Alumel wire was oxidized the most heavily in air. The photomicrographs in Figs. 3, 4, and 8–13 show that this is also the trend in CO-CO_2 environments although not to the extent observed in air. Due to the strong tendency of chromium to form a carbide, carburization is primarily a problem with the Chromel-P wire. If the carbide formed is assumed to be of the Cr_4C type, 0.1 wt % C can react with about 1.74 wt % Cr. Hence, the chromium concentration in solution would be reduced and the thermocouple would drift negative. Chemical analyses have indicated a substantial increase in the carbon content of the thermocouples exposed to pure carbon monoxide but indicated no increase in carbon content as a result of exposure to carbon dioxide and the CO_2–5 vol % CO mixture. At least two possible explanations can be given for the initial positive drifts observed in the thermocouples in the CO_2–5 vol % CO environment. One possibility is that the chromium content of the Chromel-P lay somewhat above the composition which gives the maximum thermal electromotive force. As the thermocouple was held at temperature, some of the chromium was consumed to form chromium carbide with a resulting increase in the thermal electromotive force. Another possible explanation is that the effects of cold working were being removed by annealing. The latter process has been shown to lead to positive drifts in calibration.[2]

Although it is known that the loss of soluble chromium decreases the output of these thermocouples, it is quite possible that the loss of other alloying elements may significantly alter the calibration of Chromel-P–Alumel thermocouples. However, data are not available which allow an estimate of the magnitudes of such changes.

CONCLUSIONS

It has been shown that the thermal output of Chromel-P–Alumel thermocouples decreases as a result of exposure to CO-CO_2 mixtures at elevated temperatures. These calibration changes are significantly greater than

---

[3]L. S. Darken and R. W. Gurry, Physical Chemistry of Metals, p 349, McGraw-Hill, New York, 1953.

those observed for these thermocouple materials in air. In CO_2-rich mixtures the negative drift is felt to be due primarily to the loss of chromium from solution in the Chromel-P wire as a result of oxidation. In CO-rich mixtures carburization in addition to oxidation removes chromium from solution thus causing the thermal electromotive force of the thermocouple to decrease.

ACKNOWLEDGMENT

The assistance of E. D. Bolling and M. D. Allen who prepared the metallography and B. McNabb and K. W. Boling who made the experimental measurements is gratefully acknowledged.

DISTRIBUTION

1–2. Central Research Library
3. ORNL – Y-12 Technical Library Document Reference Section
4–8. Laboratory Records
9. Laboratory Records, ORNL RC
10. ORNL Patent Office
11. G. M. Adamson, Jr.
12. J. E. Cunningham
13. J. H. DeVan
14. D. A. Douglas, Jr.
15. J. H Frye, Jr.
16–18. M. R. Hill
19. H. Inouye
20. H. G. MacPherson
21. W. D. Manly
22. W. R. Martin
23–32. H. E. McCoy, Jr.
33. D. L. McElroy
34. C. A. Mossman
35. P. Patriarca
36. J. F. Potts
37. W. T. Rainey
38. W. C. Thurber
39. J. T. Venard
40. J. R. Weir, Jr.
41. M. S. Wechsler
42. J. W. Woods
43–57. Division of Technical Information Extension (DTIE)
58. Research and Development Division (ORO)
59–60. Reactor Division (ORO)