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STABILITY OF BASE-METAL THERMOCOUPLES IN AIR FROM 800° TO 2,200° F

By Andrew I. Dahl

ABSTRACT

A study has been made of the changes in the emf of Chromel-Alumel and iron-constantan thermocouples heated in an oxidizing atmosphere at various temperatures and for various periods of time. The thermocouples were held at definite temperatures, ranging from 800° to 2,200° F, in steps of 200° F. Calibrations were made of the thermocouples in their original condition, and again after heating them at each temperature for total times of 10, 50, 100, 200, 400, 600, 800, and 1,000 hours, or as long as the thermocouples remained serviceable. The thermal emf of each element against platinum was measured in order to determine the relative stability of the individual elements. A few tests were made to determine the effect of wire size on the stability. The effects of changing the depth of immersion of thermocouples after they had been used under controlled conditions were also studied.

Since all tests were made in an atmosphere of clean air, the results give no information on stability except under oxidizing conditions.

CONTENTS

I. INTRODUCTION

With the widespread use of base-metal thermocouples for temperature measurement and control in industrial processes, there are numerous instances where high accuracy is of vital importance. Some processes require that a given temperature be maintained within narrow limits for an extended period of time, if efficiency in operation and uniformity in production are to be maintained. In order to meet these requirements, a more complete knowledge of the thermoelectric stability of base-metal thermocouple materials is necessary.

Practically all base-metal thermocouple wire produced in this country is annealed or given a stabilizing heat treatment by the manufacturer. For most purposes this treatment renders the product sufficiently stable, so that further changes which may occur while the thermocouple is in service may be neglected. However, when high accuracy is required throughout the useful life of the thermocouple, these changes must be taken into account. In many industrial processes, thermocouples, when placed in service, are left undisturbed until there is evidence of either mechanical failure or of serious error in the temperatures indicated. However, long before this occurs, the thermocouple may have changed to such an extent as to make it unreliable for accurate temperature measurement. The changes in the thermoelectric characteristics of thermocouple materials due to ordinary service conditions are usually gradual and cumulative. They depend upon such factors as the temperatures encountered, the length of time in service, and the atmosphere surrounding the thermocouple. The various types of thermocouple materials are affected in various ways and to various degrees.

When the reference-junction temperature is maintained constant, the emf developed by a homogeneous thermocouple depends only on the temperature of the measuring junction. The emf developed by an inhomogeneous thermocouple depends not only on the temperature of the measuring junction but also on the temperature distribution throughout the inhomogeneous portions of the wires. All base-metal thermocouples become inhomogeneous with use at high temperatures. However, if all the inhomogeneous portions of the thermocouple wires are in a region of uniform temperature, the inhomogeneous portions have no effect upon the indications of the thermocouple. Therefore, an increase in the depth of immersion of a used couple has the effect of bringing previously unheated portions of the wires into the region of temperature gradient, and thus the indications of the thermocouple will correspond to the original emf-temperature relation, provided the increase in immersion is sufficient to bring all of the previously heated part of the wires within the zone of uniform temperature. If the immersion is decreased, the more inhomogeneous portions of the wires will be brought into the region of temperature gradient, thus giving rise to a change in the indicated emf. Furthermore, a change in the temperature distribution along inhomogeneous portions of the wire nearly always occurs when a couple is removed from one installation and placed in another, even though the measured immersion and the temperature of the measuring junction are the same in both cases. Thus the indicated emf is changed.

Although it is recognized that there are differences in composition and thermoelectric properties between various lots of thermocouple materials of the same general type, it is believed that the changes in the thermoelectric properties of a few selected lots of material will give a general idea of the changes which would occur in other lots of the same general type, provided that all the lots have received the same initial heat treatment.

II. MATERIALS INVESTIGATED

The thermocouple materials studied were Chromel *P*, Alumel, iron, and constantan. Chromel *P* and Alumel wire of No. 18 gage and iron and constantan of No. 14 gage were used for the tests at 800° and 1,000° F. For the tests at 1,200° F and above, No. 8 gage wires were used. To determine the relation of wire size to the thermoelectric stability, additional tests were made on No. 18 and No. 22 gage Chromel and Alumel at 1,200° and 1,600° F, and on No. 18 gage iron and constantan at 1,200° and 1,400° F.

Samples of the various materials were secured from several sources. Each of the materials used in the investigation had the temperature-emf relation characteristic of the large percentage of the material of its particular type now being manufactured. All of the wires had been heat treated by the manufacturers in the manner considered standard for the particular type of wire.

III. TEST METHODS

Since Chromel *P* is generally used in combination with Alumel, and iron with constantan, the materials were paired in this manner. In addition to determining the temperature-emf relation for each pair, the thermal emf of the individual elements of each pair against the platinum standard [1] Pt 27 was determined. In this way the thermoelectric changes of each thermocouple material were determined independently. The difference of the thermal emfs of the individual elements of a thermocouple against a third material is equal to the emf of the thermocouple. As all three were measured in this work, any two served as a check upon the third.

The temperatures were measured with a standard platinum to platinum—10 percent rhodium thermocouple calibrated in accordance with the specifications for the International Temperature Scale.[2] The platinum working standard used was checked periodically against Pt 27.

The pair or pairs of wire under test were insulated by two-hole porcelain insulators. The platinum reference wire was protected by a glazed porcelain tube and was sealed through the end of the protection tube with a Pyrex glass, leaving about 1 cm of the end of the wire protruding beyond the seal. The platinum-rhodium thermocouple, insulated with a two-hole porcelain tube inside a glazed porcelain protection tube, was likewise sealed through the end of its protection tube with a Pyrex glass, leaving the welded junction protruding about 1 cm beyond the seal. The ends of the base-metal wires, the platinum reference wire, and the standard thermocouple were then welded together to form a single composite junction.

The furnace used in this work was of the resistance type wound with platinum-rhodium wire. The furnace tube of Alundum was 60 cm long and 3-cm inside diameter. The wires under test, together with the platinum reference wire and the platinum-rhodium thermocouple, were placed in the furnace with the composite junction at about the midpoint. The wires were then securely clamped with respect to the furnace. Although the ends of the furnace tube were closed with asbestos wool to promote temperature uniformity, no attempt was made to exclude air from the heated chamber, so that the atmosphere prevailing within the tube was oxidizing. The reference junctions were maintained at 32° F during all the measurements. The temperature of the furnace was maintained practically constant during any observation at a given point by means of a hand-operated voltage regulator in the power circuit.

To obtain data on the effect of long-time exposure to high temperatures upon the thermoelectric properties of the materials, the following procedure was adopted. The initial measurements were made on the sample as received from the manufacturer. Measurements of the

[1] The thermoelectric reference standard maintained at the National Bureau of Standards.
[2] G. K. Burgess, BS J. Research **1**, 635 (1928) RP22.

thermal emfs of the various combinations were made at intervals of 200° F up to and including in each case the temperature at which the effect of heating was to be determined. The furnace was then allowed to cool to room temperature, and the measurements were repeated. The differences between the two sets of measurements were ascribed to the initial heating and will be referred to as the "initial changes." Similar measurements were then made after the materials had been held at the test temperature for total elapsed times of 10, 50, 100, 200, 400, 600, 800, and 1,000 hours, or as long as the materials remained serviceable. The test temperatures included every temperature from 800° F to and including 2,000 °F, in steps of 200° F. Chromel *P* and Alumel were also tested at 2,200° F. A fresh sample was used for the test at each temperature. During heating periods, the temperature of the furnace was maintained constant within ±5° F by means of an automatic temperature controller.

The procedure followed in studying the effect of decreasing the depth of immersion was as follows:

The materials were heated in the electric furnace for a period of 20 hours at a constant temperature. Following this heat treatment, the thermal emf of the samples was determined, the position of the samples being maintained the same as that during the 20-hour heating period. The furnace was then allowed to cool to room temperature, and the immersion was decreased 3 inches and the thermal emf determined in this new position. The difference between the observations for a given sample is due only to the change in immersion, since no heating took place between the two sets of measurements. This type of test was carried out on No. 8 gage iron and constantan at temperatures from 600° to 1,800° F, in 200° F steps, and on No. 8 gage Chromel *P* and Alumel from 600° to 2,200° F.

IV. RESULTS

1. TEMPERATURE EXPOSURE TESTS

(a) CHROMEL P AND ALUMEL

Figures 1 and 2 show the results obtained on No. 18 gage Chromel *P* and Alumel heated at 800° and 1,000° F, respectively. The changes in the completed Chromel-Alumel thermocouples are also shown. The changes in the individual elements are in the same direction, so that each becomes thermoelectrically positive to the material in its original condition. The convention followed in regard to sign is as follows:

If in a simple thermoelectric circuit the current flows from metal *A* to metal *B* at the colder junction, *A* is thermoelectrically positive to *B*. On the basis of this convention, Chromel *P* is positive to Alumel. Therefore, a positive change in Chromel *P* will increase the emf of a Chromel-Alumel thermocouple, while a positive change in Alumel will decrease the emf of the thermocouple. The changes observed in the tests at 800° and 1,000° F are small, in all cases less than the equivalent of 1° F for a Chromel-Alumel thermocouple.

Figures 3 to 8, inclusive, show the results obtained with No. 8 gage Chromel *P* and Alumel at temperatures from 1,200° to 2,200° F, inclusive. The changes in the emf of Chromel *P* are in the positive direction throughout all tests, with the exception of the test at 2,200° F, where a negative change was observed at temperatures above 1,600°

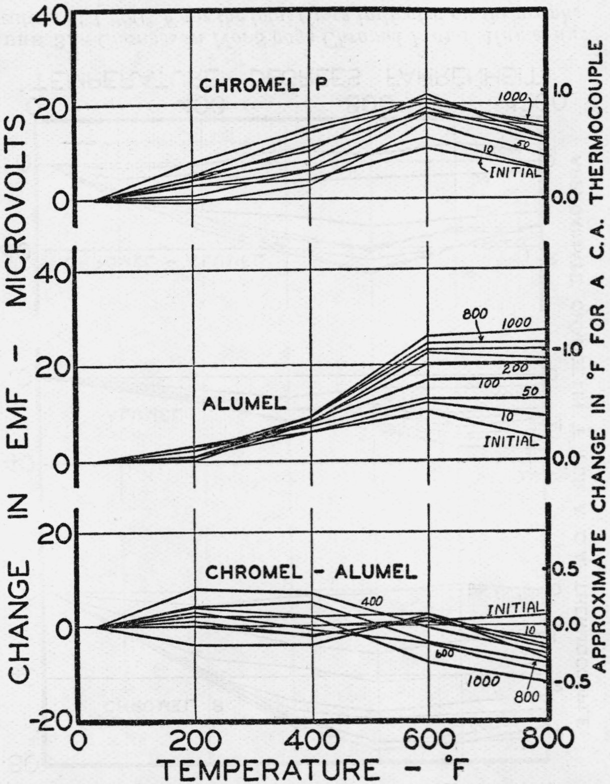

FIGURE 1.—*Changes in No. 18 gage Chromel P and Alumel due to heating at 800° F for the total times indicated on the graphs.*

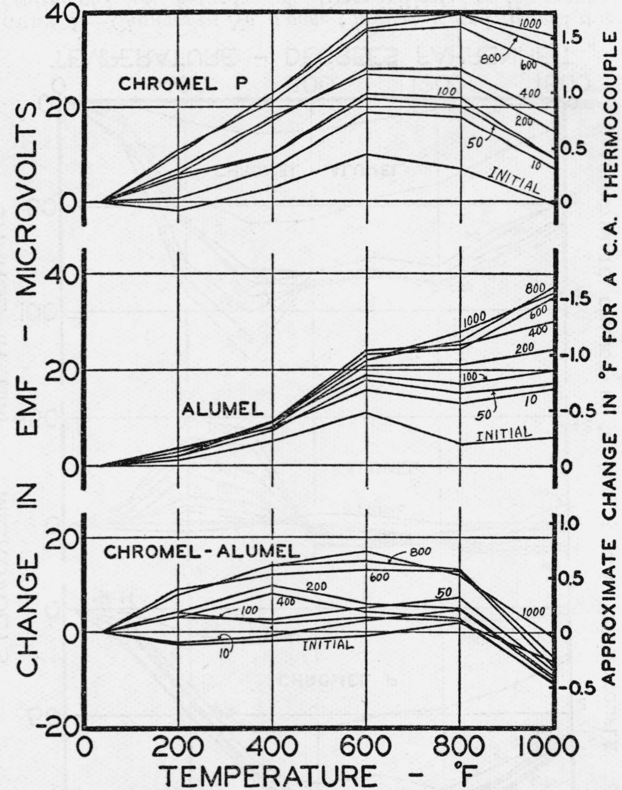

FIGURE 2.—*Changes in No. 18 gage Chromel P and Alumel due to heating at 1,000° F for the total times indicated on the graphs.*

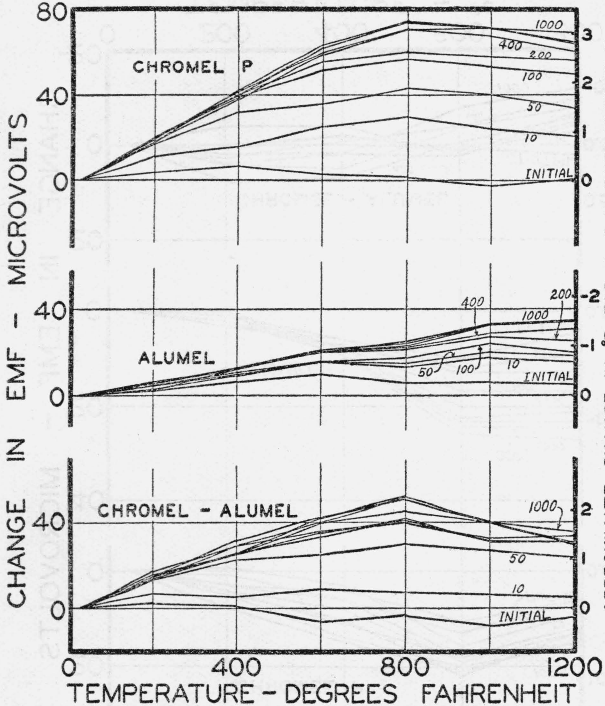

FIGURE 3.—*Changes in No. 8 gage Chromel P and Alumel due to heating at 1,200° F for the total times indicated on the graphs.*

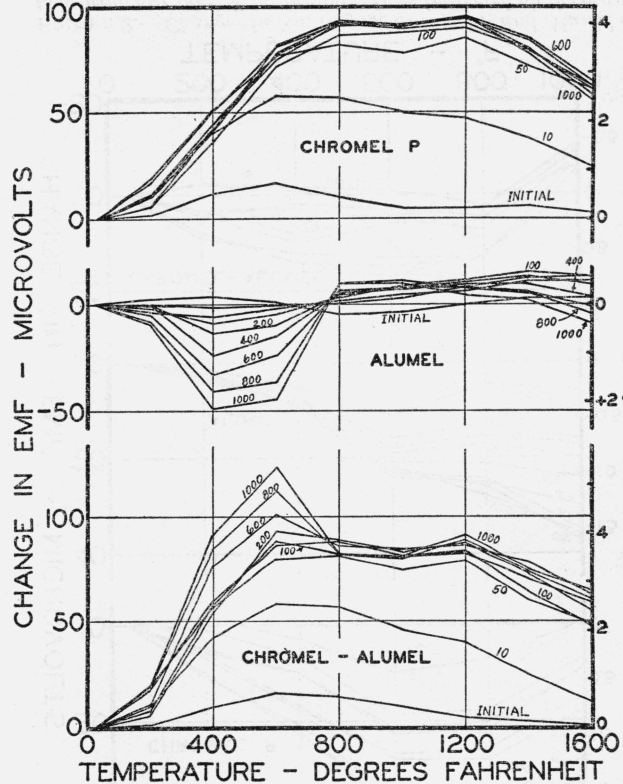

FIGURE 4.—*Changes in No. 8 gage Chromel P and Alumel due to heating at 1,400° F for the total times indicated on the graphs.*

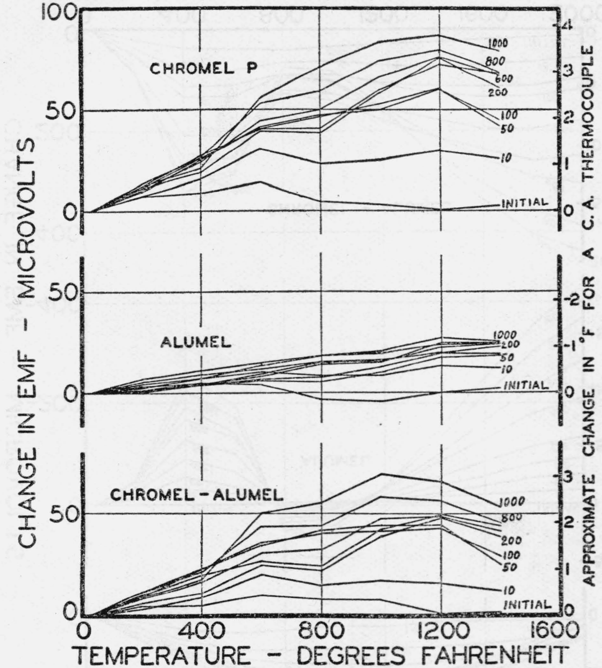

FIGURE 5.—*Changes in No. 8 gage Chromel P and Alumel due to heating at 1,600° F for the total times indicated on the graphs.*

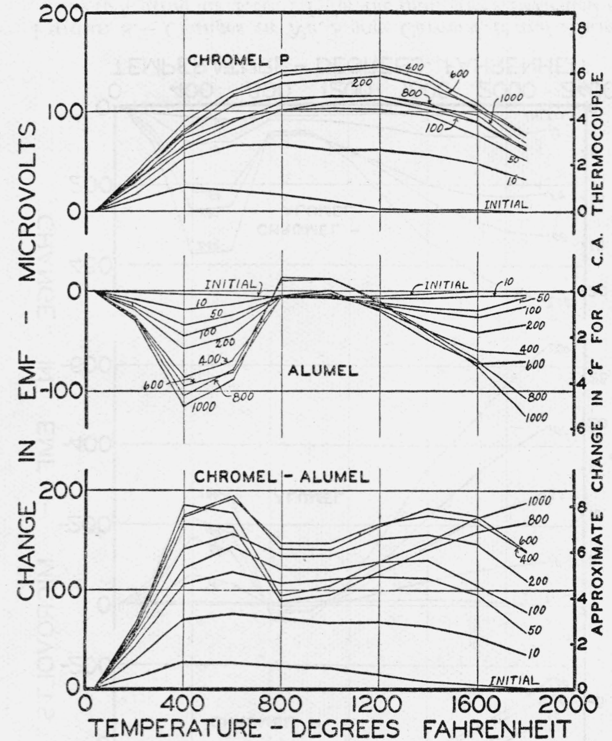

FIGURE 6.—*Changes in No. 8 gage Chromel P and Alumel due to heating at 1,800° F for the total times indicated on the graphs.*

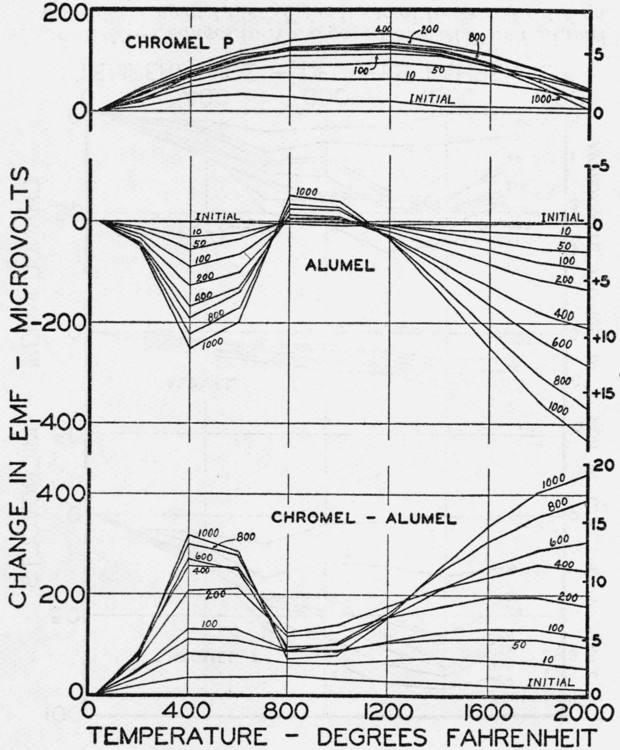

FIGURE 7.—*Changes in No. 8 gage Chromel P and Alumel due to heating at 2,000° F for the total times indicated on the graphs.*

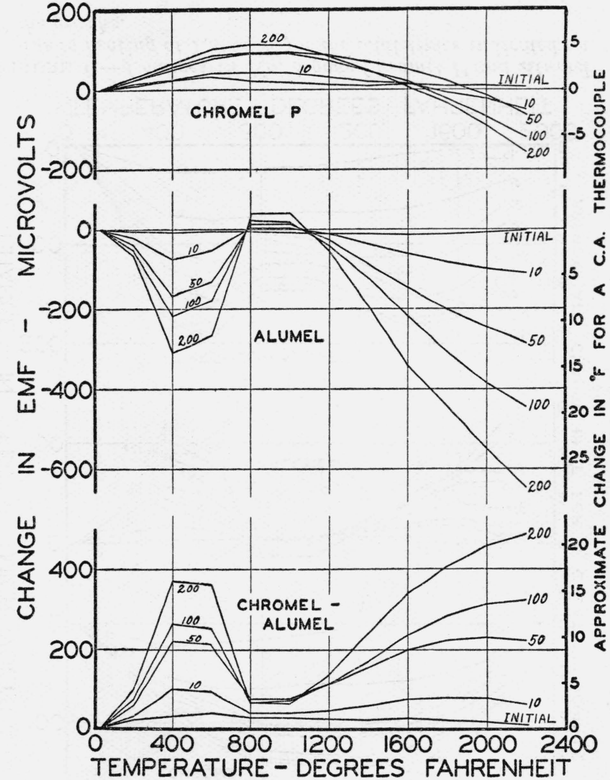

FIGURE 8.—*Changes in No. 8 gage Chromel P and Alumel due to heating at 2,200° F for the total times indicated on the graphs.*

F. The magnitude of the changes is, in nearly all cases, in the order of the duration of the heating periods, the maximum change occurring at about 1,200° F. The changes in the Alumel are in the positive direction throughout the tests at 1,200° and 1,400° F. In the tests at 1,600° F and above, the changes in the emf of the Alumel between about 800° and 1,100° F are extremely small. Above 1,100° F the changes are negative and of appreciable magnitude. This is most clearly shown in figure 7. The materials used in the test at 2,200° F failed after about 300 hours of heating.

Tests of No. 8, No. 18, and No. 22 gage Chromel-Alumel thermocouples heated at 1,200° F for a total of 1,000 hours indicated that

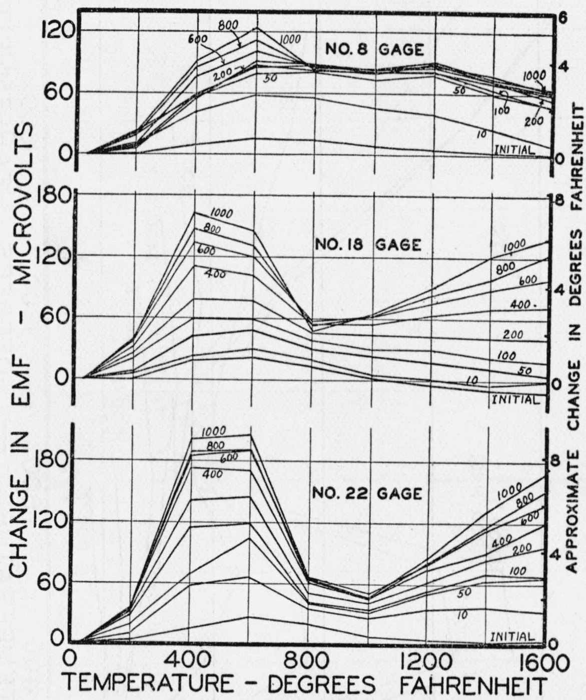

FIGURE 9.—*Changes in No. 8, No. 18, and No. 22 gage Chromel-Alumel thermocouples due to heating at 1,600° F for the total times indicated on the graphs.*

the changes in the thermocouples of the various sizes were nearly the same, and in all cases less than the equivalent of 2.5° F. Figure 9 shows the effects on the same sizes of Chromel-Alumel thermocouples when heated at 1,600° F. The change in calibration at 400° F is largest in the smallest size, but the reverse is true for the change at 1,000° F.

The changes in the emf of the Chromel-Alumel thermocouples produced by the total heating time in each of the tests are shown in figure 10 (reproduced from fig. 1 to 8, inclusive). In the test at 2,200° F the change after only 200 hours is shown, this being the elapsed time when the last measurements preceding failure were made. The peculiar change in the Alumel previously mentioned is reflected in change of the thermocouples.

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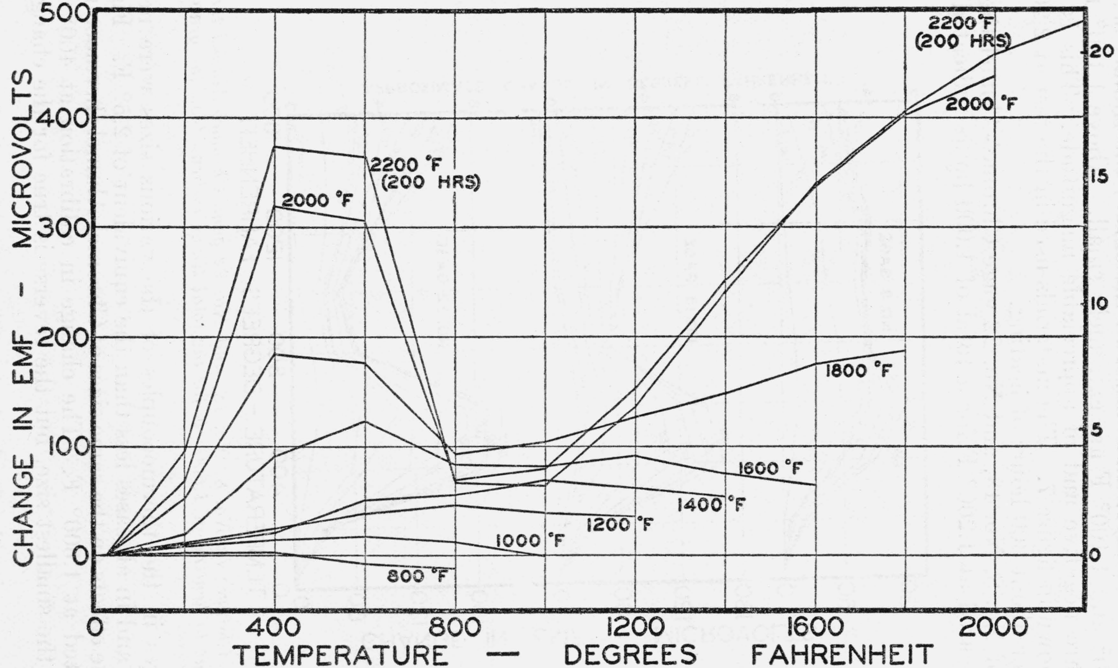

FIGURE 10.—*Changes in Chromel-Alumel thermocouples due to 1,000 hours of heating at temperatures indicated on the graphs.*

(b) IRON AND CONSTANTAN

Figures 11 and 12 show the results obtained on No. 14 gage iron and constantan tested at 800° and 1,000° F, respectively. The changes in all cases are small, being less than the equivalent of 1° F.

The results on No. 8 gage iron and constantan tested at 1,200° to 2,000° F, inclusive, are shown in figures 13 to 17. The time intervals between calibrations were shortened for the tests at 1,800° and 2,000° F, since at these temperatures the materials change at a rapid rate. The tests were continued until the materials failed.

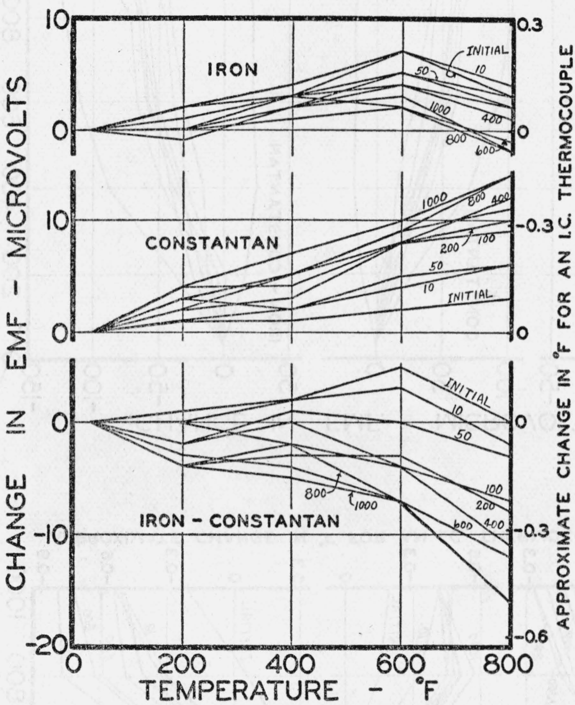

FIGURE 11.—*Changes in No. 14 gage iron and constantan due to heating at 800° F for the total times indicated on the graphs.*

The relative thermoelectric stability of No. 8 and No. 18 gage iron-constantan thermocouples heated at 1,400° F is shown in figure 18. As might be expected, the emf changes in the smaller wire proceed more rapidly. The No. 18 gage thermocouple failed after about 400 hours of heating, while the No. 8 gage remained serviceable throughout the 1,000 hours of the test. However, the measurements made on the thermocouple at the end of the 1,000-hour period indicated that failure was near. A test on these same sizes at 1,200° F showed no appreciable difference in their thermoelectric stability at this test temperature, the maximum change after 1,000 hours of heating being about the equivalent of 4° F.

The change in the emf of constantan was gradual and cumulative throughout each test. In the case of iron the change in emf was relatively small until failure of the wire was approached. When this stage was reached, the change was rapid and relatively large. This

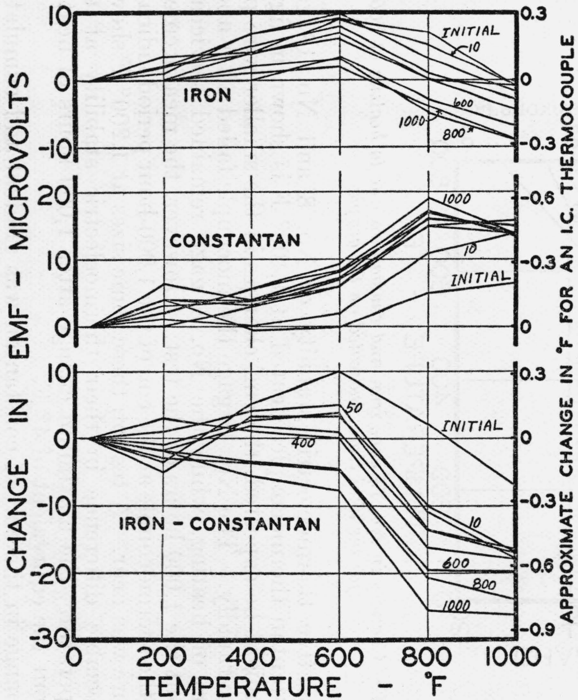

FIGURE 12.—*Changes in No. 14 gage iron and constantan due to heating at 1,000° F for the total times indicated on the graphs.*

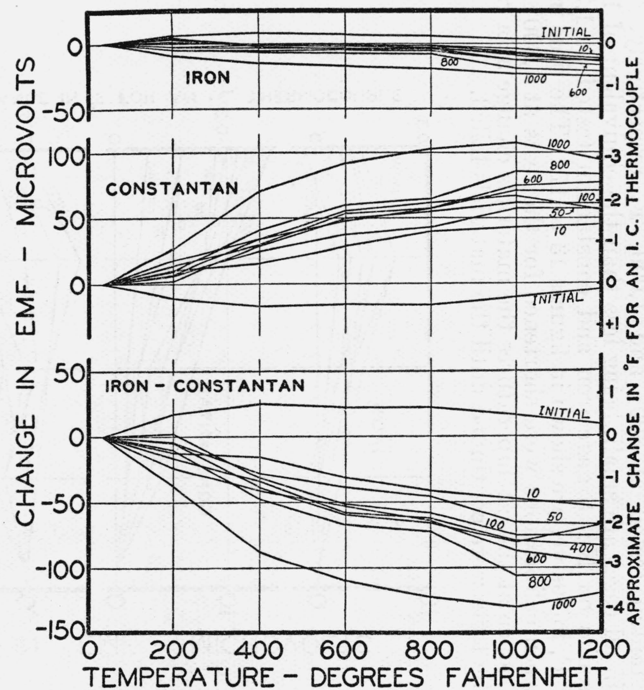

FIGURE 13.—*Changes in No. 8 gage iron and constantan due to heating at 1,200° F for the total times indicated on the graphs.*

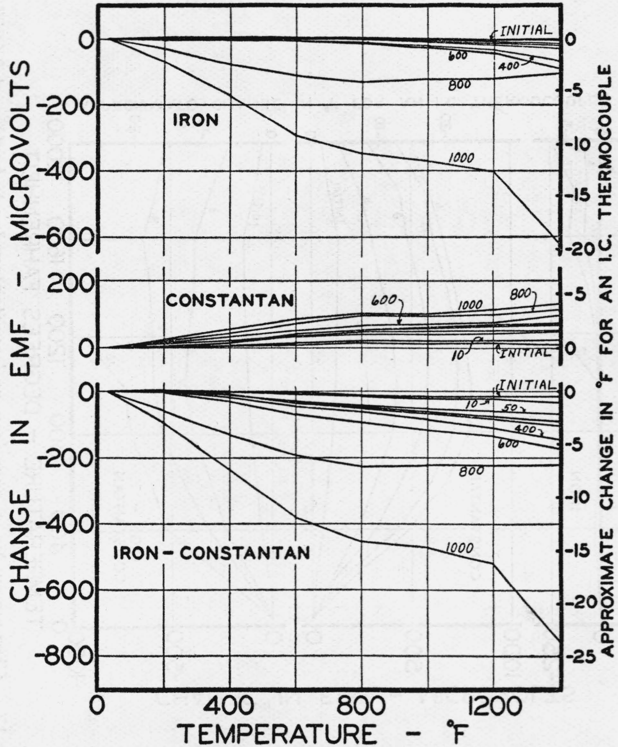

FIGURE 14.—*Changes in No. 8 gage iron and constantan due to heating at 1,400° F for the total times indicated on the graphs.*

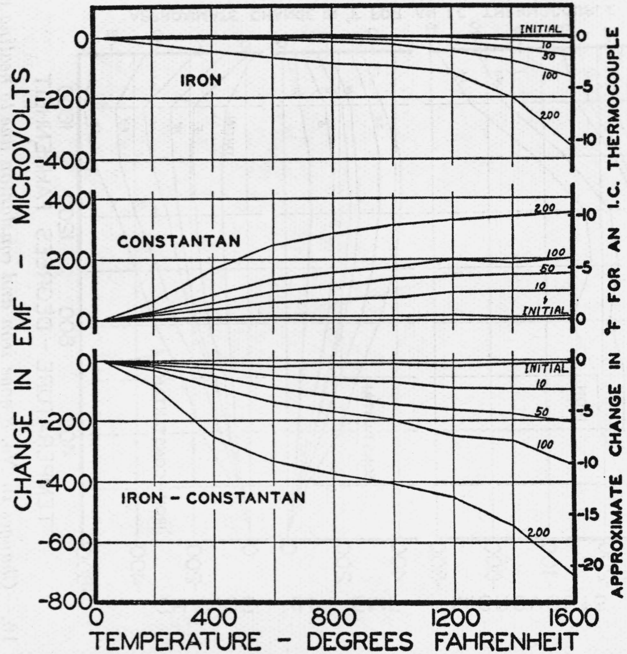

FIGURE 15.—*Changes in No. 8 gage iron and constantan due to heating at 1,600° F for the total times indicated on the graphs.*

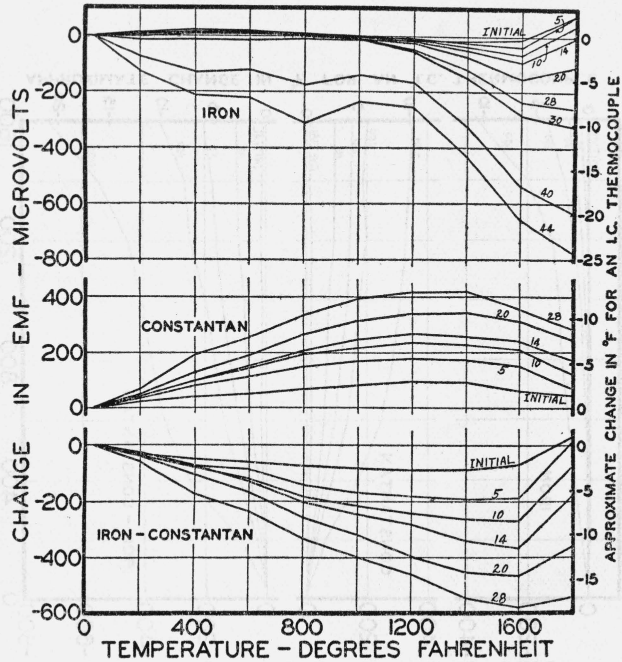

FIGURE 16.—*Changes in No. 8 gage iron and constantan due to heating at 1,800° F for the total times indicated on the graphs.*

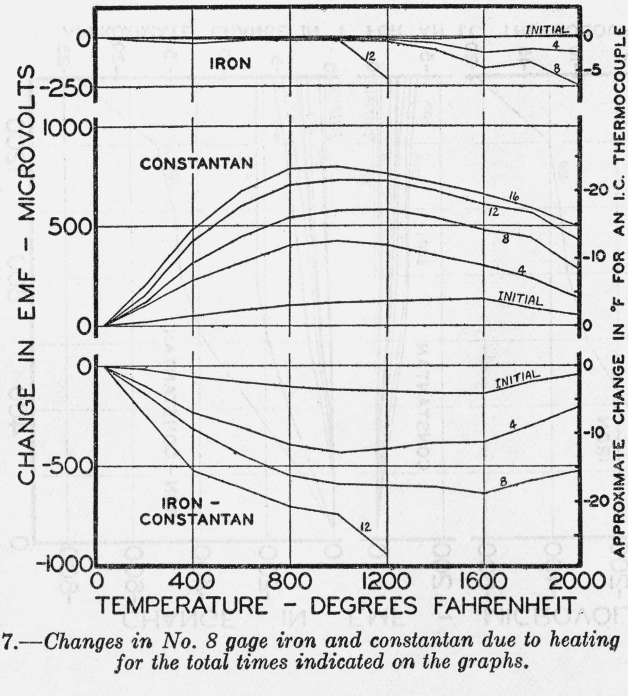

FIGURE 17.—*Changes in No. 8 gage iron and constantan due to heating at 2,000° F for the total times indicated on the graphs.*

was true for all tests in which iron was heated until failure occurred. The life of the iron element was found to be approximately the same as that of the constantan.

2. IMMERSION TESTS

Table 1 gives the observed changes in the thermal emf of No. 8 gage iron and constantan produced by a 3-inch decrease in immersion following the 20-hour heating period. The changes in both of the elements are gradual and regular throughout, the magnitude of the emf changes in constantan being everywhere considerably greater than in the case of iron. Figure 19 shows the change in the emf of the iron-constantan thermocouple under the various conditions of heating (test at 1,800° F not shown in graph). A greatly increased, though regular, change is clearly shown for the test at 1,600° F. At 1,800° F the change is about four times as great as that observed at 1,600° F.

TABLE 1.—*Changes (in thermal emf) at various temperatures caused by decreasing the depth of immersion 3 inches, after heating the wires in air at the temperatures indicated for 20 hours*

Calibration temperature	Heating temperature						
	600 °F	800 °F	1,000 °F	1,200 °F	1,400 °F	1,600 °F	1,800 °F
IRON							
°F	μv	μv	μv	μv	μv	μv	μv
200	1	5	3	1	−2	−1	−2
400	0	7	4	3	−2	−4	−9
600	1	8	3	4	−2	−7	−18
800		7	2	4	−3	−12	−29
1,000			3	4	−6	−19	−43
1,200				1	−9	−30	−58
1,400					−13	−43	−72
1,600						−57	−80
1,800							−100
CONSTANTAN							
200	4	10	13	14	14	25	83
400	7	18	20	30	28	62	224
600	9	27	26	43	41	93	374
800		35	37	52	53	127	504
1,000			49	60	54	156	615
1,200				65	65	182	735
1,400					68	208	837
1,600						223	935
1,800							1,078
IRON-CONSTANTAN							
200	−3	−5	−10	−13	−16	−26	−85
400	−7	−11	−16	−27	−30	−66	−233
600	−8	−19	−23	−39	−43	−100	−392
800		−28	−35	−48	−56	−139	−533
1,000			−46	−56	−60	−175	−658
1,200				−64	−74	−212	−793
1,400					−81	−251	−909
1,600						−280	−1,015
1,800							−1,178

Table 2 gives the observed effects for No. 8 gage Chromel *P* and Alumel of changes in immersion, as outlined above. In the tests up to and including 1,600 °F the effect is gradual and approximately regular. At 1,800 °F and above, the Alumel element exhibited an irregular effect, somewhat similar to that observed in the exposure tests, which became more pronounced as the heating temperature was increased. Figure 20 illustrates the results for the Chromel-Alumel thermocouples.

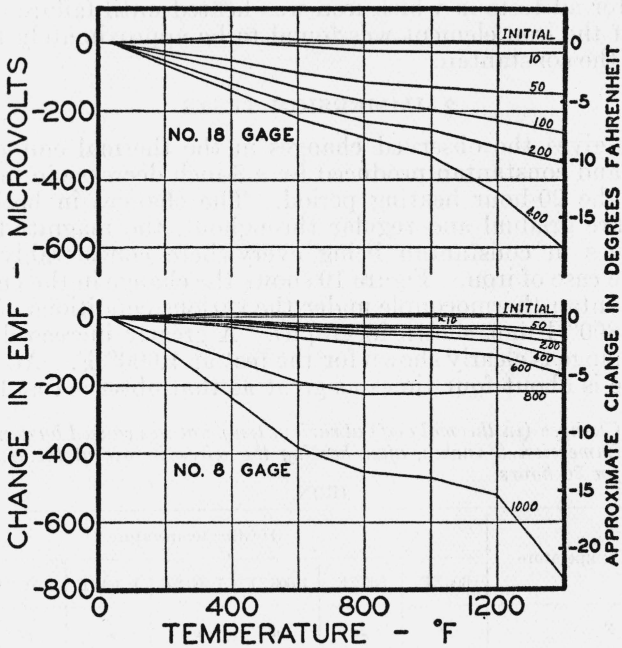

FIGURE 18.—*Changes in No. 8 and No. 18 gage iron-constantan thermocouples due to heating at 1,400° F for the total times indicated on the graphs.*

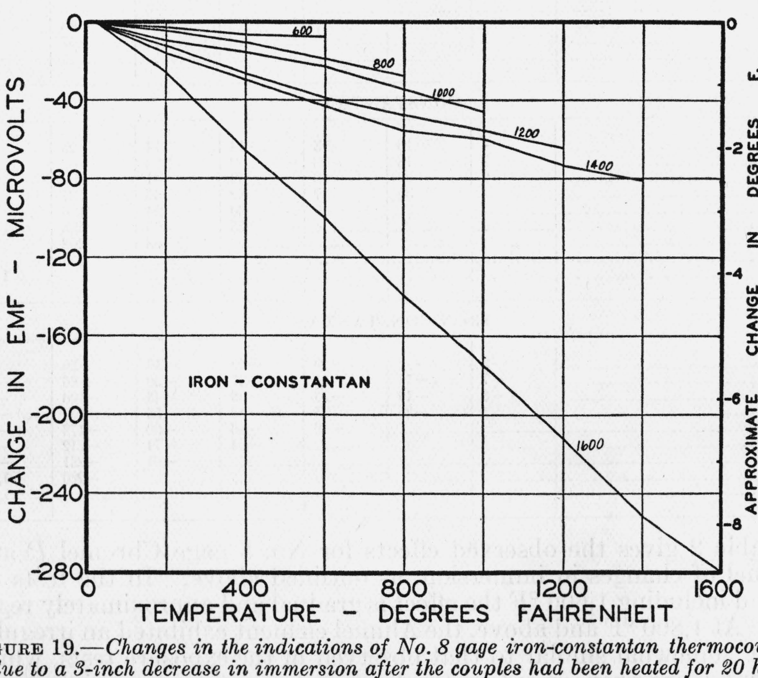

FIGURE 19.—*Changes in the indications of No. 8 gage iron-constantan thermocouples due to a 3-inch decrease in immersion after the couples had been heated for 20 hours at the temperatures indicated on the graphs.*

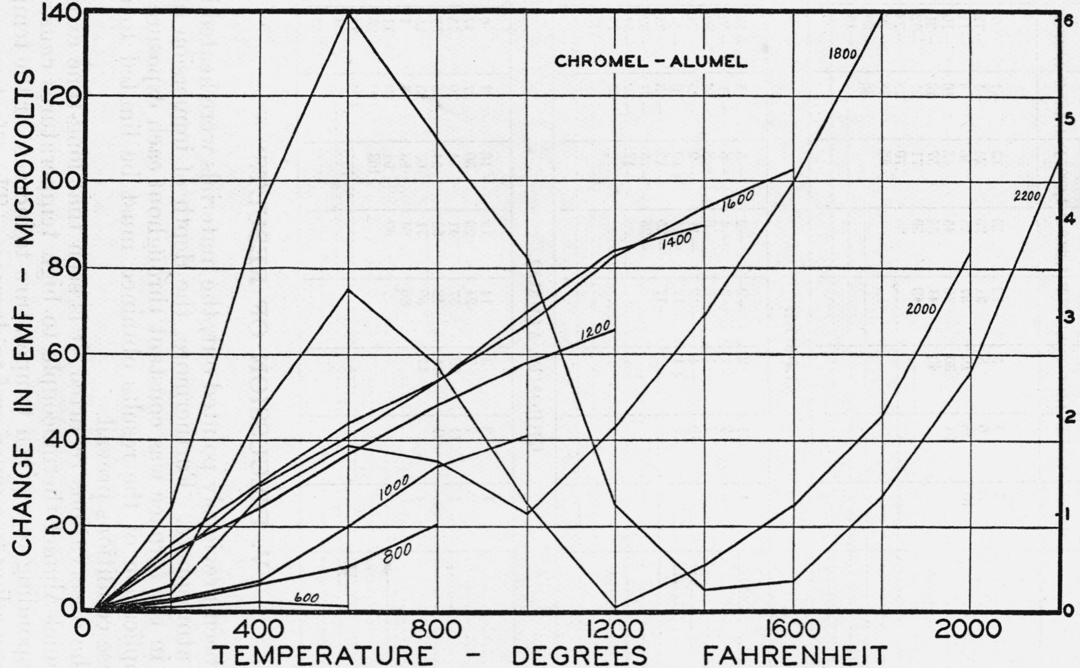

Figure 20.—*Changes in the indications of No. 8 gage Chromel-Alumel thermocouples due to a 3-inch decrease in immersion after the couples had been heated for 20 hours at the temperatures indicated on the graphs.*

TABLE 2.—*Changes (in thermal emf) at various temperatures caused by decreasing the depth of immersion 3 inches after heating the wires in air at the temperatures indicated for 20 hours*

Calibration temperature	Heating temperature								
	600° F	800° F	1,000° F	1,200° F	1,400° F	1,600° F	1,800° F	2,000° F	2,200° F
CHROMEL *P*									
°F									
200	2	4	5	12	10	13	−1	−7	−7
400	5	9	8	21	25	24	+1	−12	−35
600	10	18	19	31	35	36	4	−14	−50
800		31	30	36	45	45	10	−16	−49
1,000			40	41	54	57	13	−21	−52
1,200				49	59	71	31	−32	−53
1,400					65	79	48	−28	−81
1,600						86	68	−29	−103
1,800							95	−28	−130
2,000								−18	−158
2,200									−176
ALUMEL									
200	1	1	2	−2	−2	−3	−5	−13	−31
400	3	2	1	−3	−4	−6	−26	−59	−128
600	9	7	−1	−6	−6	−8	−35	−89	−193
800		10	−4	−12	−11	−9	−25	−73	−159
1,000			+1	−17	−17	−10	−10	−46	−134
1,200				−17	−25	−12	−13	−33	−78
1,400					−25	−15	−21	−39	−86
1,600						−17	−32	−54	−110
1,800							−45	−74	−157
2,000								−102	−214
2,200									−281
CHROMEL-ALUMEL									
200	1	3	3	14	12	16	4	6	24
400	2	7	7	24	29	30	27	47	93
600	1	11	20	37	41	44	39	75	140
800		21	34	48	55	54	35	57	110
1,000			41	58	71	67	23	25	82
1,200				66	84	83	43	1	25
1,400					90	94	69	11	5
1,600						103	100	25	7
1,800							140	46	27
2,000								84	56
2,200									105

V. DISCUSSION OF RESULTS

As has been previously pointed out, the materials were heated in an oxidizing atmosphere. Furthermore, the depth of immersion of the materials in the furnace was constant throughout each exposure test. Direct application of the results obtained must be limited to cases where these conditions prevail.

From the observations reported, it is seen that long-time exposure of a Chromel-Alumel thermocouple to high temperatures causes the emf corresponding to a given temperature to increase or the temperature corresponding to a given emf to decrease. The effect on an iron-constantan thermocouple is just the reverse.

Failure of a Chromel-Alumel thermocouple (No. 8 gage) occurred within the 1,000-hour heating period only in the test at 2,200° F. In this case an open circuit was indicated after 300 hours, and examination of the sample showed that the metal forming the welded junction and the individual wires for some distance from the welded junction were oxidized nearly through.

The 1,000-hour heating periods at 2,000° and 1,800° F for No. 8 gage Chromel *P* and Alumel also produced appreciable oxidation of the materials. In the test at 2,000° F the diameter of the wires, after the oxide was removed, was 2.3 mm for the Alumel and 2.6 mm for the Chromel *P*, as compared with 3.3 mm for the original diameters. For the test at 1,800° F the diameter, after removing the oxide, was 2.6 mm for the Alumel and 3.1 mm for the Chromel *P*. In the tests at 1,600° F and below, the oxidation had not materially decreased the diameter of the wires.

The exposure tests on No. 8 gage iron-constantan thermocouples showed failure of the materials within the 1,000-hour heating time for the tests at 1,600° F and above. Failure occurred after 12 hours at 2,000° F, after 28 hours at 1,800° F, and after 300 hours at 1,600° F. The No. 18 gage iron-constantan thermocouple failed after about 500 hours at 1,400° F, while the No. 8 gage thermocouple remained serviceable throughout the 1,000-hour test at 1,400° F. However, at the conclusion of the test the diameters of the No. 8 gage materials had been reduced to about one-tenth of their original value.

A summary of the changes observed for Chromel-Alumel, iron-constantan, and Chromel-constantan thermocouples produced by long-time exposure to various temperatures is given in table 3. The values for Chromel-constantan were obtained indirectly by combining the changes in the individual elements. Though the changes in both Chromel *P* and constantan are considerably larger than those of the completed thermocouple, the directions are such that the changes counteract each other, so that the change in a Chromel-constantan thermocouple is small. The life of this thermocouple is limited by that of the constantan element.

TABLE 3.—*Changes in the calibration of base-metal thermocouples heated in air in an electric furnace*

Exposure temperature	Chromel-Alumel		Iron-constantan		Chromel-constantan	
	Hours of exposure	Maximum change	Hours of exposure	Maximum change	Hours of exposure	Maximum change
°*F*		°*F*		°*F*		°*F*
800	1,000	<1	1,000	<1	1,000	<1
1,000	1,000	<1	1,000	<1	1,000	<1
1,200	1,000	+2	1,000	−4	1,000	−1
1,400	1,000	3	800	−7	1,000	−2
1,600	1,000	5	100	−10	100	−4
1,800	1,000	8	28	−18		
2,000	1,000	19	8	−19		
2,200	200	21				

The relatively large changes in calibration observed for Chromel-Alumel thermocouples at 400° and 600° F, after the couples have been exposed to temperatures of 1,600° F and above, are not as serious as may at first appear. When a thermocouple is used for accurate measurement of temperatures of 1,600° F or above, it is seldom required that this same couple be used for accurate measurements at temperatures as low as 400° or 600° F. Therefore, the relatively large changes at these lower temperatures are of no great importance. A thermocouple which is to be used for accurate measurements below 1,000° F should not be exposed to the higher temperatures. If this procedure is followed, the relatively large changes at 400° and 600° F will be avoided.

The results on the immersion tests emphasize the importance of never decreasing the depth of immersion of a thermocouple after it has once been placed in service. The practice of using a single base-metal thermocouple for high-temperature measurements in a number of different installations should be avoided. It is even difficult to obtain consistent and accurate results by using a thermocouple in a single installation if the couple is withdrawn and replaced between periods of service. The results obtained by removing a used base-metal couple from an installation to determine the corrections to the original calibration by testing it in a laboratory furnace are unreliable. The temperature gradients in the two furnaces usually differ widely, and hence the results will not be applicable to the actual service conditions. If it is practicable by any means to remove the inhomogeneous portions of the thermocouple from the temperature gradient, then the original calibration of the couple is applicable.

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