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Instruments

PROGRESS REPORT I

THERMOCOUPLE RESEARCH REPORT

FOR THE PERIOD

NOVEMBER 1, 1956 TO OCTOBER 31, 1957

D. L. McElroy

OAK RIDGE NATIONAL LABORATORY
OPERATED BY
UNION CARBIDE NUCLEAR COMPANY
Division of Union Carbide Corporation
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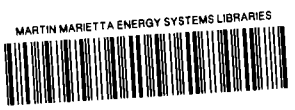

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PROJECT PERSONNEL

Permanent Station Personnel:

David L. McElroy: Research Engineer
B. S. in Metallurgy, University of Alabama, 1951
M. S. in Metallurgy, University of Alabama, 1953
PhD in Metallurgy, University of Tennessee, 1957

E. E. Stansbury: Consultant
Professor of Metallurgy, University of Tennessee
B. S. in Chemical Engineering, North Carolina State, 1940
M. S. in Metallurgy, University of Cincinnati, 1943
PhD in Metallurgy, University of Cincinnati, 1947

Fred Wallace: Machinist

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Individually they have expressed thanks for the financial aid they have received from the contractor for their efforts. In several cases this aid has been the sole support for the continuation of their education.

Wayne Grooves: Laboratory Assistant
Undergraduate: Chemical Engineering--University of Tennessee 1959

Forrest Hall, Jr.: Laboratory Assistant
Undergraduate: Electrical Engineering--University of Tennessee 1959

Larry Hendrix: Laboratory Assistant
Co-op. Undergraduate: Electrical Egnineering--University of Tennessee 1959

Ed Hina: Laboratory Assistant
Undergraduate: Mechanical Engineering--University of Tennessee 1959

Don C. Holt: Laboratory Assistant
Undergraduate: Electrical Engineering--University of Tennessee 1959

Jere Nichols: Laboratory Assistant
Undergraduate: Chemical Engineering--University of Tennessee 1958

Jamie Scantlin: Secretary
Undergraduate: English Education--University of Tennessee 1959

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T. H. Blewitt
C. J. Borkowski
G. I. Cathers
J. H. Crawford
J. T. DeLorenzo
D. A. Douglas
C. S. Harrill
R. N. Lyon
C. A. Mossman
D. S. Toomb

CHAPTER I

SUMMARY

This document describes the first year of progress in the investigation of thermoelectric thermometry at the University of Tennessee Engineering Experiment Station. The purpose of this work is to provide means for improving the art of thermoelectric measurement through a better understanding of the fundamental behavior of thermocouples. Toward this end: (1) Exchange of ideas and experience with people versed in the field is being stimulated. (2) Correlation of current data with those existing in the literature is being made. (3) Detailed laboratory study is proceeding on existing nickel-base thermocouples (eg. Chromel-Alumel) in the range 500 °C to 1100°C.

Attention is being focused on the Chromel-Alumel system because it is almost universally used in this temperature range, and because recent increased demands on the stability and consistency of temperature measurement have increased the significance of a number of questions regarding the performance of this thermocouple. Although the literature contains a large amount of information on thermocouple technology, scant information is available on the fundamental causes for observed thermocouple behavior. It is felt that a study of a particular system and variations thereof leads to a better fundamental understanding. It has been necessary to duplicate certain data from the literature for the purpose of establishing uniformity of test conditions where extrapolative experiments are needed. This is always necessary in a system involving as many intangible variables as presently exist in thermoelectric measurements. Ultimately we will be able to correlate our new findings with existing literature data and present the results in such a manner that quantitative estimates of the performance of a thermocouple in a given application can be made along with recommendations which will permit maximum utilization of the thermocouple.

This report presents a description of the experimental equipment constructed and operated for (a) thermocouple calibration, (b) time-at-temperature studies of changes in thermal emf, (c) heat treating of wires. A brief literature survey, based on nearly 4000 references, has been included to summarize the large amount of information existing on thermocouple technology (annotated bibliography forthcoming).

Chemical analyses of a number of the Chromel-Alumel-type alloys have been obtained and show that the following two general classes of both alloys exist: (1) complex alloys containing significant amounts of eight or nine components, and (2) simple alloys which contain only two or three components in significant amounts. Some of the alloying components are added to facilitate fabrication and some are added to match the alloy to a particular calibration curve.

The following conclusions have been drawn from this study:

1. Major variations in calibrations of individual thermocouples are caused by composition variations in the alloys.

2. A mercury U-tube connection in the geometrical center of a Dewar flask is a convenient device to limit reference-junction errors to less than 0.1°C.

3. The emf generated by a thermocouple is not influenced by the method of hot-junction preparation if the hot-junction exhibits adequate electrical continuity and mechanical strength.

4. Large errors in thermal emf have been observed in thermocouples containing both mechanical and chemical inhomogenieties which vary from wire-to-wire and from producer-to-producer. Mechanical inhomogenieties may be removed by short-time annealing. Chemical inhomogenieties are not so readily removable, but may be altered in magnitude by annealing in air or vacuum or by pickling.

5. The recrystallization temperature for Chromel is 1160°F for 70 percent cold work, and for Alumel it is 1100°F.

6. With proper consideration of etchants, satisfactory microstructures of the two alloys can be prepared. Chromel and Alumel are single-phase alloys and the microstructure varies somewhat from vendor to vendor. Chromel is extremely resistant to oxidation, as evidenced by the microstructure of exposed material. In contrast, Alumel undergoes appreciable oxidation in similar situations; this is seen in the microstructure. Grain growth is quite evident in Chromel and Alumel exposed for long times at high temperatures.

7. The emf generated by Chromel-Alumel thermocouples changes with time at temperature in the range 500° to 1100°C. In general, the magnitude and direction of the average drift depend on the test temperature and environment, and show the most change at high temperatures.

8. Accurate calibrations performed on Chromel and Alumel wires indicate that the calibration on the first heating on an as-received material differs from the calibration on cooling, and from the calibration on reheatings and coolings. Changing the depth of immersion of a thermocouple causes a change in calibration of the thermocouple.

An hypothesis based on compositional changes has been presented to explain the variations in emfs with time at temperature, and experiments are being conducted to check this hypothesis. The current study has suggested treatments for presently available thermocouples to give improved performance. The exact criteria for judging the performance of a particular thermocouple (stability, consistency, alloying element, costs, etc.) are still not precisely known; however, they are more clearly understood now than at the beginning of this study. The separation of fact from fiction has been fairly well accomplished. In any case, these criteria will be conditional, depending upon the accuracy desired and the thermocouple environment.

It should be remembered that this document describes the progress of the first year of investigation on thermocouple thermometry. Some of the conclusions here presented may need further consideration, however, it is strongly felt that most of the conclusions drawn from the experimental results are fundamentally sound and will remain essentailly unchanged.

CHAPTER II

INTRODUCTION

General Thermocouple History

In 1826, Thomas Seebeck (1) discovered that an electric current is maintained in a circuit of two dissimilar metals when their junctions are held at different temperatures. This type circuit is called a thermocouple. Seebeck's discovery was supplemented in 1834 by a fundamental discovery made by Jean Peltier (2) that when a current exists in one direction across the junction of two dissimilar metals, heat is absorbed and the junction cooled, and that when the current is maintained in the opposite direction the junction is heated. This phenomena is called the Peltier effect and is reversible. In 1848, William Thomson (3) (later Lord Kelvin) concluded from thermodynamic reasoning and the characteristics of thermocouples that the Peltier effect was not the only reversible heat effect in a thermoelectric circuit, and he was able to show that in certain homogeneous metals, heat is absorbed or released when there is an electric current from colder to hotter parts. This heating or cooling is called the Thomson effect and is reversible and occurs only where there is a temperature gradient in a metal.

These phenomena have been coupled with accurate experimental measurements on many thermoelectric circuits to establish three laws which govern thermocouple behavior:

1. The law of the homogeneous circuit: An electric current cannot be sustained in a circuit of a single homogeneous metal by the application of heat alone.

2. The law of intermediate metals: The algebraic sum of the thermoelectric forces in a circuit composed of any number of dissimilar metals is zero, if all of the circuit is at a uniform temperature.

3. The law of intermediate temperatures: The thermal emf developed by any thermocouple of homogeneous metals with its junctions at any two temperatures T_1 and T_3 is the algebraic sum of the emf of the thermocouple with one junction at T_1 and the other at any other temperature T_2 and the emf of the same thermocouple with its junctions at T_2 and T_3.

Since the development of these laws a number of useable thermocouple combinations have been developed and used in the measurement of temperatures.

Practical considerations of the characteristics of materials which will yield a good thermocouple element can be summarized as follows:

1. The thermal emf increases continuously with increasing temperature over the range of use.

2. The thermal emf is large enough to be measured with reasonable accuracy.

3. The thermoelectric characteristics are not appreciably altered during calibration and use either by internal changes, or by chemical contamination in the environment in which the thermocouple is used. This is to say, the metals should be resistant to any action such as oxidation, corrosion or volatilization which alters the wire.

4. The thermocouples are reproducible and readily obtainable in uniform quality at a reasonable price.

One finds that these qualifications restrict the number of feasible thermocouple systems for measuring temperatures. There are only five thermocouples in prominent use today and each is restricted in use by the specific environments and temperature ranges. In 1886, Le Chatelier (4) (also Barus (5)) introduced a thermocouple consisting of one wire of platinum and the other of 90 percent platinum-10 percent rhodium. This combination (I. S. A. Type S)* defines the International Temperature Scale from 630°C to 1063°C. The platinum-87platinum-13rhodium thermocouple (I. S. A. Type R) was introduced by Heraeus and is called the Heraeus (6) thermocouple. Both types find wide use in industry. In an effort to find less costly metals for use in thermocouples a number of combinations of metals were investigated. Iron and nickel are both useful and cheap. Pure nickel however becomes very brittle upon oxidation, but investigations showed an alloy of about 60 percent copper 40 percent nickel (Constantan, Advance, Ideal) was free of this difficulty. Hence the Iron-Constantan (I.S.A. Type J or I.S.A. Type Y) came into use. Another important pair of thermocouple alloys arose when Hoskins Manufacturing Company was formed to produce the alloys patented by M. L. Marsh in 1906. These alloys, as still being produced for thermocouples, are a 90 percent nickel, 10 percent chromium alloy as the positive wire, and a 95 percent nickel, 5 percent aluminum, manganese, silicon alloy as the negative wire. This patented and trademarked combination is known as Chromel P-Alumel (I.S.A. Type K) and has proven to be very useful. Another combination, Copper-Constantan (I.S.A. Type T) is particularly useful from 350° C to

*I.S.A. Instrument Society of America, Recommended Practice applicable to thermocouple wires for industrial use.

to sub-zero temperatures. The characteristics of these thermocouples are given in Table I. Many other combinations such as carbon-tungsten, Nickel-nickel molybdenum, carbon-silicon carbide, chromel-stainless steel, and chromel-constantan have been used but have never gained wide acceptance. In recent years several new combinations for particular applications have been developed: Geminol P and Geminol N (242-33) by Driver Harris Corporation; Kanthal (+) and Kanthal (−) by Kanthal Corporation; NiCr (+) and NiAl (−) by A. C. Scott, Ltd.

Thus when faced with a temperature measuring problem, one finds several combinations are available for use and the final choice of thermocouple depends on the accuracy desired, the environment of the system, and the equipment and money available. As shown in Table I certain thermocouples are not reliable in reducing environments but will satisfactorily perform in oxidizing and neutral systems within certain temperature ranges, and vice versa, performance may be superior in reducing environments as compared to oxidizing environments.

Of the thermocouples, in industrial application in the temperature interval from 1000° to 2000°F, the chromel-alumel type finds widespread use. Many experiments are committed to the use of chromel-alumel in this temperature interval without full realization of this combinations' limitations. The rather wide tolerances quoted on this economical combination are from nuclear considerations much better than can be given to more costly combinations. Thus it seemed that initial efforts could be directed profitably toward the chromel-alumel type thermocouple.

Chromel-Alumel Thermocouple History

The present research project developed from a number of reasons which are related to the aforementioned characteristics and limitations. Briefly the problem might be stated: How reliable are chromel-alumel thermocouples for measuring temperatures and temperature differences in the interval 1000° to 2000°F? Why is this combination good or bad, and does any combination exist which is better, and if so why. Thus the first goal of this project was not to find a panacea for all temperature measuring problems, but to try to rationalize the basic factors governing the behavior of chromel-alumel thermocouples in service.

TABLE I

TYPE	Pt-PtRh		CHROMEL P-ALUMEL		IRON-CONSTANTAN		COPPER-CONSTANTAN	
Composition %/100	100 Pt 100 Pt	.90Pt-.10Rh .87Pt-.13Rh	.90Ni-.10Cr.	.95Ni-.02Al- .02Mn-.01Si	.999Fe	.55Cu-.45Ni	.999Cu	.55Cu-.45Ni
Usual Temp. range Maximum temp.	0 to 1450°C (0 to 2650°F) 1700°C (3100°F)		-200 to 1200°C (-300 to 2200°F) 1350°C (2450°F)		-200 to 750°C (-300 to 1400°F) 1000°C (1800°F)		-200 to 350°C (-300 to 650°F) 600°C (1100°F)	
Polarity	-	+	+	-	+	-	+	-
Melting temp.	1773°C	1830°C	about 1430°C		1535°C	1190°C	1083°C	1190°C
Influence of environment	Resistance to oxidizing atmosphere good; poor for reducing atmosphere. Susceptible to chemical alteration by As, Si, P vapor in reducing gas (CO_2, H_2, H_2S, SO_2). Pt corrodes easily above 1000°C. Used in a gas-tight protecting tube.		Resistance to oxidizing atmosphere good; poor for reducing armosphere. Affected by reducing or sulfurous gases, SO_2 and H_2S.		Oxidizing and reducing gases have little effect on accuracy. Protect from moisture and sulfur. Resistance to oxidation good up to 400°C but poor above 700°C.		Subject to oxidation and alteration above 400°C due Cu, above 600°C due constantan wire. Required protection from acid fumes obtained by nickel-plating Cu tube. Resistance to oxidizing and reducing atmospheres good.	
Particular Applications	International standard 630 to 1063°C - Pt/90Pt10Rh		Used in oxidizing atmosphere in electric furnaces, ceramic kilns, tube stills.		Industrial uses up to 800°c, especially for reducing atmospheres. Steel annealing, boiler flues, tube stills.		Industrial uses, as a tube element in steam lines, internal combustion engines, low temperature measurements.	
Extension wire color code	Green		Yellow		Black		Blue	
	Red	Black	Yellow	Red	White	Red	Blue	Red
Manufs'. Guar. acc. (I.S.A. STD. acc.)	+2 to 0 at 1220°C **		32-530°F ±4°F 530-2300°F ±3/4% *		32-530°F ±4°F 530-1400°F ±3/4%		-75-200°F ±1.5°F 200-700°F ±3/4% *	

**See B. Brenner

* Closer tolerance on request

In order to understand the changes which occur in a particular thermocouple, some background discussion is pertinent on what is known about thermocouples in general. Particularly important is information which may be gained by examining the methods of testing and calibrating thermocouple systems which have slowly developed during the last 50 years. These have been summarized in a number of outstanding articles on thermocouple technology.

In 1935 Roeser, Dahl, Gowens and Wensel (9, 10) described in detail the methods for testing thermocouples and thermocouple materials at the National Bureau of Standards. The precautions which must be observed in order to attain various degrees of accuracy in calibrations at fixed points and by comparison methods were detailed. In addition methods of interpolating between the calibration points are given. Under a section entitled "General Considerations" the authors point out some of the well-known but too often disregarded facts about thermocouples. To wit:

> The temperature-emf relation of a homogeneous thermocouple is a definite physical property and therefore does not depend upon the details of the apparatus or method employed in determining this relation. (A homogeneous thermocouple, in both chemical composition and physical condition throughout its length.) However, the output of an inhomogeneous thermocouple will not be determined solely by the temperature of the hot junction and of the reference junction, as with a new homogeneous thermocouple, but also by the temperature gradient between the hot and cold end, and the pattern of inhomogeniety in the temperature gradient zone. For this reason a used thermocouple should not be removed from its installed location and placed in a calibrating furnace for checking, since it is highly improbable that the temperature gradients in the two locations will be the same. Furthermore the effects of inhomogeniety in both wires may be either additive or subtractive and as the emf developed along an inhomogeneous wire depends upon the temperature distribution, it is evident that corrections for inhomogeniety are impracticable if not impossible.
>
> Regarding the annealing of base-metal thermocouple wires: Practically all base metal wire produced in this country is annealed or given a "Stabilizing heat treatment" by the manufacturer. Such treatment is generally considered sufficient and seldom is it found advisable to further anneal the wire before testing.

Whether the statements in the last paragraph are still generally true statements remains open to question. Roeser, et. al, also point out that in the measurement of the emf of thermocouples an instrument is usually available whose performance is such that the accuracy of the calibration

need not be limited by the accuracy of the emf measurements. While this is certainly true in any standards laboratory, one must be constantly aware of the necessary precautions in the use of any instrument. In general, the calibration techniques in use at the University of Tennessee are the same as those reported in the article by Roeser et. al, and are reported in detail in a later section.

In 1941 a number of articles relating to thermocouple thermometry and its application to measurement of temperature appeared in a book, Temperature, Its Measurement and Control In Science and Industry, Volume I (22). Volume II (23) of this series was published in 1955. Of particular importance to the present research are the findings of Dahl (11) on the stability of base metal thermocouples from 800° to 2200°F. Dahl points out that changes in calibration of chromel-alumel thermocouples start almost immediately upon reaching temperatures in the range 800° to 2200°F. When good temperature control is required this change in calibration cannot always be neglected. For instance, chromel-alumel thermocouples heated in air at 800°F for 1000 hours are out of calibration less than 0.5°F at 800°F, whereas chromel-alumel thermocouples heated in air at 2000°F for 1000 hours are out of calibration by nearly 20°F at 2000°F, and wires heated at 2200°F for only 200 hours are out of calibration 20°F at 2000°F. In addition to reporting serious changes in calibrations which occur, the effect of a change in the depth of immersion of the chromel-alumel thermocouple are reported. Wires heated at 2000°F for 20 hours showed a change in calibration of nearly 100°F when the depth of immersion was decreased by 3 inches. These results emphasize the importance of never decreasing the depth of immersion of a thermocouple after it has once been placed in service, which is to say that the inhomogeneous portion of the thermocouple should be kept in a uniform temperature zone where it has no effect on the thermocouple output.

Other articles of utmost importance relating to thermocouples, combinations, general thermoelectric thermometry, and methods of testing thermocouples are contained in references 22 and 23.

In 1955 Martin and Berry (12) reported the results of an investigation test to determine thermocouple immersion errors. These results, as those of Dahl, indicate that the change in calibration is very serious if the depth of immersion is decreased (25°C for 6 inch decrease) but not too serious if the

depth is increased (2°C for 6 inch increase). Results on wires held at 800°C for 50 days strongly indicate that the thermoelectric characteristics of a thermocouple are affected by exposure to elevated temperatures. The reported results also indicate that the stability of a chromel-alumel thermocouple can be improved to some extent by heat treatment prior to use. Martin and Berry also state:

> ...another solution to the problem of stability is to adopt the use of Pt/PtRh thermocouples. Although these thermocouples will develop inhomogenieties during use, they are markedly superior in this respect to chromel-alumel thermocouples in an oxidizing atmosphere. In some instances, considerations of over-all economy may make mandatory the use of "expensive" materials.

In 1955 Spooner and Thomas (13) reported the results of tests on increasing the stability of chromel-alumel thermocouples by (1) controlling the thermocouple well size (L/D ratio) and (2) by controlling the atmosphere around the thermocouple by sealing the system with a titanium "getter" for oxygen removal. When the length of the well is extremely large compared to the diameter of the well the effective conditions around the thermocouple wires are reducing and the observed drift of the thermocouple output is high and decreasing in value (-80°F in 24 hours at 1800°F). When the length to diameter ratio is small, oxidizing conditions are maintained around the wire by convection currents and the drift of the thermocouple is small. Likewise when the system is sealed with a "getter", the oxygen is consumed and an inert (N_2) atmosphere surrounds the wire. This prevents the preferential oxidation of chromium from the chromel and the observed drift is zero in 24 hours at 1800°F. These results emphasize the importance of the thermocouple surroundings and make it imperative that the details of the geometry of all drift tests be given.

In order to evaluate any thermocouple system, and chromel-alumel in particular, one is faced with the need of an understanding of the results of the cited articles. Calibration methods appear to have been adequately resolved by the Bureau of Standards, however recent results of the Oak Ridge National Laboratory and University of Tennessee standards laboratories which will be discussed later, indicate that difficulties still exist here. The stability tests of Dahl and those of Spooner and Thomas indicate that changes can occur in chromel-alumel thermocouples and that the magnitude can be expected to change at a constant temperature depending upon the geometry of the test. Thermocouple immersion errors reported by Dahl, and Martin and Berry,

indicate that both initial and induced thermocouple inhomogeniety is a major source of error and may mask other factors contributing to instability. These are but a few of the problems involved in understanding the basic factors governing chromel-alumel thermocouple behavior.

CHAPTER III

EQUIPMENT

It is the purpose of this chapter to describe in some detail the equipment which has been constructed and placed in operation. This includes drift test equipment, individual wire testing equipment and equipment for the cataloging of the literature survey of thermocouples.

Literature Survey

The objective of the present project is to understand observed phenomena in chromel-alumel thermocouples. A comprehensive literature survey of what is known about temperature measurement by thermocouples in general thus constitutes an important portion of this objective. A rather comprehensive literature survey has been conducted and a number of the references obtained have been studied. More than 4000 references have been cataloged in a punched card system (McBee Keysort WCX-869). These references were assembled from abstracting journals (Chemical Abstracts 1907-1957, Metals Review 1945-1956, Ceramics Abstracts 1930-1957) and from references cited in text books on temperature measurement. The cataloging system is divided into eight major divisions, 104 subdivisions and 34 minor divisions. The major divisions are:

1. Thermocouple Theory
2. Thermocouple Systems
3. Individual Thermocouple Properties
4. Thermocouple Measurements and Control
5. Thermocouple Applications
6. Thermocouple Life
7. Thermocouple Processing
8. Temperature Sensing Devices

This survey was conducted from the viewpoint that returns comparable to the total work expended might not be immediate, but that as particular problems arose, the value of having on hand an essentially complete set of references in a specific field would justify the project. Several of these references have been cited in the introduction as sources of background information on the problems existing with chromel-alumel thermocouples. Several other references of importance which have been collected are: (1) The original work by Seebeck between 1820 and 1830. (2) The patents on chromel and alumel by A. L. Marsh (15).

(3) The extensive work by W. P. White and L. H. Adams (16) on detection of spurious thermals due to inhomogenieties. (4) The recent patents by C. L. Carter (17) on enameling of high temperature thermocouples for oxidation protection. It is thought that this list of references will prove to be of increasing value as the research continues. A major effort is being made to keep this listing up-to-date and a comprehensive listing will be prepared for distribution by February 1, 1958.

Thermocouple Drift Test Equipment

In order to establish the magnitude of the drift error and to define further the present problem, a number of drift tests have been run at the University of Tennessee and at Oak Ridge National Laboratory. The method of testing the stability of thermocouples at high temperatures used, was to place the thermocouples in a furnace at a temperature and monitor the output of the thermocouples as a function of time. To accommodate a large number of samples at approximately the same temperature, special drift blocks were constructed from copper blocks sheathed in inconel for oxidation protection. The copper blocks measured 2" x 2" x 14" and contained wells of inconel tubing 9 inches deep and .300 inches inside diameter. Six drift blocks were constructed and contained 9 holes with the geometry of the holes as shown in Figure 1. Figure 1 also shows the temperature distribution in the test blocks at 600°, 800°, and 1000°C. The thermocouples being studies were placed in holes 1, 2, 3, 4, 6, 7, 8, 9, and the comparison or reference thermocouple was placed in hole 5, the latter being used only when the emf of test thermocouples was being determined. The comparison temperature was determined with a 30 gauge Pt-90Pt10Rh low mass thermocouple. This small thermocouple was used so that insertion into the system would minimize changes of the temperature distribution in the massive copper block.

Test thermocouples were insulated by using six-hole one inch long porcelain beads, 0.240 inches O.D. (2200°F maximum temperature). These beads allowed three thermocouples per hole in the copper block and thus 24 test thermocouples could be placed in each block. The furnaces were well insulated with Sil-O-Cel insulation and employed nichrome resistance windings. The voltage to the windings was adjusted with a variable transformer and after

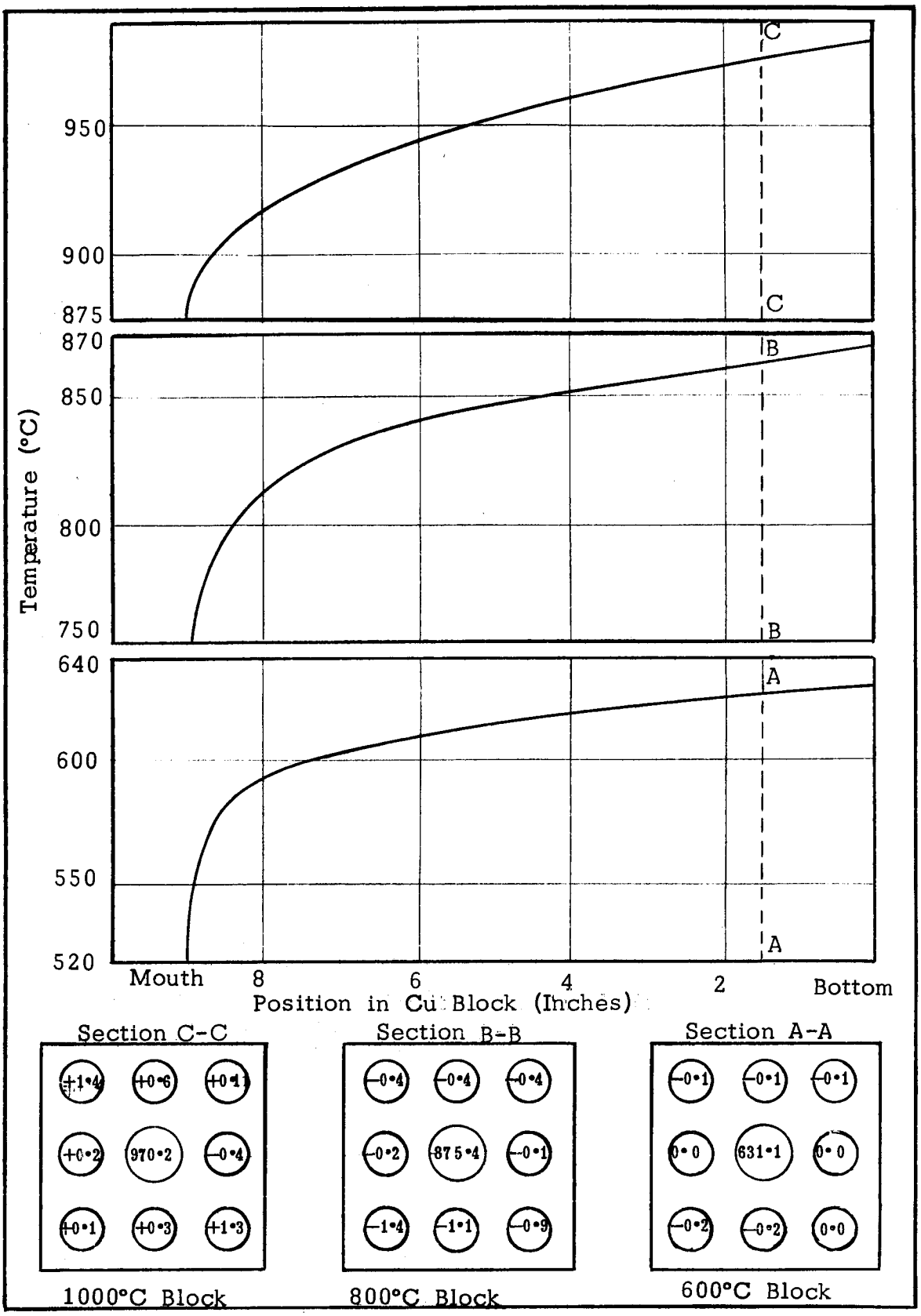

FIGURE 1 - DRIFT BLOCK TEMPERATURE PROFILES

steady state conditions were reached in the furnace surroundings, the average furnace temperature was found to change by less than 5°C over a testing period which usually lasted for several weeks. This performance was surpisingly good and avoided the necessity of elaborate temperature control equipment.

All emf measurements were made using a reference junction of 0°C and comparisions were made with a platinum-rhodium working standard thermocouple to obtain the absolute temperature. If the test chromel-alumel thermocouple emf indicated a temperature above the absolute temperature, the drift was considered as positive, and vice versa. All emf measurements were made using a type K-2 potentiometer.

Chromel-Alumel thermocouples generate 40 to 42 microvolts per °C, depending upon the temperature. The potentiometer is considered accurate to better than ±3 microvolts, thus the measurement of the thermocouple emf contains an error of less than ±0.1°C. At least two other errors occur in the drift test data. First there is some variation in the hole to hole temperatures in the copper block, as well as some variation of hole temperatures due to line voltage fluctuation. Typical hole variations are illustrated in Figure 1 and are seen to be ±0.3°C at 630°C, ±0.7°C at 875°C and ±0.9°C at 970°C. It is believed that corrections can be applied to the thermocouples in a given hole to bring their indicated temperature closer (within ±0.2°C) to the temperature of the reference or comparison thermocouple. The temperature variation during the data taking period is corrected for by taking readings with the comparison thermocouple after every six test thermocouples are read. A second error arises due to the individual thermocouples of a particular type (say, Kanthal) varying somewhat in temperature indication within a given hole. Recent results indicate that by proper positioning of the individual hot junction beads the variation can be reduced to less than ±0.2°C. These three sources of error give a cumulative error of less than ±0.5°C for a set of chromel-alumel thermocouples in a drift test. The results of the drift tests are reported in the following chapter, however corrections have not been applied for the latter two errors. The results are considered to be accurate to within ±3°C without these corrections.

Equipment for Thermocouple Calibrations

The following sections will be devoted to the calibration room equipment and its operation, to equipment for the determination of thermocouple homogeniety, to equipment for the heat treatment of thermocouples and thermocouple wires, and to metallographic equipment for the examination of the metal microstructures.

With the exception of the results found for the drift tests, the effect of a treatment given to thermocouple wire is determined from the resulting calibration of the treated product. Considerable attention has been given to the construction of standards room equipment which would be capable of arriving at the above decision with the minimum expenditure of effort, but the maximum attainable accuracy. The two methods of calibration which are being employed in the University of Tennessee standards room are the comparison method and the fixed melting point method (both methods are described in detail by Roeser and Wensel (10)).

In the fixed melting point method, a thermocouple is calibrated at the melting or freezing point of a number of metals. The present equipment consists of a bank of four furnaces each of which contains a standard metal. The standard metal is contained in high purity graphite crucibles, which are positioned in refractory tubes as shown in Figure 2. The equipment is constructed to allow a helium gas blanket to be maintained over the standard metal. The thermocouple to be calibrated is inserted in the axial refractory tube and thus it is open to the atmosphere but separated from the melt by a carbon tube and the closed-end refractory tube. This system has the advantage that the melt is protected from contamination by oxidation, but it has the disadvantage that the melt cannot be stirred to reduce temperature nonuniformity prior to cooling. However the thermal conductivity of liquid metals is extremely high and as a further aid in creating a uniform temperature distribution, a copper sleeve has been added outside the graphite crucible. The fixed points which are being accepted for use are given in Table II. The first six of the above have been melted into high purity graphite crucibles and the latter two are available in wire form for determining the melting points by the open circuit method. With the furnace bank it is possible to run four melting points in less than two hours with a minimum of trouble in changing the thermocouple from one point to the next. The thermocouple emf measurements for these calibrations are made with a Leeds and Northrup K-3 potentiometer and a galvanometer system which has a sensitivity of a 1.6 cm deflection/microvolt. The limit of error of the K-3 potentiometer as advertised by the manufacturer is ± (0.015% + 0.5 microvolts). The reference junction for calibrations by the fixed point method is an ice bath (0°C).

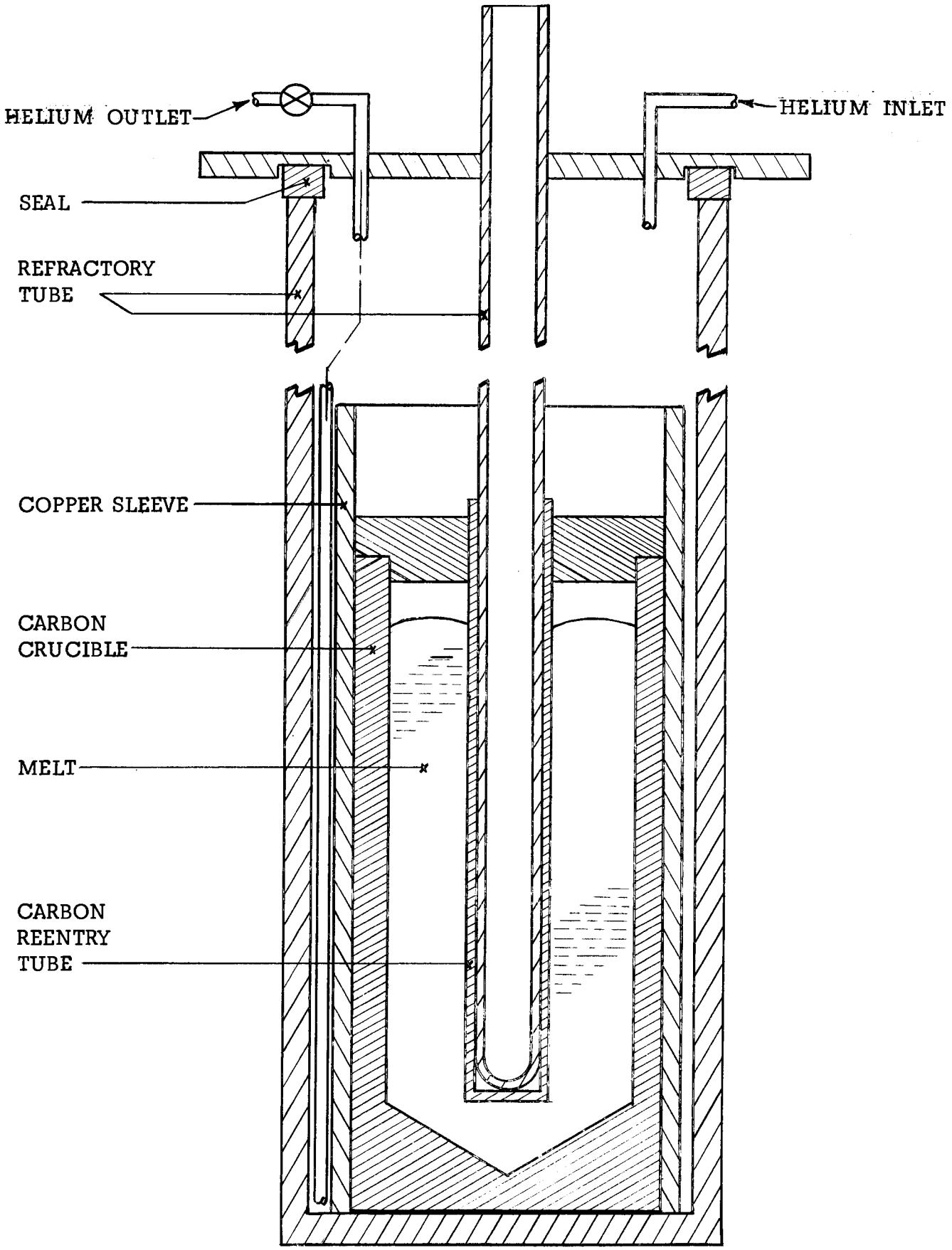

FIGURE 2 - STANDARD MELTING POINT APPARATUS

For calibrations by the comparison method the thermocouple to be calibrated is compared to a known standardized thermocouple. In most cases this is a platinum-90platinum 10rhodium working standard thermocouple which has been carefully calibrated against a standard Pt-90Pt 10Rh thermocouple. The

Table II

Fixed Point Metals

Metal	Source	Melting Point
Tin	N.B.S.	231.9°C
Lead	N.B.S.	327.4°C
Zinc	N.B.S.	419.5°C
Aluminum	N.B.S	659.7°C
Antimony (99.999%)	Assoc. Lead Mfg. Ltd.	630.5°C
Silver (99.99%)	Handy and Harmon	960.5°C
Gold	Handy and Harmon	1063.0°C

standard thermocouples are normally calibrated by the melting point method covering the entire range of use and this thermocouple is then used only to check the working standard thermocouples. Thus the possibility of contaminating this thermocouple with base metal constituents is reduced since it is never directly used in a base metal calibration.

The working standard thermocouple is brought into good thermal contact with the thermocouple to be calibrated and this combination is heated through the desired range for calibration. A separate potentiometer is used to measure each emf, one connected to each thermocouple, and each potentiometer is provided with a galvanometer system. Simultaneous readings are obtained by setting one potentiometer so that at one instant both thermocouples are balanced. Readings may be taken at any number of points with a slowly rising or falling temperature in the region of concern.

In order to calibrate a thermocouple in the least possible time by this method, it was necessary to construct a furnace that heated and cooled rapidly. This was accomplished by constructing the rapid heating and cooling furnace

utilizing a heating element of a Hastelloy B tube which is 1-3/4 inches inside diameter, 2 inches outside diameter and 29 inches in length. The large current necessary to heat the tube is obtained from a special high current transformer. A large cylindrical shield of sheet metal is mounted around the heating tube to reduce the radiation loss. To minimize lag no thermal insulation is used between the heating tube and the radiation shield. The central portions of this furnace is practically at a uniform temperature and the water-cooled terminals produce a very sharp temperature gradient at each end. This furnace is capable of reaching 1000°C in 5 to 7 minutes. A schematic circuit is shown in Figure 3. Figure 4 is a photograph of the standards room equipment showing the rapid heating furnace, the bank of furnaces for the fixed melting point determinations and the K-3 potentiometer and galvanometer system.

In addition to these two methods of thermocouple calibration, a method of comparison to a calibrated platinum resistance thermometer has been utilized. This calibration is carried out in a large copper block which is designed to position the resistance thermometer in a central hole in the block and the thermocouples to be calibrated are placed in surrounding holes. The copper block is heated by nichrome resistance windings and there is no detectable temperature difference between the various holes if sufficient time is given for stabilization at any given temperature. In this method the absolute temperature of the furnace is determined by the resistance thermometer and the corresponding emf of the thermocouple is measured on a Rubicon Type C Microvolt Potentiometer. Thus the absolute temperature can be determined to at least 0.05°C and the major limitations are in the emf measuring equipment and spurious thermal effects in the thermocouple circuit. This type of calibration is somewhat slow because of the slow response of the copper block. Calibrations can only be made up to 630°C because of the temperature limitation on the resistance thermometer. As a low temperature check on the standard thermocouples this speed is not objectionable, but it is unlikely that this apparatus will ever be used for obtaining rapid calibrations.

Homogeniety Test Equipment

As pointed out in the introduction, for the emf of a thermocouple to significantly indicate the temperature of the hot junction, the thermocouple wires must

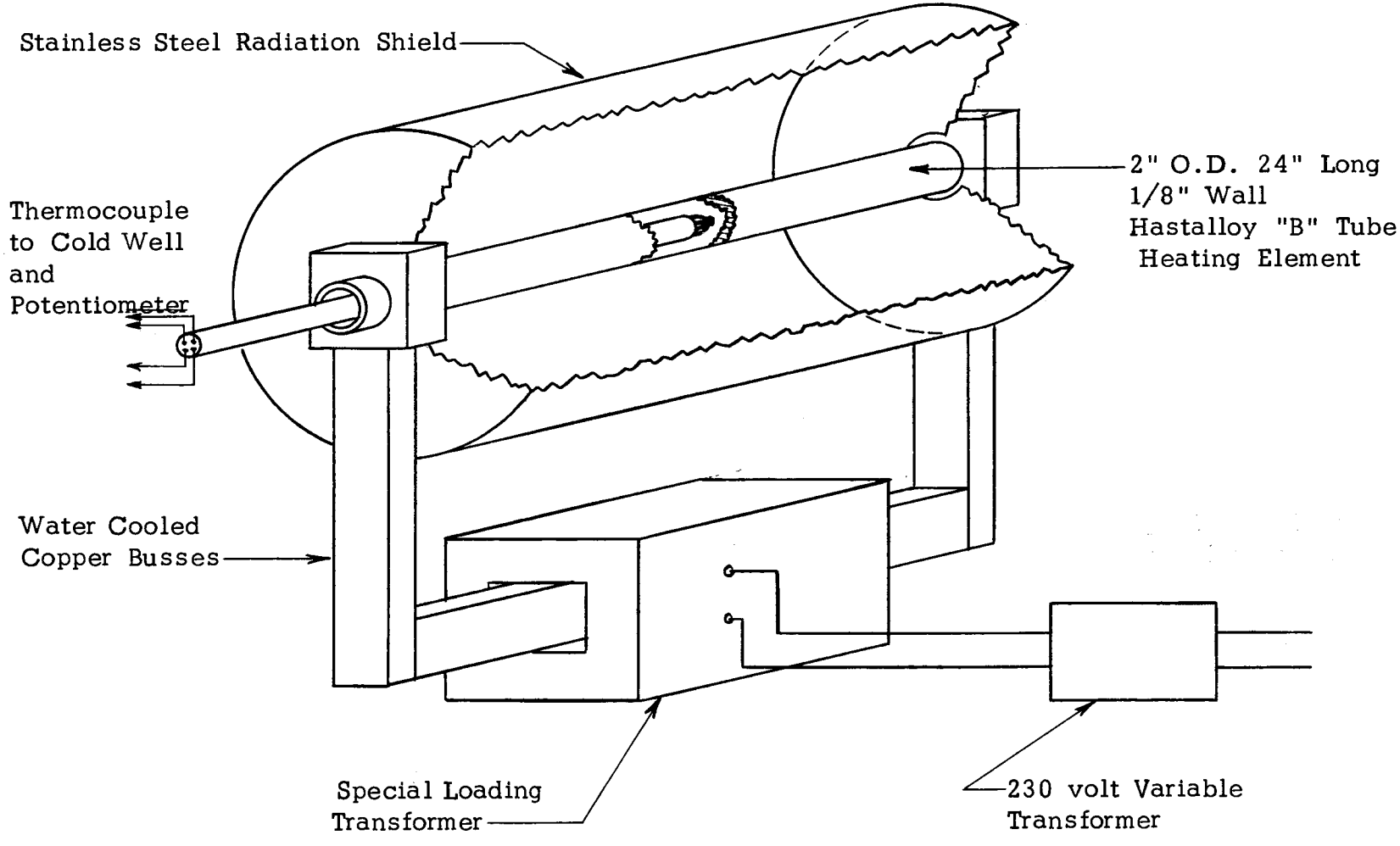

FIGURE 3 - SCHEMATIC DRAWING OF THE RAPID HEATING COMPARISON CALIBRATION FURNACE

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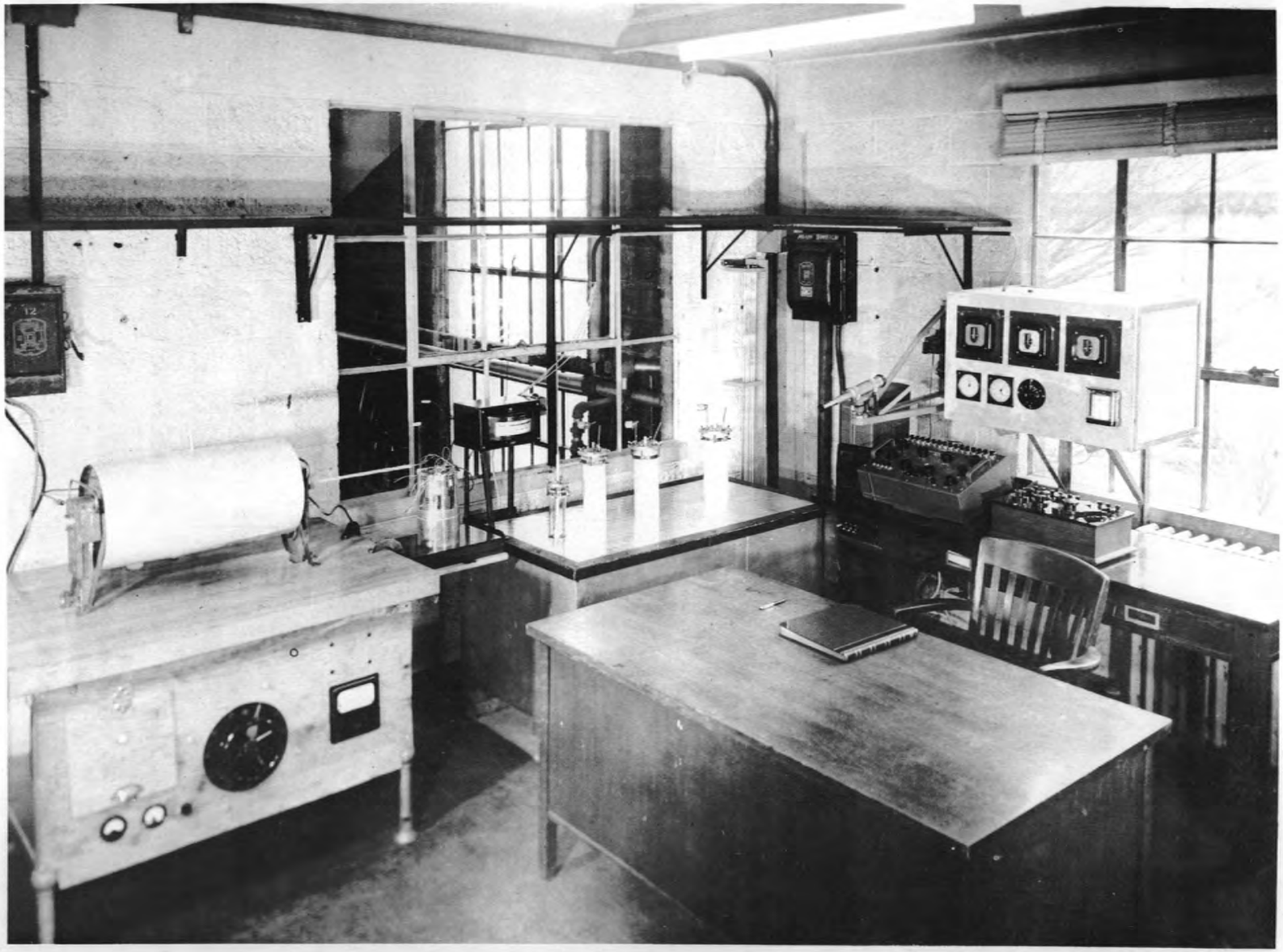


FIGURE 4 – PHOTOGRAPH OF THE STANDARDS ROOM EQUIPMENT

be homogeneous throughout. Several methods are described in the literature for testing for inhomogenieties in thermocouples either initially present or introduced during service. Basically each of these methods involves exposing a closed loop of a single wire of the thermocouple to a temperature gradient. Experimentally this has been accomplished with a piece of chromel or alumel, which passes through a furnace in which the temperature gradients are known and the ends are in a cold well (0°C) from which copper leads are taken to suitable measuring equipment. As the furnace passes over this length of wire the spurious emf is detected alone and in the present investigation is recorded by means of a microvolt amplifier and an electronic strip chart recorder.

Two quite different types of gradient furnaces have been utilized, and yielded the temperature gradients shown in Figure 5.

In addition to these two furnaces a third furnace based on a different concept is under construction at the present time which is believed to be superior to both of the above techniques. This latter furnace method is patterned after a design W. P. White and L. H. Adams (15) made in 1915 for the investigation of inhomogenieties in constantan for use in calorimetric measurements. A schematic drawing of this apparatus is shown in Figure 6. This method compares a length of wire passing through a temperature gradient to a piece of wire from the same spool or a piece of wire of known behavior in a second fixed temperature gradient. The testing apparatus consists of two spools mounted in the same plane with one spool at ambient temperature and the other contained in a furnace. The wire is coiled from one spool to the other and in doing this it passes through the temperature gradient (entry Gradient) upon entering or leaving the furnace. The wire is introduced into the apparatus in such a manner that the ends of the wire pass out the axes of the spools and go to cold wells and on to the recording system. In this manner the wire lead from the spool at room temperature is exposed to virtually no temperature gradient in passing into the ice well, but the wire lead passing from the axis of the spool in the furnace is exposed to a very large temperature gradient (axial gradient). The axial gradient may be quite different from the entry gradient, but the fact that the wire lead is fixed in the axial gradient enables a comparison of the behavior of overall length of the wire as it is exposed to the entry gradient. The design of this appa-

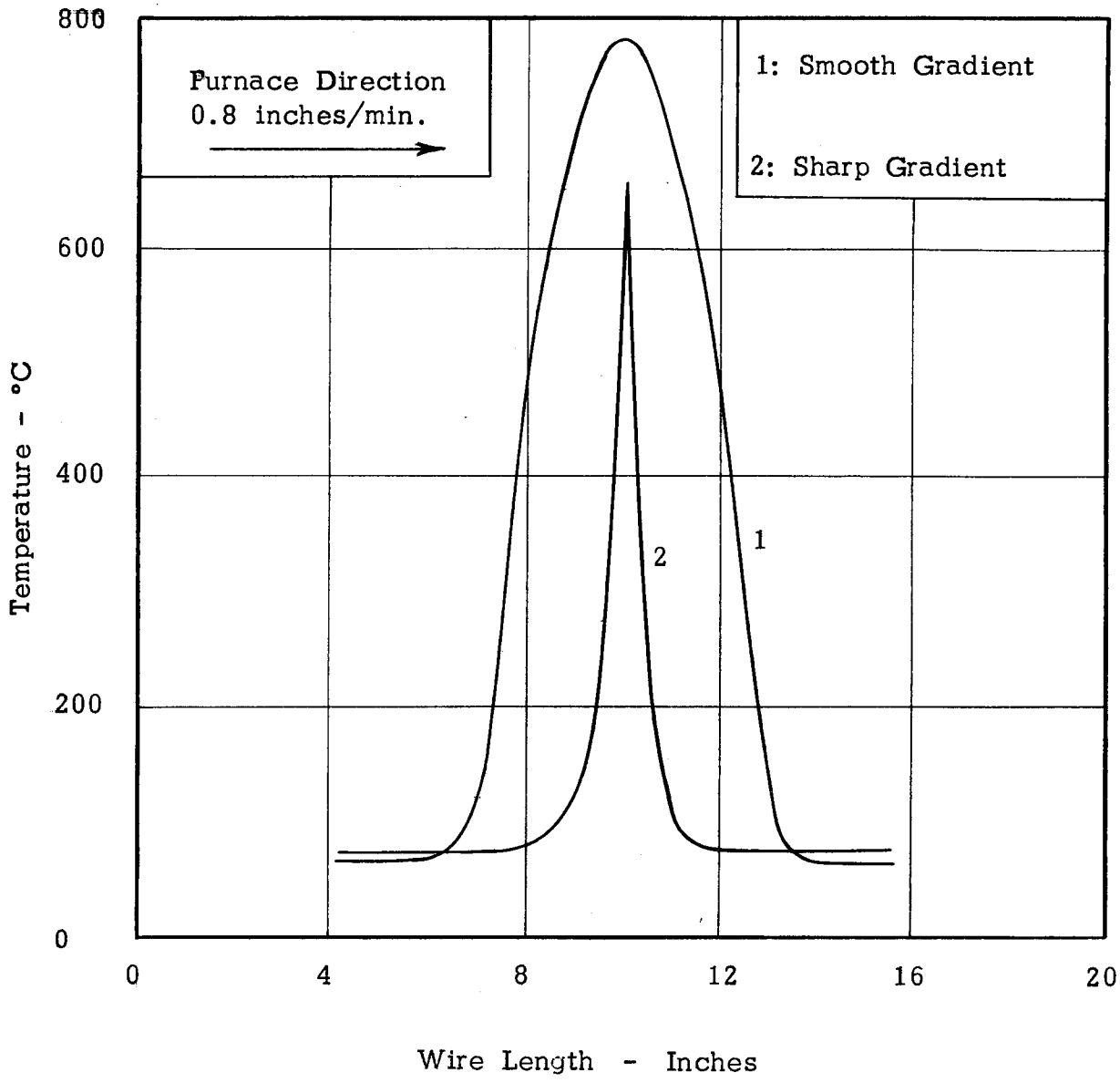


FIGURE 5 - TEMPERATURE PROFILE OF SMOOTH AND SHARP GRADIENT FURNACES

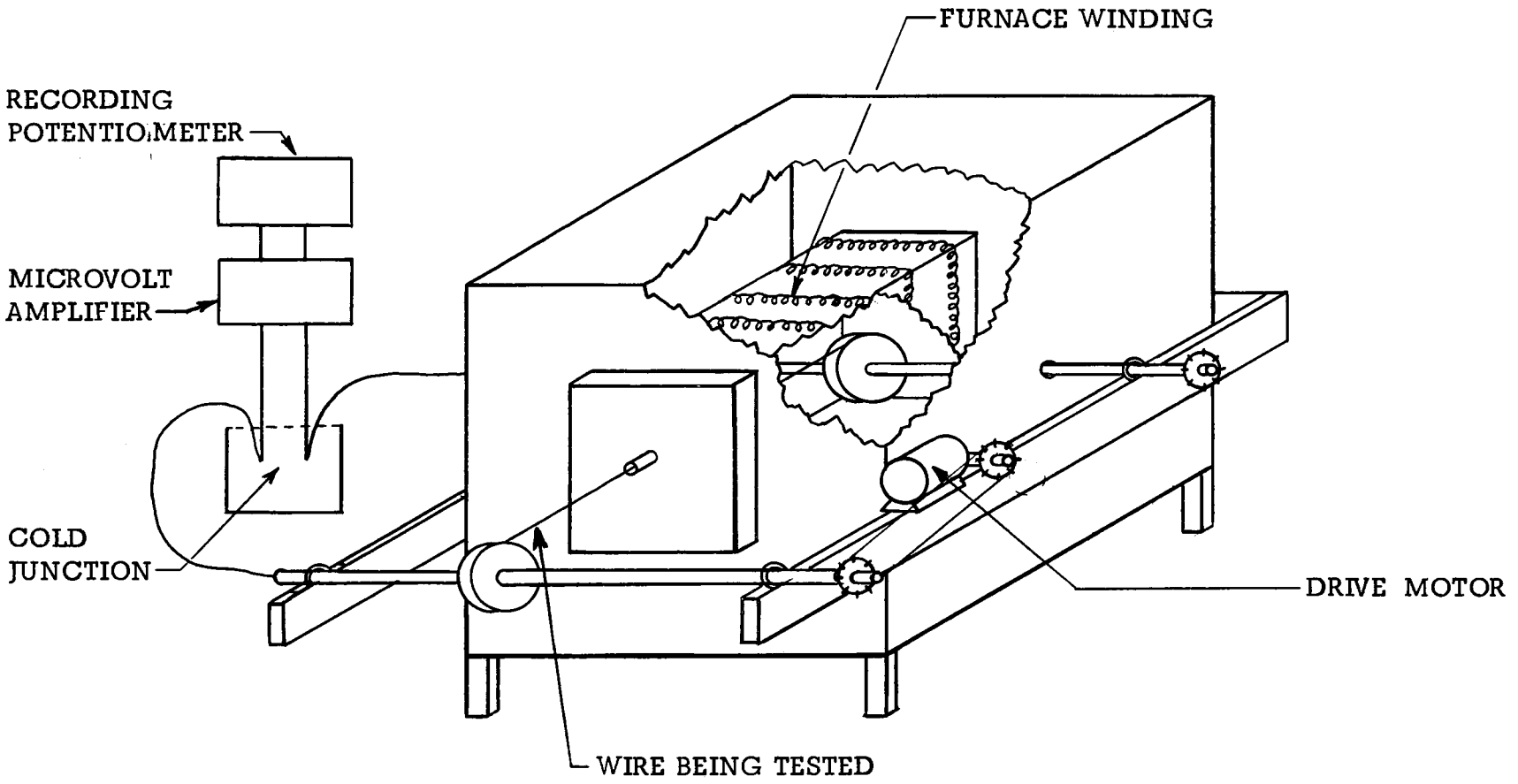


FIGURE 6 - SCHEMATIC DRAWING OF THE UNILATERAL GRADIENT FURNACE

ratus will enable one to test up to 300 feet of wire at one time. The preliminary results from this apparatus and the results of the original temperature gradient furnaces are reported in the following chapter.

Heat Treating Equipment

Reference has been made to the "Stabilizing Heat Treatment" given to thermocouple wires by thermocouple suppliers and to the possible improvement of performance of thermocouples by heat treatments. To investigate a possible improvement of performance by heat treatment, annealing and heat treatment facilities have been constructed. This equipment is such that annealing can be done in vacuum or under an atmosphere of almost any gas. Electrical heating is used with the wires being directly heated in vertically mounted pyrex tubes. The tube for annealing under an atmosphere is 6 inches inside diameter and 10 feet tall. The wires are suspended vertically in the tube and heated by passing an electric current through them. This tube has rubber gasket seals at the top and bottom and the gas inlet and outlet is such that complete purging of the system is possible. The vacuum annealing apparatus tube is 3 inches inside diameter and 8 feet tall and the heating is done in the same manner as for the gas annealing. A vacuum of the order of 10^{-5}mm of mercury can be maintained in this tube for prolonged treatments. Annealing in air is done by two methods: either by suspending the wire from two electrodes and passing a current through the wire or by placing the wires in one of the high temperature furnaces. The furnace bank for the melting point calibrations may also be used for annealing wire in an inert or reducing atmosphere. In this latter case the standard metal is removed from the refractory container and replaced by the wire to be heat treated. This latter technique has the advantage that creep of the wire is reduced during the test. This is important since it is conceivable that reduction in the wire size could cause localized heating due to a decrease in cross section in the directly heated wire area and this could mask the results of the test. Several preliminary heat treatments have been run in these apparatuses and the results of these tests are reported in the following chapter.

Metallographic Equipment

Metallographic equipment has been constructed and assembled for processing

samples of thermocouples for examination of the metal microstructures for the detection of possible metallurgical changes in the wire which could explain some of the observed phenomena in the thermocouples. Samples of thermocouple wires have been prepared using this equipment and microstructures of some of these samples and their interpretations are reported in the following chapter.

CHAPTER IV

EXPERIMENTAL RESULTS AND DISCUSSION

Introduction

The primary purpose of this chapter is to report the results obtained in this investigation to date utilizing the equipment which has been described. The reasons for utilizing the specific approaches will be re-emphasized as well as those results which have been pertinent in establishing more definitely the future approach necessary for the completion of the original objectives. Many of the results which are here reported are from experiments still in progress. The final interpretation of some of this work will not be possible until completion of these experiments.

Because of the widespread use of thermocouples and the many environments of operation, one finds that in the practical applications of thermocouples their behavior is influenced by many variables. First, information obtained from references resulting from the literature survey on thermocouple thermometry has proved to be extremely helpful in the interpretation of observed phenomena. Second, discussions between the staffs of the University of Tennessee and the Oak Ridge National Laobratory as well as a visit made to the major thermocouple producers and vendors has helped maintain the proper prospective of more basic studies in thermocouple thermometry. Since experimental data and/or "handbook rules" without the proper interpretation are of very limited practical value, considerable time has been spent in studying the literature for thermocouple characteristics. Some of the pertinent reference material relative to chromel and alumel was given in Chapter II. These and additional references will be considered in greater detail in the following sections.

Thermoelectric Characteristics of Chromel and Alumel

Chromel P and Alumel are patented alloys produced by Hoskins Manufacturing Company, Detroit, Michigan. These alloys are advertised as follows (17):

> "They are processed only by special methods under closely controlled conditions. And, when sold, they are unconditionally guaranteed to register true temperature-emf values within close specified limits. Chromel, or Chromel-P is essentially a heat-resistant nickel-chromium alloy containing

> nearly ten times as much nickel as chromium, but also incorporating nine additional minor constituents which must be carefully controlled. This alloy has an inherent temperature-emf relation that is very positive to almost every known metal or alloy. Alumel is the negative wire in a thermocouple. It is a heat-resistant alloy, but more complex than Chromel P. It contains nickel, manganese, aluminum, and silicon with appreciable percentages of the last three elements...plus eight other minor constituents which must also be carefully controlled. Alumel has an inherent temperature-emf relation that is negative to most metals and alloys. Both Chromel P and Alumel are controlled with reference to a mutual standard, the resultant emf of a thermocouple made from them is also automatically controlled. Thus any length of genuine Chromel P can be used with any length of genuine alumel to produce a thermocouple which will operate within the Hoskins Accuracy Guarantee." (See Table 1, page 7 of this report.)

It is significant to find that for each alloy there are so many additional minor constituents which must be closely controlled. One would think that closer control could be maintained if only two elements were added to produce the alloy. However production problems, such as removal of sulfur from the melt with manganese, deoxidation of the melt with aluminum or magnesium, and the improvement of fabrication performance by the addition of minor constituents, are involved in producing a satisfactory alloy. The present alloys are designed to be stable and meet the accepted calibration curve. To accomplish this, elements have to be added to the alloy to compensate for some of the undesirable effects which the intentionally added elements may have on the calibration of the material. The patents on Chromel and Alumel by Marsh (14) expired in 1923, yet the fact that Hoskins Manufacturing Company is the only producer of these materials in the United States must be considered as an indication of the skill and ability which this company has acquired in producing these alloys.

A re-evaluation of the present complicated chromel and alumel alloys would be in order if it were possible to produce simple stable alloys of the same general type, although not necessarily meeting the present Chromel/Alumel table. This possibility is being studied with interest..

Realizing that many additions are made to the melts for a number of reasons, one might ask why do these alloys generate such a large thermoelectric force? The fundamental answer to this question is beyond the scope of this report. The primary thermoelectric properties of Chromel/Alumel thermocouples are due to the additions of chromium, and of silicon, manganese,

aluminum respectively. It is fortunate that the minor additions do not largely alter the magnitude of the thermoelectric properties of these alloys. The chosen alloys are the compositions which are closest to the peak of the curve in a plot of emf generated versus composition at a constant temperature. Hunter and Jones (24) report this dependence as shown in Figure 7. If the emf generated by a chromel-platinum thermocouple and an alumel-platinum thermocouple is measured at increasing temperatures, then a plot such as appears in Figure 8 is obtained. The net emf of a chromel-alumel thermocouple is the algebraic sum of the above two emfs at a constant temperature and a plot of this is shown in Figure 9.

Roeser and Wensel (10) have stated:

> "Little success has been met in the past in fitting equations to the calibration of chromel-alumel thermocouples in the range 0° to 300°C. A cubic equation of the form $e = at + bt^2 + ct^3$ will be in error by 1°C at 50°C if the constants are determined by calibration at about 100°, 200°, and 300°C. However, it will be accurate to about 0.5°C at 150°C and to about 0.2°C between 200° and 300°C."

As a result the method of interpolating between calibration points has been one which utilizes an experimentally determined difference curve and a reference table. A smoothed reference table with 10°C intervals in which the emf is tabulated to 1 microvolt has been prepared by Hoskins Manufacturing Company (#270, #271 series). This does not mean that an arbitrary thermocouple is accurate to 1 microvolt in the range of its application. Rather, the table is a reference from which difference curves may be based and temperatures obtained. Hoskins' state that their alloys individually meet this table to within ±3/8 percent and this is to be interpreted that there is no need to match chromel and alumel wires for accuracies within ±3/4 percent. Examination of the Hoskins tables indicates that while the thermal emfs of the chromel-alumel, chromel-platinum and alumel-platinum thermocouples are monotonically increasing functions of temperature, the derivative of the emf with respect to temperature are not such functions and in fact vary considerably, though somewhat smoothly. This is shown in Figure 10 with the curves displaced on an expanded absissa. Whether or not theoretical implications can be derived from such a plot is not yet known, but this is being studied with interest. This plot does show some small irregularities

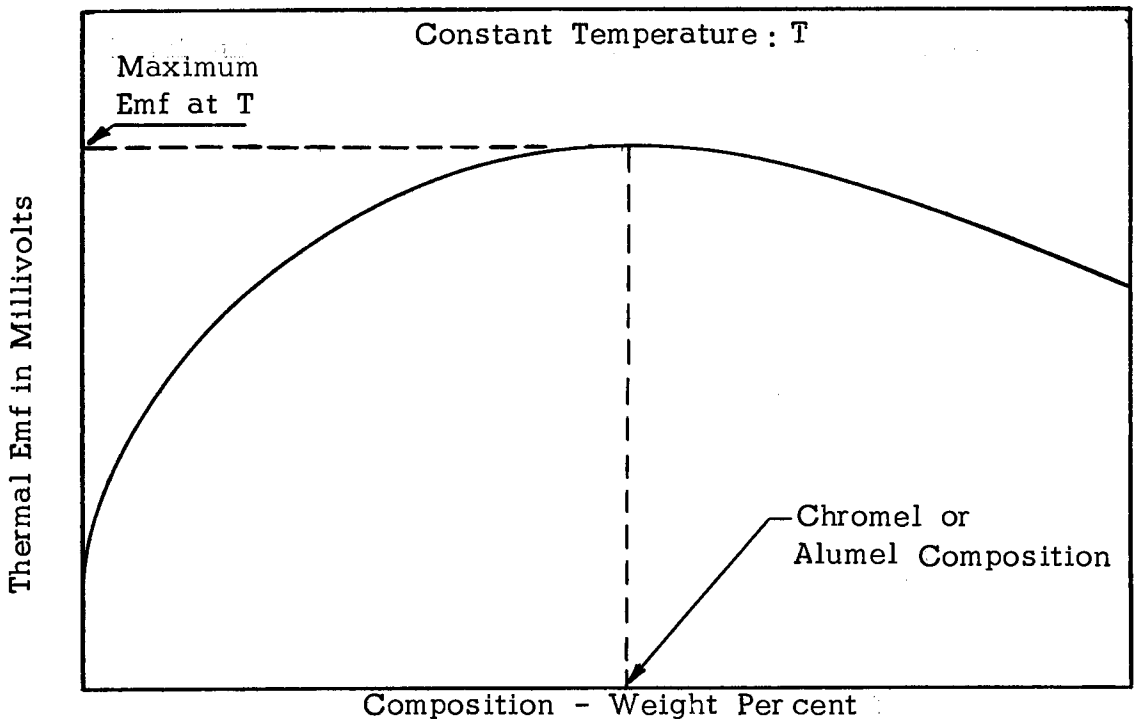


FIGURE 7 - SCHEMATIC DRAWING OF COMPOSITION VERSUS EMF AT A CONSTANT TEMPERATURE

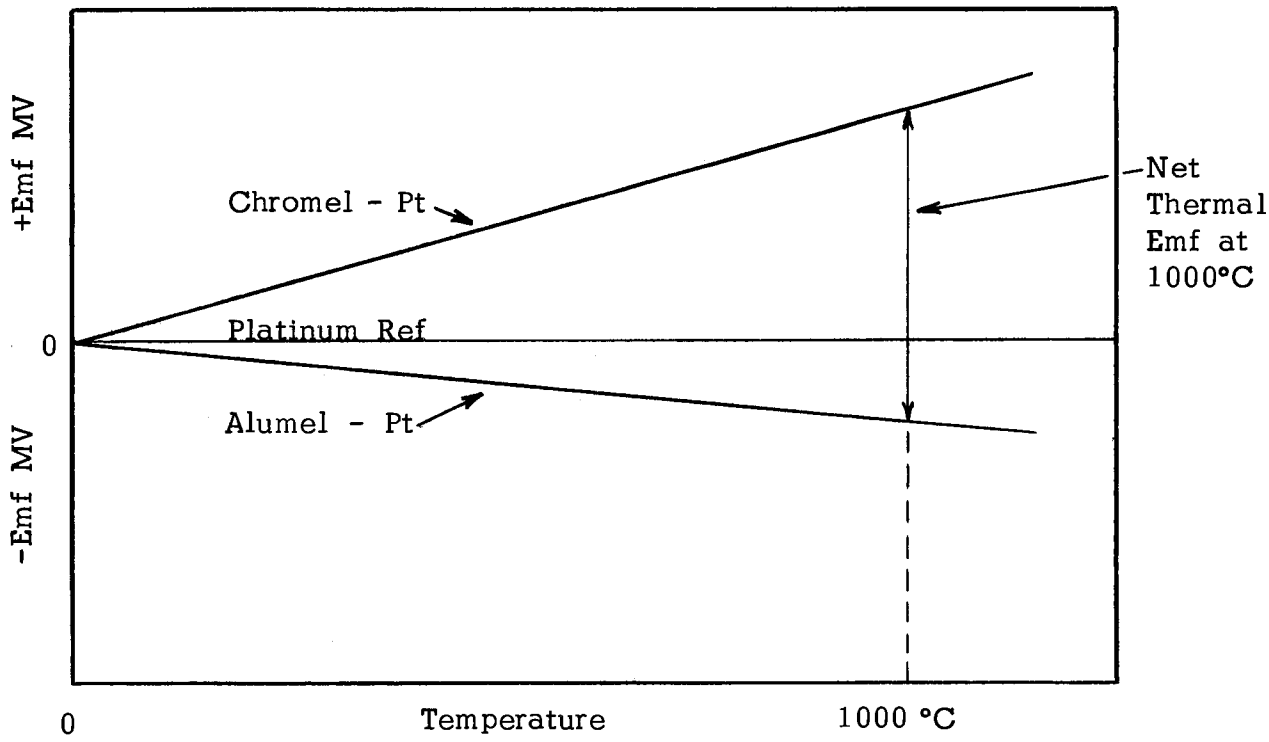


FIGURE 8 - SCHEMATIC DRAWING OF CHROMEL/PLATINUM AND ALUMEL/PLATINUM EMF VERSUS TEMPERATURE

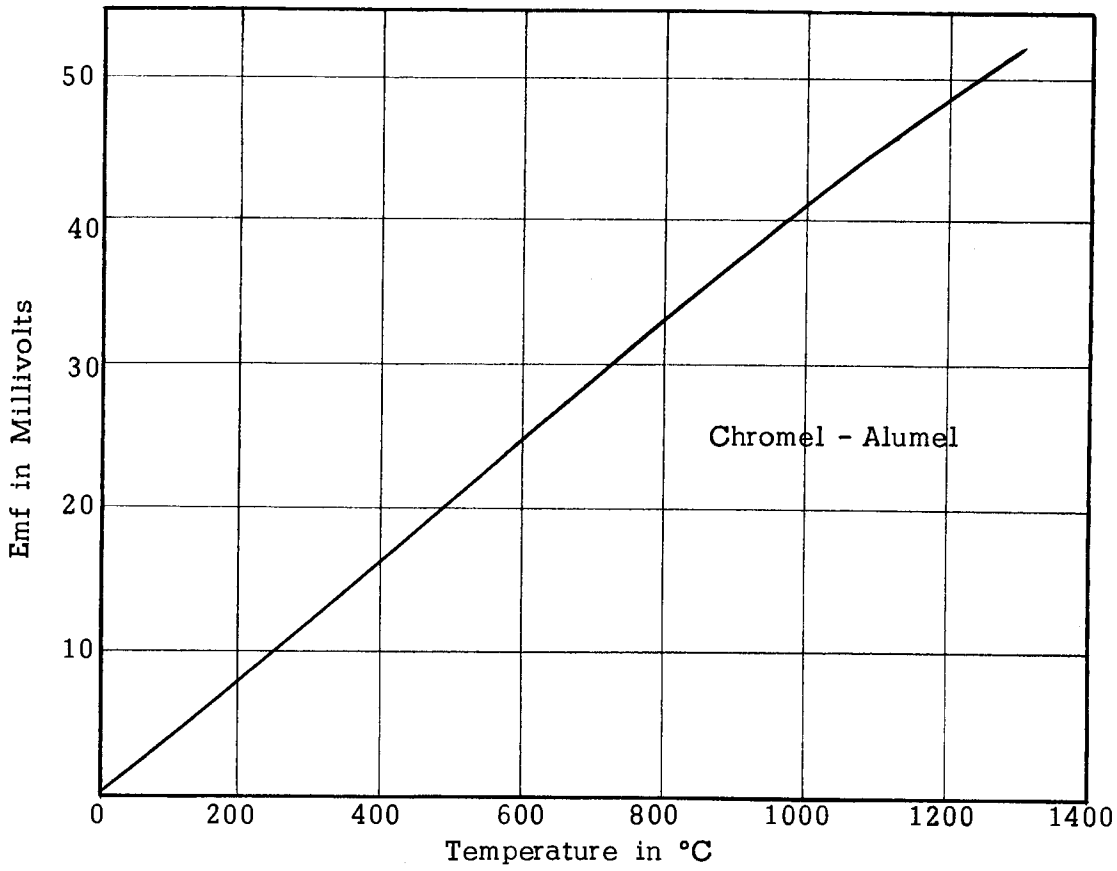


FIGURE 9 - THERMAL EMF OF CHROMEL/ALUMEL

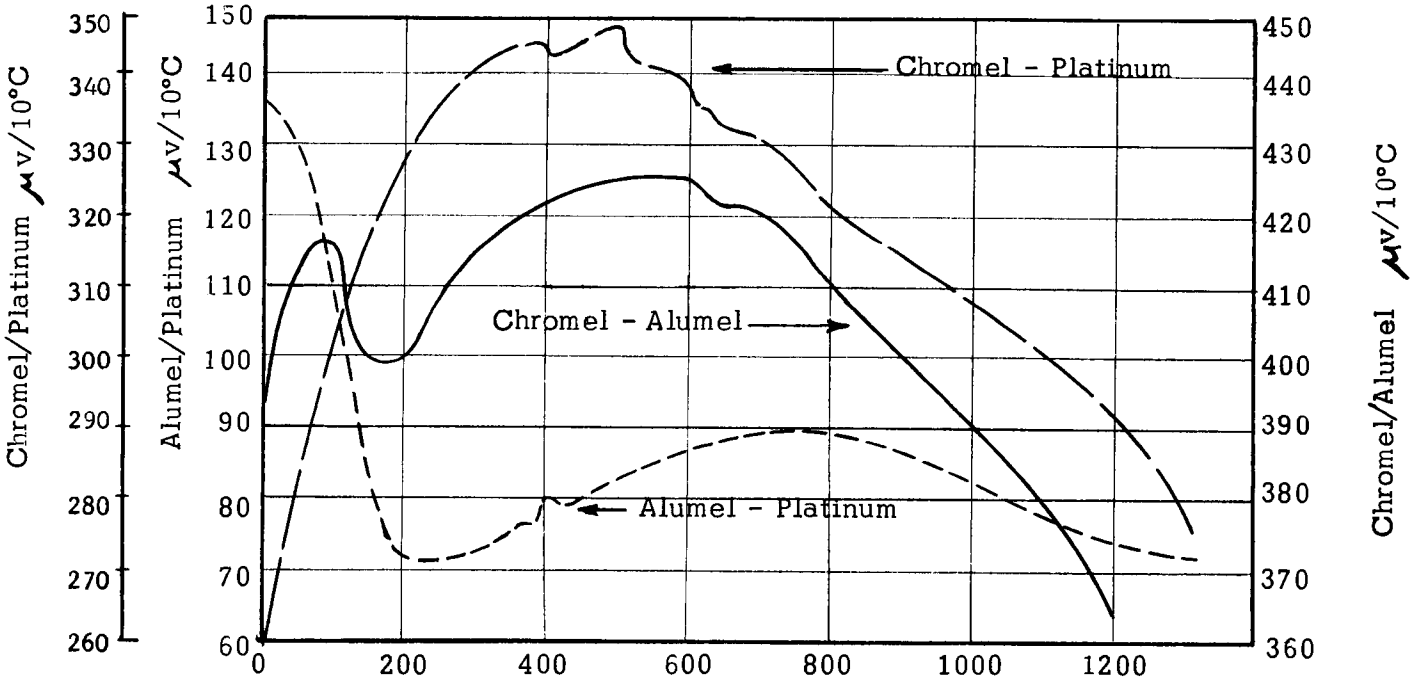


FIGURE 10 - (dE/dT)10°C VERSUS TEMPERATURE FOR CHROMEL/PLATINUM, ALUMEL/PLATINUM, AND CHROMEL/ALUMEL

which may or may not be characteristic of chromel/alumel thermocouples. (500°C-Chromel/Pt.) A revised table has been constructed at Oak Ridge National Laboratory which is smooth to ±1/2 a microvolt and consistent to ± 1 microvolt. This table removes the previously mentioned irregularities in the Hoskins table.

Chemical Analysis of Chromel and Alumel Type Alloys

To obtain additional information on the modern chromel and alumel type alloys, chemical analyses were procured. The exact effects of certain minor elements are not known and it was thought that the chemical analyses would supplement future results in the interpretation of thermocouple characteristics.

Two methods of analysis were chosen. The first method was a qualitative spectrographic analysis on the alloys to indicate which elements were present in major and minor proportions. The second method was a quantitative chemical analysis for major elements, established as present to 0.1% or greater by spectrographic analysis. Carbon was determined by the conventional method. Two laboratories were engaged in performing analysis: Lucius C. Pitkin Company, New York, New York and Oak Ridge National Laboratories, Oak Ridge, Tennessee. The same type samples were submitted to both laboratories and these sets of samples contained certain duplicates to serve as an estimate of the possible variation in results. The samples submitted are listed in Appendix A. The resulting analyses are given in Table III.

This table not only includes the analyses of the alloys now being produced by Hoskins, but also includes an analysis which was obtained from A. I. Dahl on alloys being produced around 1940, (2) an analysis obtained from Thomas and Spooner of the Hoskins Manufacturing Company in 1957, and (3) a proposed analysis by R. C. Lever (19) of the General Electric Company. When the specimens were being prepared for analysis it was decided to include some of the thermocouple wire being produced by vacuum melting by the A. C. Scott, Ltd., NiCr+ and NiAl-. This thermocouple generated an emf which matches the chromel-alumel emf table. Two of the wires listed as Leeds and Northrup undoubtedly are chromel and alumel which was recieved from Hoskins. Wire from this spool was selected because previous comparison

TABLE III

Negative Element Chemical Analysis

Elements	Hosk.	Dahl	G. E.	Hoskins wire L. P.	Hoskins wire ORNL	Hoskins wire ORNL	L and N L. P.	L and N ORNL	A. C. Scott L. P.	A. C. Scott ORNL	Kan.	20 ga. Gem. N	24 ga. Gem. N
Ni	94.32	94.77	93.68	94.27	95.58	95.57	93.73	94.77	96.67	98.80	96.1	96.43	96.78
Si	1.2	1.0	1.35	1.15	0.96	1.14	1.13	1.03	1.50	1.10	2.40	2.75	2.75
Al	1.6	1.9	2.50	1.26	1.61	1.74	1.54	1.91	0.01	0.21	-----	-----	-----
Mn	1.75	2.00	1.90	2.03	2.29	2.31	2.89	3.25	0.43	0.47	0.04	-----	-----
Fe	0.10	0.35	0.58	0.02	0.038	0.018	0.02	0.038	0.04	0.053	0.02	-----	-----
Co	-----	-----	-----	0.38	-----	-----	0.41	0.63	0.01	0.025	-----	-----	-----
Cu	-----	-----	-----	0.0X	-----	0.01	0.0X	0.01	0.69	0.1	-----	-----	-----
C	0.02	0.08	-----	0.03	0.01	0.01	0.022	0.01	0.014	0.01	92ppm	.01	0.01
Cr	-----	-----	-----	-----	-----	-----	-----	----	----	-----	.001-.01	0.005	0.005
Cb	-----	-----	-----	-----	-----	-----	-----	----	-----	----	0.001	0.05	0.05

* L. P. - Lucius Pitkin Co.

ORNL - Oak Ridge National Laboratory

L and N - Leeds and Northrup

G. E. - General Electric

TABLE III

Positive Element Chemical Analysis

Ele-				Hoskins wire			L and N		A. C. Scott			20 ga.	24 ga.
ments	Hosk.	Dahl	G. E.	L. P.	L. P.	ORNL	L. P.	ORNL	L. P.	ORNL	Kan. +	Gem. P	Gem. P
Ni	89.93	89.42	89.73	89.02	89.33	89.53	89.34	90.45	88.22	88.71	89.7	78.67	79.03
Cr	9.46	9.25	9.44	9.53	9.43	9.04	9.42	9.19	9.21	8.93	9.11	17.92	18.07
Si	0.4	0.10	0.46	0.36	0.34	0.33	0.36	0.35	0.28	0.26	0.367	0.74	0.85
Mn	0.05	0.80	----	0.03	0.03	0.02	0.01	0.02	2.09	2.40	0.035	----	----
Al	----	----	----	0.01	0.01	----	0.01	0.1	0.01	----	-----	----	----
Co	----	----	----	0.17	0.15	----	0.13	0.072	0.01	----	-----	----	----
Fe	0.20	0.35	0.37	0.59	0.63	0.052	0.65	0.048	0.02	0.05	0.05	0.73	0.76
Cu	----	----	----	0.0X	0.0X	-----	0.0X	0.01	0.0X	----	102ppm	0.02	0.03
C	0.02	0.08	----	0.0144	0.022	0.02	0.019	0.01	0.014	0.01	-----	----	----
Cb	----	----	----	-----	-----	----	-----	----	-----	----	-----	0.99	0.94

calibrations had revealed that it had a very small deviation from Hoskins Table 271.

The analyses show some variations occur for each element and certainly this is to be expected. The analytical techniques have fixed limits of accuracy and considerable spread exists in the results for the chemical analysis. In addition some of the variation must be attributed to wire inhomogenieties. The results would undoubtedly be of much greater value had a sufficient number of samples each been submitted to permit a statistical treatment.

Also shown in this table are analyses for the Kanthal (±) and Geminol (P/N) thermocouples. As can be seen their negative wires are very similar in composition, whereas the positive wires are quite different.

It is evident that the chemical analyses show some composition differences in wires being supplied as chromel and alumel. Further experimentation is needed to show whether these differences are truly significant. Admittedly, extremely close control of composition must be attained if accurate measurements are to be made on the chromel-alumel performance. Recent information coupled with the above analyses indicate that some possible hope may exist for obtaining a conditional emf tolerance on chromel-alumel closer than the present ones. Private communications with Mr. R. C. Lever of the General Electric Company and Mr. Bjorn Edwin of the A. B. Kanthal Company indicate the following:

> 1. By extremely close control of the raw materials used in melting the original alloy and by closer control of melting conditions, one can produce alloys which have very small variations in composition. ---Lever
>
> 2. The weakest link in the thermocouple is the alumel wire--the less oxidation resistant material. Preferrential oxidation of several constituents (Mn, Al, and Si) has a serious effect on the net emf of the alumel wire. By choosing the alloying constituent for the alumel to be only silicon, one finds that the net change in composition due to loss of only silicon has much less effect on the net emf of the alumel wire. (These results are partially verified later in this Chapter). ---Edwin

As more is learned about these thermocouple alloys, their calibration and their drifts, the overall picture of a better thermocouple seems to be evolving.

The Thermocouple System

Any thermocouple system can be divided into three distinct regions and each

has an effect on the net emf of the thermocouple system. These three parts are: The thermocouple hot junction, the thermocouple reference junction and the thermocouple wires connecting the hot junction and the cold junction. The relative importance of each of these three regions is of definite interest to the thermocouple user, and yet the magnitude of the possible error contribution from each of these regions does not seem to be well-defined in the literature.

Studies Relating to the Thermocouple Reference Junction

At least two methods of accounting for the cold junction temperature are in use today. In many industrial thermocouple applications thermocouple extension leads are used and a reference junction compensation is incorporated in the measuring units. The errors associated with this technique are usually greater than those associated with the laboratory practice of using an ice bath reference junction. However there are definite errors which can be encountered with the latter method unless proper precautions are observed.

Experiments have been conducted on the materials used in preparing an ice bath. By using a resistance thermometer as the temperature sensing device ice baths were made using the following materials:

1. Distilled water ice-distilled water liquid
2. Distilled water tap water ice
3. Tap water ice-tap water liquid
4. Tap water-distilled water ice

If the ice is crushed to less than 1/4 inch granules, then one finds an apparent variation of less than 0.03°C. Variation of a point in the various bath temperature, is as shown in Figure 11. Thus for most thermocouple experiments the third combination is quite satisfactory.

There are several techniques for producing a copper to thermocouple wire connections in the ice bath. Perhaps the most convenient is to use a glass or polyethylene U-tube with the thermocouple wire in one side of the tube and the copper wire in the other side of the tube. The electrical connection between the two can be made by mercury contained in the U-tube. Because the mercury is at 0°C there is a tendency for water to condense on the top of the mercury and eventually lead to a galvanic cell being established in the cold junction which could invalidate all readings. Care must be exercised to avoid this and the system requires continual inspection to preclude the occurrence

of this type cell. In addition studies are being conducted to wet chromel and alumel with mercury to preclude the occurrence of this cell. The results using the U-tube method are most satisfactory and the convenience of the method is a real asset in taking a number of measurements from different thermocouples with a single reference tube apparatus.

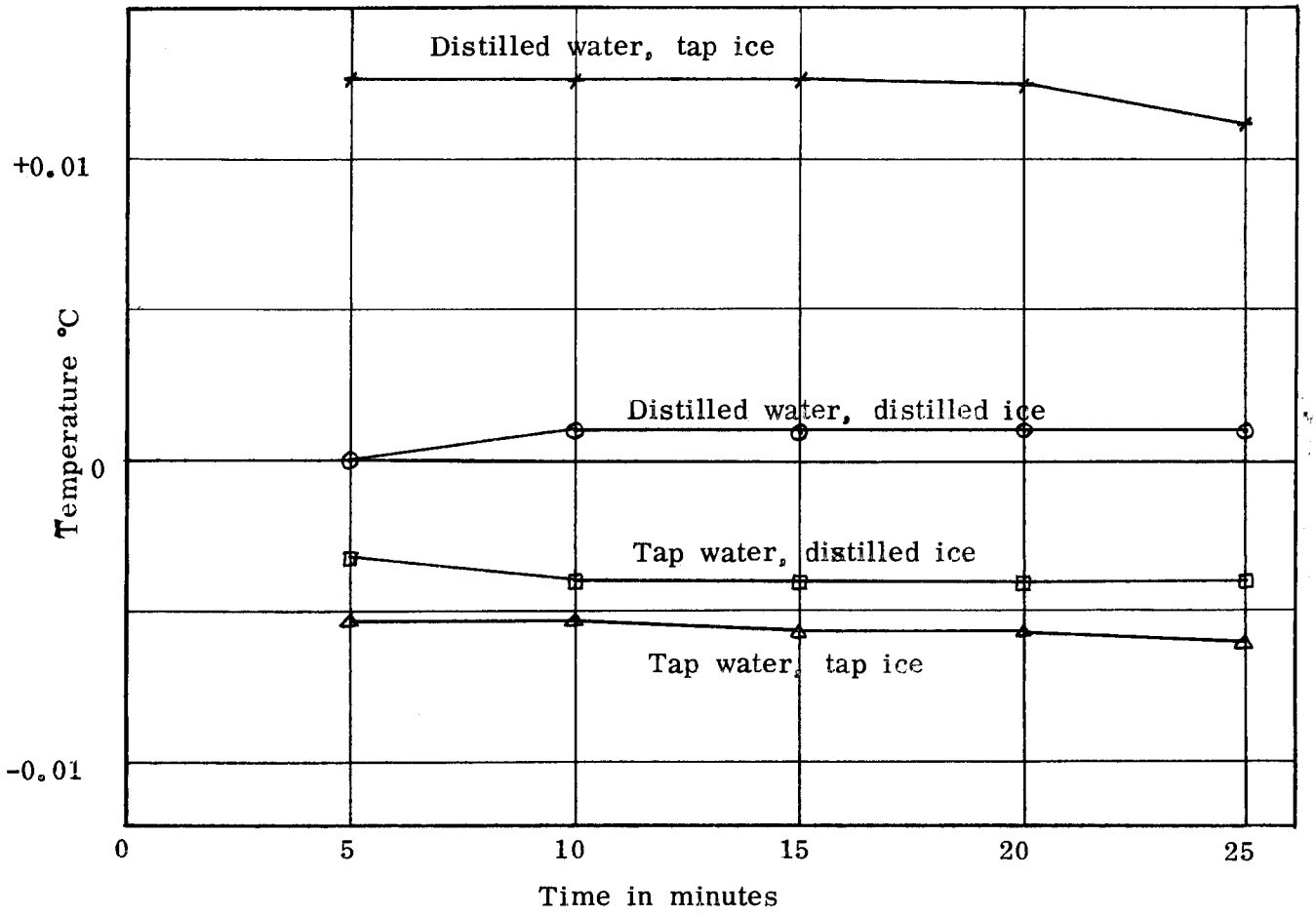


FIGURE 11 - TIME TEMPERATURE CURVES FOR VARIOUS ICE BATH MATERIALS

The position of the cold junction in the dewar containing the ice water mixture is also critical. One's intuition would say to place the cold junction in the geometrical center of the dewar. Careful studies have been made concerning this position and have verified the above. Errors as serious as 2° to 3°C can be encountered if the junction is too close to the bottom, top or sides

of the Dewar.

It was thought that the addition of a layer of oil on the top of the mercury columns would help in reducing the galvanic cell effect due to water condensation. The addition of oil to the cold junction did reduce this effect, but it also introduced an effect which could lead to serious errors, that of high resistance contacts. As the clean wires are introduced into the U-tube they adsorb a film of oil onto their surfaces. This has resulted in a decrease in the sensitivity of the detection system from 1.6cm/microvolt to 0.04cm/microvolt, a factor of 400 for the instrumentation used.

Studies Relating to the Thermocouple Hot Junction

According to the law of intermediate metals the only requirement on the hot junction is that the two homogeneous dissimilar metals be in good electrical contact in order to properly indicate the temperature of the junction. The first place at which the metals come into electrical contact will be the point of temperature indication of the thermocouple. Thus if a long twist is used in connecting the two wires, then the temperature quite possibly could be indicative of the first twist. In the measurement of the temperature of surfaces, certain justifiable rules of thumb have developed. If small wires are used, and thus heat conduction from the surface is minimized, then a satisfactory technique consists of individually welding the two wires to the surface. This method makes the hot junction through the surface of the material (a conductor) and closely approximates the surface temperature. If the material is a nonconductor and the thermocouple wires are not of small size, then one normally positions the hot junction so that the wires leading from the bead lie on the surface for at least ten diameters of the wire.

In recent years some attention has been called to the method of manufacture of thermocouple hot junctions. At least ten acceptable techniques exist, with the most prominent ones being those which endeavor to protect the wires from oxidation during the preparation of the junction. This tends to result in a hot junction with a better appearance and higher strength for service at high temperatures.

Studies on copper-constantan thermocouple behavior as influenced by preparation techniques have been made by Glickstein (20). This study involved

the use of duplex copper-constantan thermocouples in which the junction was manufactured by nine different techniques. These thermocouples were followed as a function of time at temperature and the resulting data indicated a consistent drift for each couple depending on its manufacture. The results are supported by photomicrographs of each junction which suggest that the different drifts observed are due to solid state reactions occurring in reaching equilibrium conditions in the hot junction. The author goes on to say that small emf's are generated by these reactions which add to or subtract from the thermal emf of the thermocouple and thus give consistent separations between the various thermocouples. Certain theoretical and practical questions arise in the interpretation of these results. There is an apparent violation of the second law of thermodynamics since the thermal emf of a thermocouple system is a thermodynamic quantity and a point function, it should not be influenced in the above manner. If there is a difference in emf of the various systems in a constant temperature region then it should be possible to construct an engine to work on the difference in energy. Certain practical considerations arise in reviewing the wires used in the experiment. The wires were duplex insulated wires and whether they were in a fully annealed state (homogeneous) is certainly open to speculation. Metallurgical changes such as stress relief and recovery could be occurring in these alloys in the regions of the temperature gradient and lead to results very similar to the ones which have been reported. The net emf of the wires thus being associated with the change in the state of physical homogeniety of the wires, rather than with the hot junction, which is supposedly at a constant temperature.

These and other considerations warranted a detailed investigation of this phenomena. The same thermocouple system has been investigated. However, individual 20 gauge copper and constantan wires were used and the thermocouples were so connected that interconnections between the various legs of the thermocouple wires could be made to check for spurious thermal emfs. Three types of thermocouple hot junctions were prepared: (1) Mercury welding with an oil protective layer, (2) Clean twist, (3) Welding by means of a singly carbon arc drawn to the twisted thermocouple. These three were chosen because their original report (20) indicated that these should have

given the greatest spread in the date. The results of the drifts in the inconel sheathed copper blocks are shown in Figure 12. An initial decrease in emf is noted, which is no doubt due to changes occurring in the wire at 550°F. However it will be noted that all of the thermocouples shifted together in this downward change. The thermocouple hot junction temperatures differed slightly from hole to hole. However, when the junctions were in the same tube in the block, they drifted together without any real differences in thermal emfs, independent of junction preparation. In addition, the interconnections between thermocouples indicated that the spurious thermals in the copper:copper combinations were never greater than 5 microvolts, and usually much less than 2 microvolts. Whereas the interconnections between the constantan:constantan wires were as large as 20 microvolts in certain wires. These results when considered with the variations observed from one thermocouple to the next are sufficient to reduce the apparent spread in the data to a random spread less than 0.3°C.

The above results are inconsistent with those reported by the University of Florida. They do indicate however that the University of Florida research probably was influenced by variables other than the method of preparation of the hot junction.

The art of preparation of the hot junction requires some skill and doubtless needs further study. The strength of the resulting hot junction is of primary interest and studies correlating the metallography and strength of the junction are being anticipated in the hopes of developing standard techniques of junction manufacture.

Studies Related to Effects of Homogeniety on Thermocouple Behavior

Foremost in the laws governing the wires used for thermocouples is that the wire must be homogeneous throughout. Both chemical and mechanical defects can contribute to the inhomogeniety of the wire. Chemical defects may be caused by variations in composition of the wire from position to position along the wire. This can probably be traced back to either (a) segregation occurring during solidification of the ingot which may not have been removed by annealing; or (b) oxidation reactions between the wire and its environment which cause the preferrential oxidation of one constituent of another or (c) local precipitation reactions involving the formation of metallic

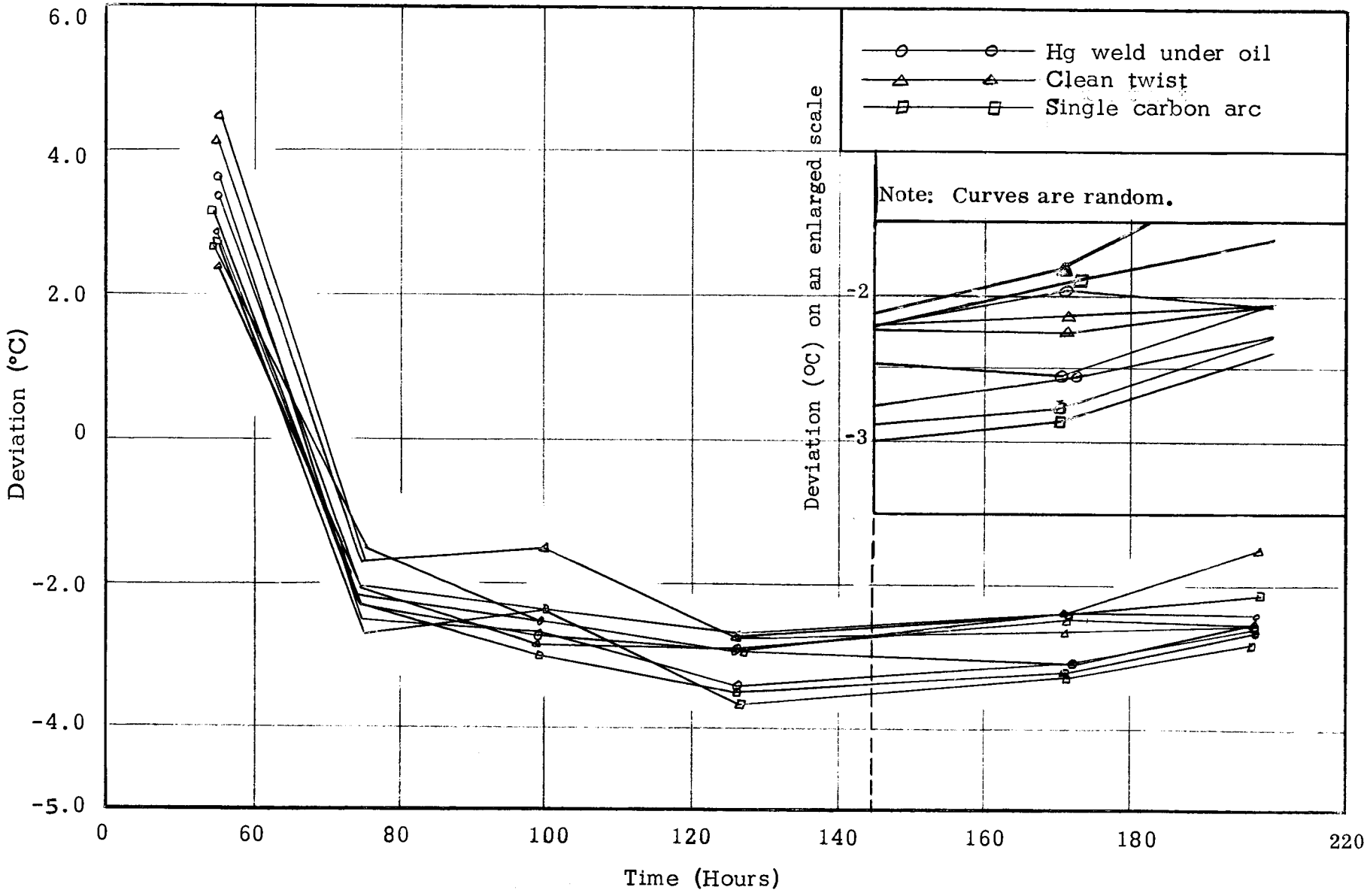


FIGURE 12 - HOT JUNCTION PREPARATION DRIFT EXPERIMENT FOR COPPER/CONSTANTAN THERMOCOUPLES AT 550°F

compounds which occur only at certain temperatures to which the wire is exposed in the temperature gradient passing to the furnace. Physical defects may be caused by variations in the mechanical state of the wire from position to position. These variations are caused by such things as cold work effects due to (a) coiling and uncoiling of the wire from the spool or (b) bending or kinking the wire in placing it in refractory tubes or in placing it in the proper position in the system or (c) erosion of the wire surface in introducing it in the refractory insulator. The magnitude of these various effects needs to be known so that proper interpretation and emphasis can be placed on thermocouple installation practices.

The testing of thermocouples for homogeniety has been reported by White and Adams (15) and the experimental equipment in present use has been largely patterned after their design, as reported in the previous chapter. Palmer (25) has presented tests on chromel, alumel, platinum and platinum-13 rhodium wires in which the quality of the wire is indicated by the record of the emf generated as a furnace passes over a length of the wire. In high quality wires, apparently homogeneous, the spurious emf generated is virtually zero microvolts. The present results show that spurious emfs as large as 1000 microvolts can be generated in the wires of chromel and alumel. White has proposed that the spurious signal can be related to the error in temperature measurement as follows:

$$\Delta t = \frac{Et_2}{et_1}$$

where:

Δt = uncertainty in temperature measurement due to inhomogeniety, °C

E = maximum inhomogeniety, microvolts

e = thermoelectric power of thermocouple used, microvolts/°C

t_1 = temperature rise produced in test, °C

t_2 = operational temperature difference, °C

If this is correct, then errors as large as 22° Celcius can be expected in some of the already tested wires.

The majority of the results being reported here are from tests run on seven foot lengths of wire with two furnaces, a smooth gradient and a sharp gradient (see Figure 5 .) Experiments have been conducted on a number of wires and only the most significant are reported. These are:

1. Alumel-Leeds and Northrup Company
2. Chromel-Hoskins Manufacturing Company
3. Alumel-Hoskins Manufacturing Company
4. Kanthal (+)-Kanthal Corporation
5. Kanthal (-)-Kanthal Corporation
6. NiCr (+)-A. C. Scott Ltd.
7. NiAl (-)- A. C. Scott Ltd.

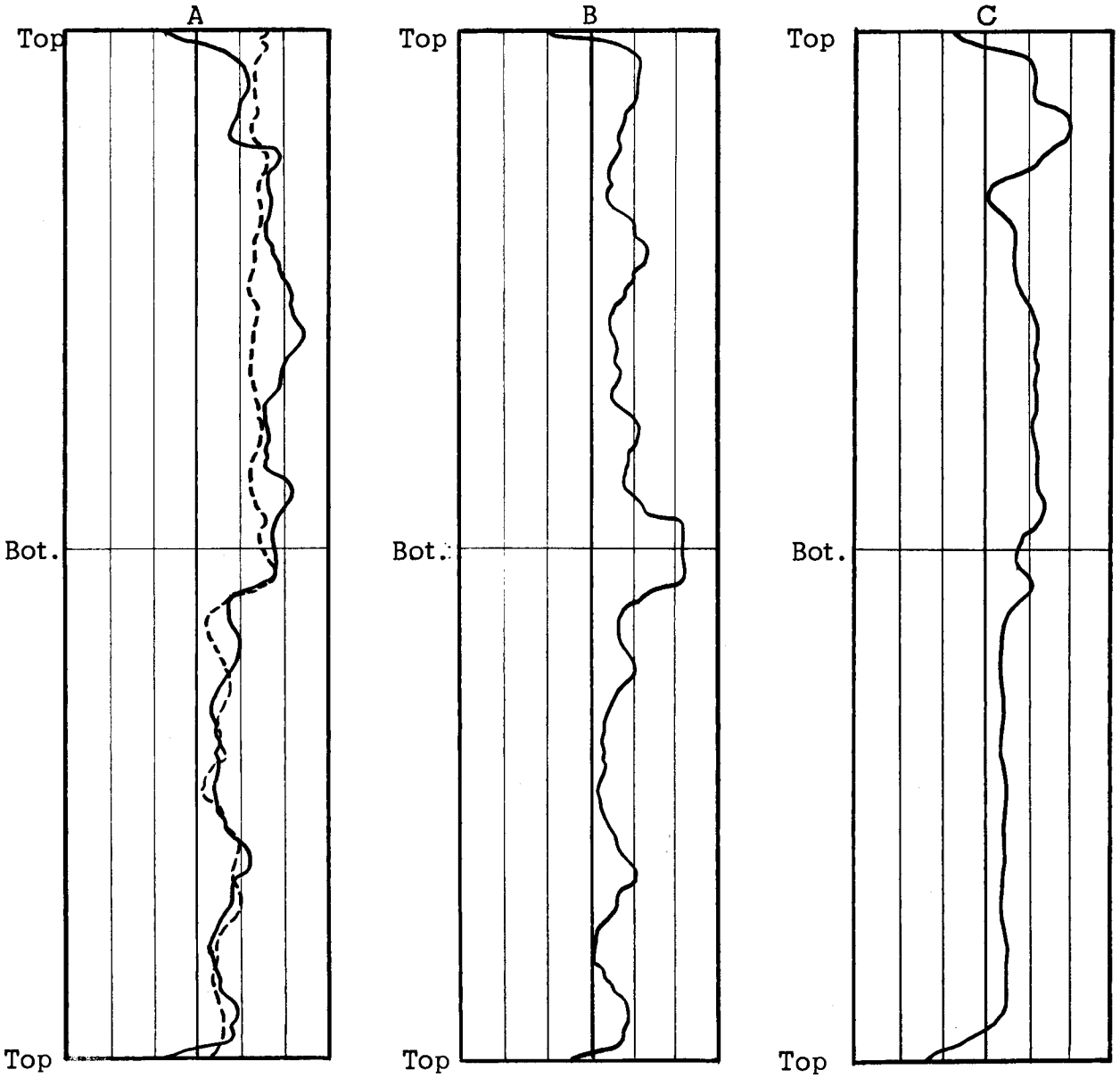
Certain of these wires have been subjected to various treatments such as annealing in air for various periods of time, annealing in vacuum for various periods of time, and pickled prior to testing. The results are shown in Figures 13, 14, 15, 16, 17, and 18.

For a homogeneous metal the spurious emf should be zero when subjected to this type test, and as can be seen this is rarely the case. In these tests the furnace travels from the top of the wire to the bottom a distance of 76 inches in 80 minutes. As the furnace travels down the wire, the emf which is generated is believed to be due to a comparison of the homogeneity in the furnace region. That is, the wire on the upper side of the furnace (wire having been exposed to the maximum temperature of the furnace) is being compared to the wire on the lower side of the furnace (wire entering the furnace). In the as-received wires there is a difference in pattern once the furnace has passed over the wire, and as the furnace continues to pass over, the record continues to shift until the pattern becomes virtually the same. This indicates that a certain amount of annealing will bring the wire to a seemingly constant condition by removal of stresses (recovery) and recrystallization. The fixed offsets which are left may be attributed to composition differences which continue to vary as annealing continues. Pickling the wire results in a record with fewer variations for alumel, thus indicating an emf variation due to the wire surface has been removed (Figure 13). This is not apparent in chromel (Figure 14). Annealing chromel wire in air at 800°C for times up to 19 hours increases the variation found in the wire (Figure 15). This indicates that localized compositional changes are occurring in the wire possibly due to oxidation. Vacuum annealing of chromel does not produce a more homogeneous wire (Figure 16). A higher gradient furnace temperature gives a greater deviation in the as-received chromel and alumel wire.

The sharper furnace gradient indicates a finer structure pattern than

ALUMEL

Leeds-Northrup : 22 Gauge : Oxidized Surface.
Smooth Gradient Furnace ≃800°C Maximum Temperature
Scale : (-150 microvolts-0 +150 microvolts)



As rec'd wire #1 (Full line)
As rec'd wire #2 (Dashed line)

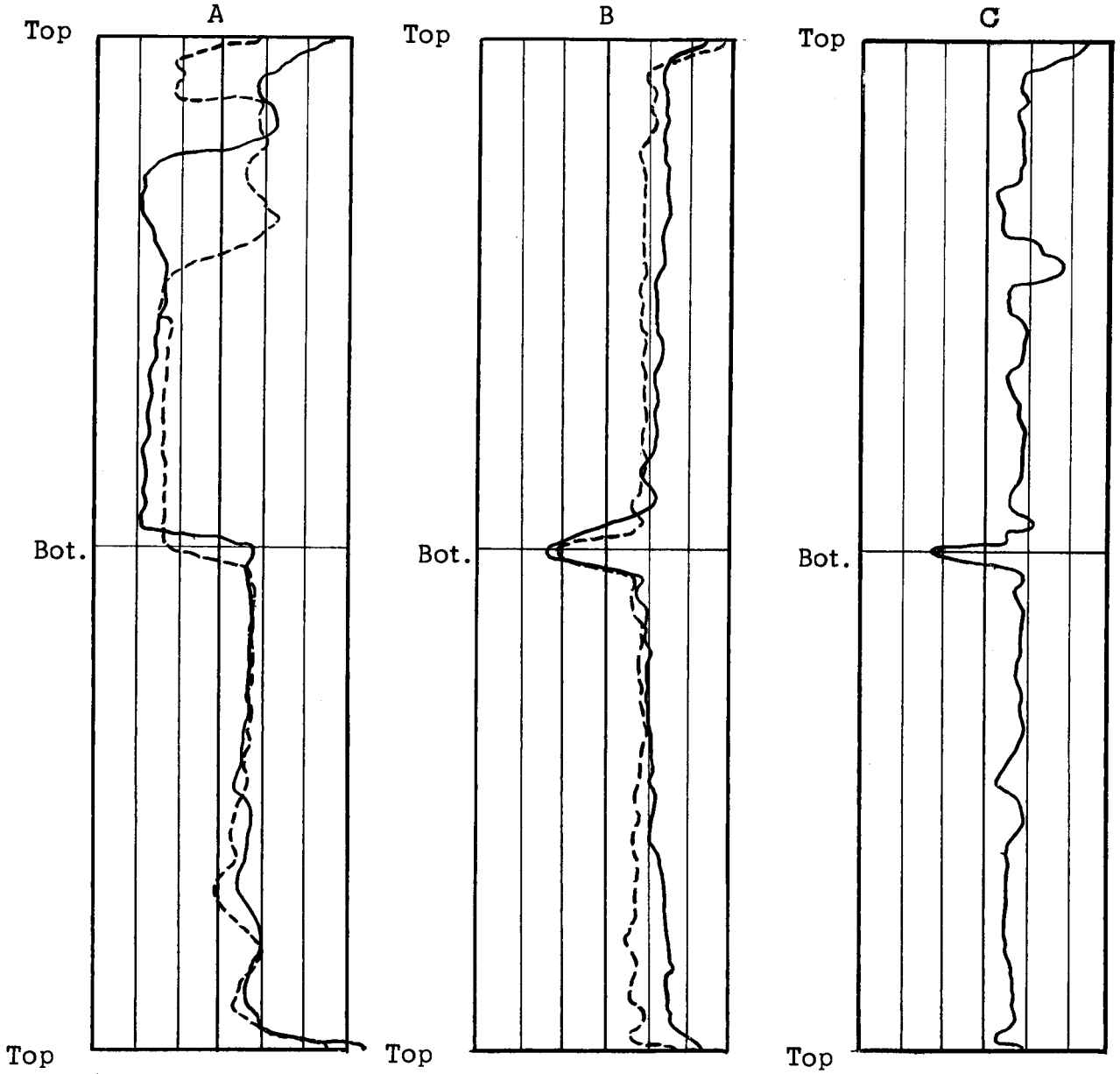
Wire #1 15 cycles later

Same wire pickled

FIGURE 13 - SMOOTH GRADIENT STUDIES ON ALUMEL

CHROMEL

Hoskins Mfg.: 22 gauge : Oxidized surface.
Smooth Gradient Furnace ≃800°C Maximum Temperature
Scale: (-150 microvolts-0 +150 microvolts)



As rec'd wire #1 (Full line)
As rec'd wire #2 (Dashed line)

15 cycles later #1 (Full line)
6 cycles later #2 (Dashed line)

#1 15 cycles later pickled

FIGURE 14 - SMOOTH GRADIENT STUDIES ON CHROMEL

CHROMEL

Hoskins Mfg. : 22 gauge: Oxidized Surface
Smooth Gradient Furnace -800°C Maximum Temperature

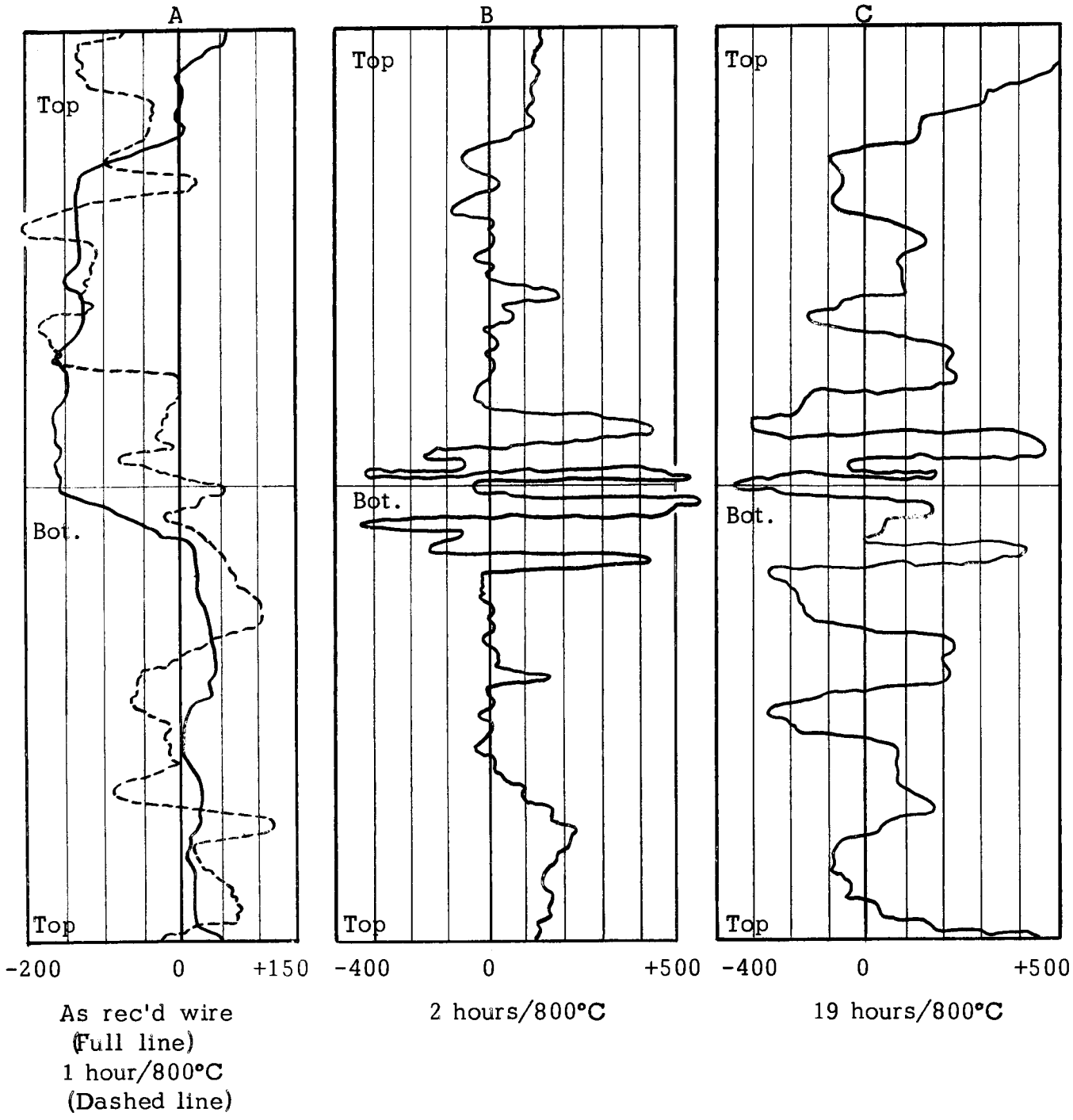


FIGURE 15 - SMOOTH GRADIENT RESULTS ON ANNEALED CHROMEL

Vacuum annealed Chromel and Alumel
Smooth Gradient Furnace

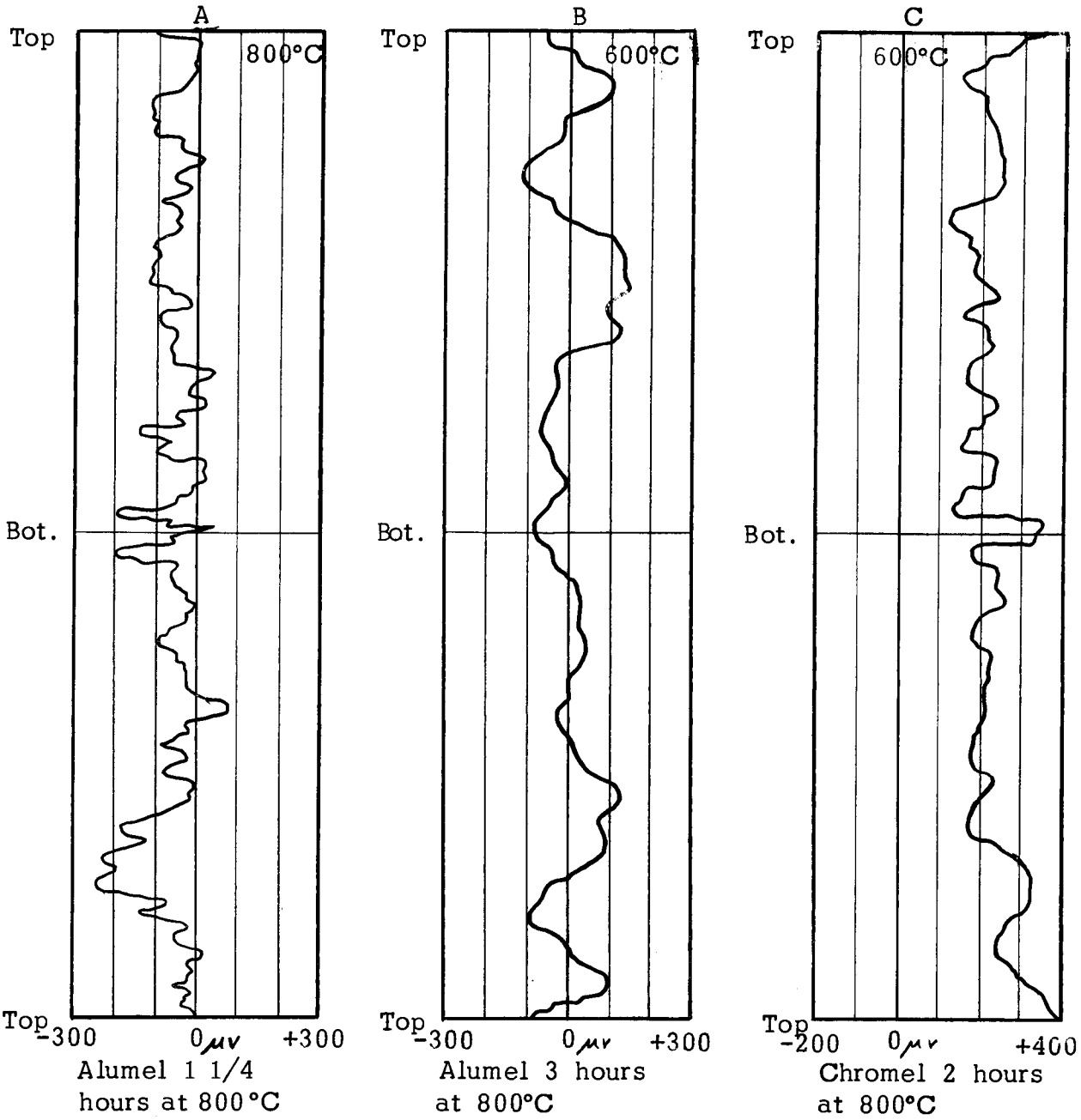


FIGURE 16 - SMOOTH GRADIENT RESULTS ON VACUUM ANNEALED CHROMEL AND ALUMEL

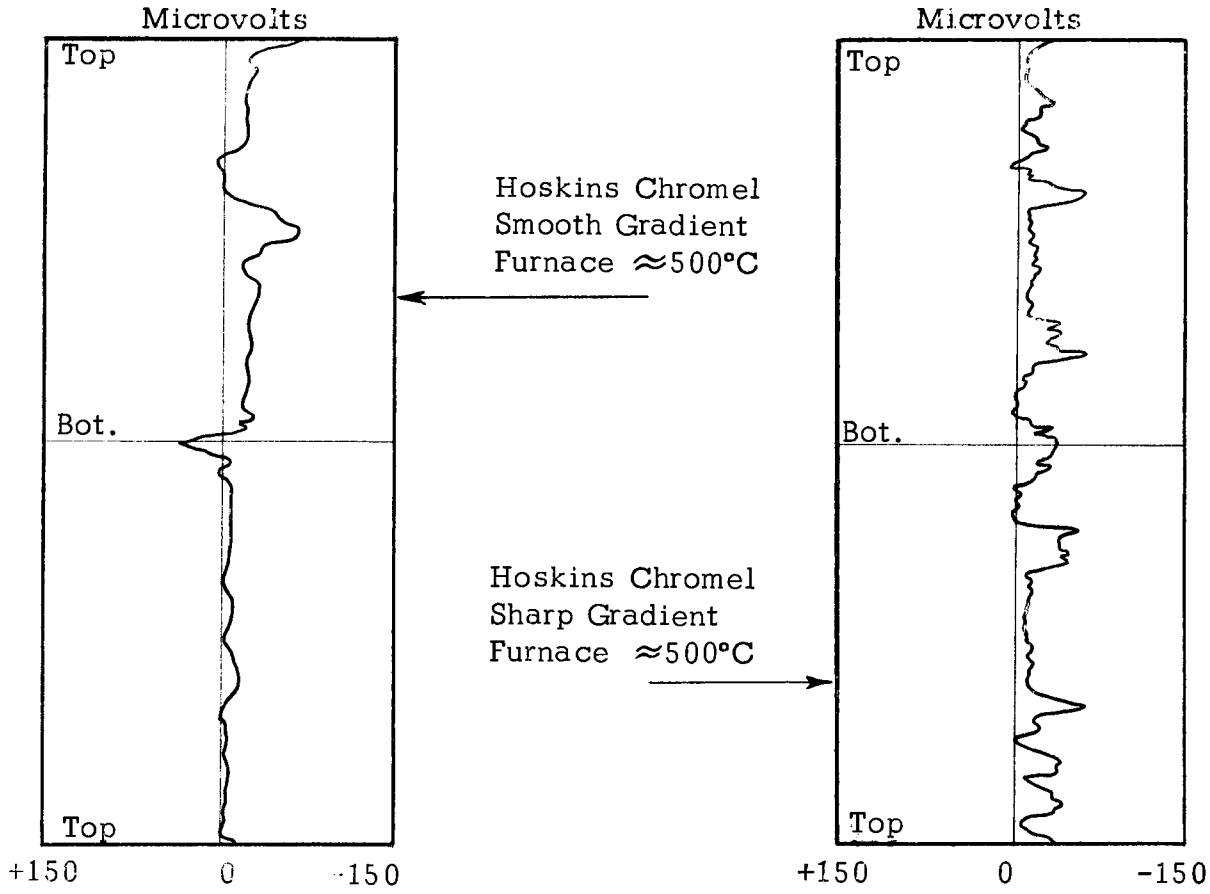
the smooth furnace gradient for chromel and alumel (Figure 17). Sharp gradient tests on Kanthal (+) and (-) indicate that these alloys have less composition gradient in the individual wire length in the as-received condition than do Hoskins' chromel and alumel. Tests on the A. C. Scott NiAl (-) indicate that the original condition of this wire will change with a short time anneal at 700°C, but that once this has occurred the variance in the wire is small (Figure 18). A. C. Scott NiCr (+) is virtually unaffected by the brief 700°C anneal, but has a greater variance than does the NiAl (-). In most of the tests the negative wire appears to be the better behaved under the temperature gradient test.

One additional point of interest is the rather large spurious emf which occurs at the wire ends. This is seen in most all traces and is believed to be due to recovery occurring in the region of the wire which does not fully enter the furnace region. Tests on bent wires at Oak Ridge National Laboratory indicate that this type test will detect a single inhomogeneity of this type quite adequately. This test does not allow a comparison of the variance in changing from one negative wire to another, but serves only to test the homogeneity of the individual wire for certain types of inhomogeneity Admittedly this is not as desirable a test as one would like, nor are the interpretaions of results although plausible thought to be completely correct. The interpretation of the results of the unilateral tests appears to be a much less formidable task and the initial experiments are being run with this apparatus.

Metallography Studies

This section of the experimental results includes metallography studies on the individual wires, in the as-received and tested conditions, and data on the cold working and recrystallization characteristics of chromel and alumel.

Mechanical inhomogenieties caused by cold working can be removed by annealing. The temperature and the time of annealing are of concern in avoiding excessive oxidation of the wire prior to use. Cold working chromel and alumel results in an increase in the wire hardness and undoubtedly



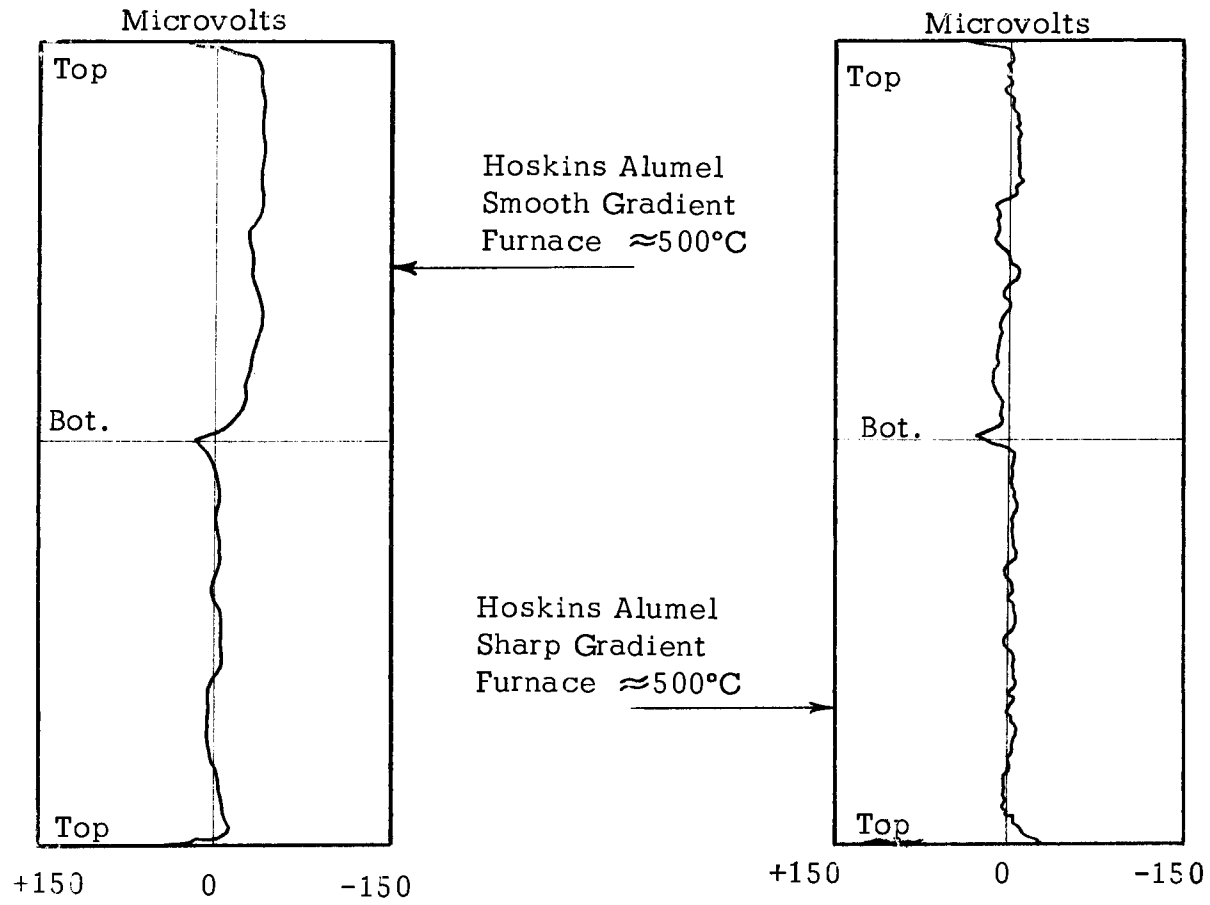


FIGURE 17 - SMOOTH AND SHARP GRADIENT RESULTS ON HOSKINS CHROMEL AND ALUMEL

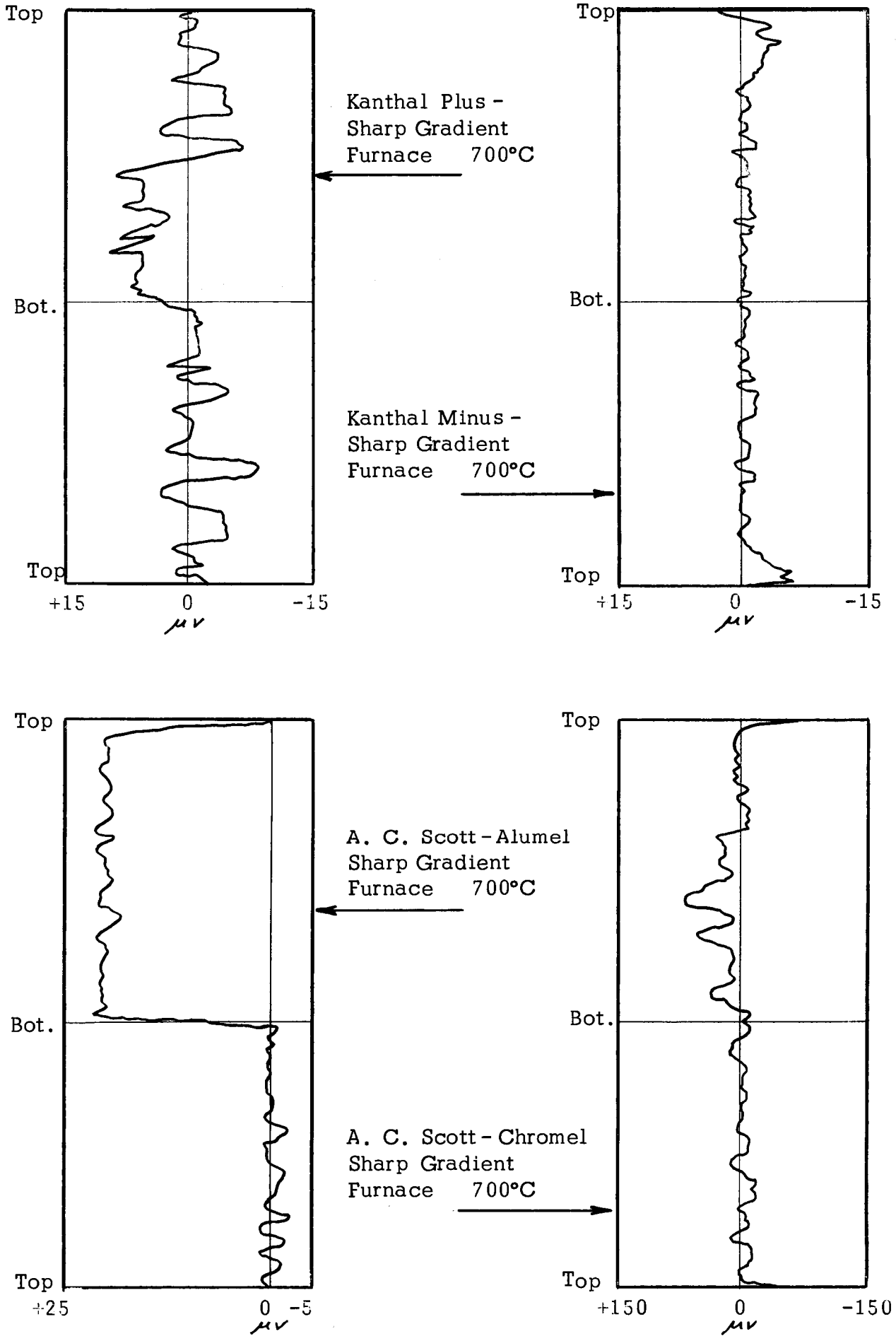


FIGURE 18 - SHARP GRADIENT RESULTS ON KANTHAL AND SCOTT CHROMEL AND ALUMEL

causes a change in the thermoelectric properties of the materials. Annealing a 70 percent cold worked material for one hour at higher and higher temperatures allows recrystallization of the wire to occur at an elevated temperature and an accompanying decrease in hardness is observed. These results are shown in Figure 19. The hardness of the chromel drops in a manner which is expected, but that of the alumel does not drop as sharply as expected. As a result the recrystallization temperature of the chromel is easier to estimate than that of alumel. However if one choses the value of 50 percent hardness change then for alumel it is 1100°C and for chromel, 1160°C. Thus for either alloy in the 70 percent cold worked condition to produce a fully recrystallized structure, it must be held at temperatures in excess of these for at least one hour.

Thermoelectric properties of cold worked metals are normally changed at temperatures below the recrystallization temperature by the process of recovery. This change has been used to indicate that recover, polygonization and recrystallization are occurring in the originally cold worked metal (21). These effects and their temperature are not known exactly for chromel and alumel, but are of interest in producing a stress free alloy in which the thermoelectric properties would not vary appreciably due to mechanical changes occurring during service. It is proposed to determine the recovery temperatures for these alloys in the unilateral temperature gradient furnace or in the rapid heating calibration furnace.

As reported in the homogeniety results some of the wires tested were given a pickling treatment. Because chromel and alumel are heat resistant alloys some work was needed on the proper pickling solutions. The two procedures which proved to be most staisfactory are given in Table IV.

The preparation of samples for metallographic studies was done in the normal manner using lucite as the mounting material and the customary polishing papers, cloths and polishing solutions. The wires were mounted so that one could study a longitudinal section of the wire. Etching chromel and alumel is a somewhat difficult task. However, several solutions have been developed which give reasonably satisfactory results. Small composition variations in the alloys seem to give different etching properties to the

various materials. The three solutions which have been used are given in Table V.

Table IV

Pickling Procedure For Chromel and Alumel

I	Alumel		Chromel	
	Water	1000 cc	Water	1000 cc
	Sulfuric	95 cc	Nitric	1000 cc
	Sodium Nitrate	65 gm	Hydrofluoric 40%	150 cc
	Sodium Chloride	110 gm		
	Temperature	180°F	Temperature	80°F
	Time	15-45 min	Time	15-45 min

After pickling either chromel or alumel, rinse in hot water and neutralize in 2% ammonia solution.

II	Solution 1		Solution 2	
	Water	1000 cc	Water	1000 cc
	Hydrochloric	500 cc	Sulfuric	100 cc
	Cupric Chloride	30 gm	Sodium Dichromate	130 gms
	Temperature	180°F	Temperature	105°F
	Time	15-30 min	Time	5-20 min

Leave wire in solution 1 for about 25 minutes, depending on the extent of oxidation. Rinse in hot water. Leave wire in solution 2 for 5-10 minutes to brighten. Rinse in 2% ammonia solution.

Table V

Etching Solutions for Chromel and Alumel

Solution 7		Solution 9		Solution 13	
Chromic acid	4 gm	Hydrochloric	30 cc	Hydrochloric	20 cc
Nitric acid	10 cc	Nitric acid	10 cc	Copper Sulfate	4 gm
Ammonium Chloride	5 gm	Cupric Chloride	(sat.)	Methanol	10 cc
Water	90 cc			Water	10 cc

These solutions have been combined in the following way to give etched structures on the following materials:

Chromel (Hoskins): Use solution #9. Swab for 7-20 seconds, dependent upon the condition of the wire.

Alumel (Hoskins): Use solution #9 and #7 in a 1:1 mixture. Swab 1-20 seconds, dependent upon the wire condition.

NiCr+ (Scott): Use solution #9. Swab for 7-15 seconds, dependent upon the wire condition.

NiAl- (Scott): Use solution #13. Swab for 5-10 seconds.

Alumel (Gordon): Use solution #9. Swab for 5-10 seconds.

Alumel (Revere): Use solution #9. Swab for 5-10 seconds.

The microstructure of an as-received Hoskins Chromel P wire is shown in Figure 20. Since chromel is a nickel-base solid solution alloy one would expect only a single phase to be present which is similar to that of nickel. Annealing twins are prominent in this structure. The microstructure of an as-received Hoskins Alumel wire is shown in Figure 21. This is a solid solution alloy with a microstructure similar to that of chromel, only with a larger grain size. All of the metallography samples are thin wires which have a tendency to round on the edges when mounted and polished, to produce regions which are out of focus on the sides of the photomicrograph. Attempts are being made with new mountings to avoid this edge effect because this region is of interest in studying the effects of environment on the alloys in service. The alloys are difficult to etch and when oxides exist on the edge of the specimen they tend to drag across the metal surface and cause scratches.

As-received Scott NiCr (+) and NiAl (-) also have single phase structures which are similar to those shown for the Hoskins products. The only apparent difference is that for the vacuum melted Scott alloys, the grains are slightly larger than those of the Hoskins alloys. There has been no real experimental evidence that the grain size of the alloys is significant. Since the Scott microstructures are so similar to those of Hoskins, no photomicrographs are shown.

As-received Kanthal (+) and (-) are shown in Figures 22 and 23. The distinguishing feature about these structures is that the Kanthal (+) has an extremely small grain size and the Kanthal (-) one which is slightly smaller

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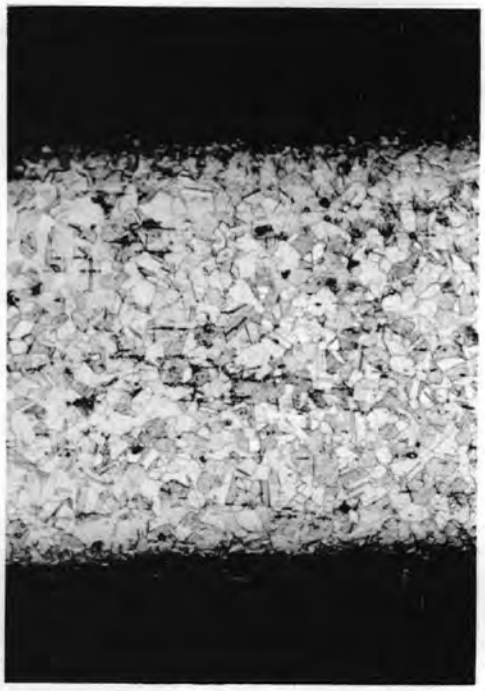

FIGURE 20 – AS RECEIVED HOSKINS CHROMEL

FIGURE 21 – AS RECEIVED HOSKINS ALUMEL

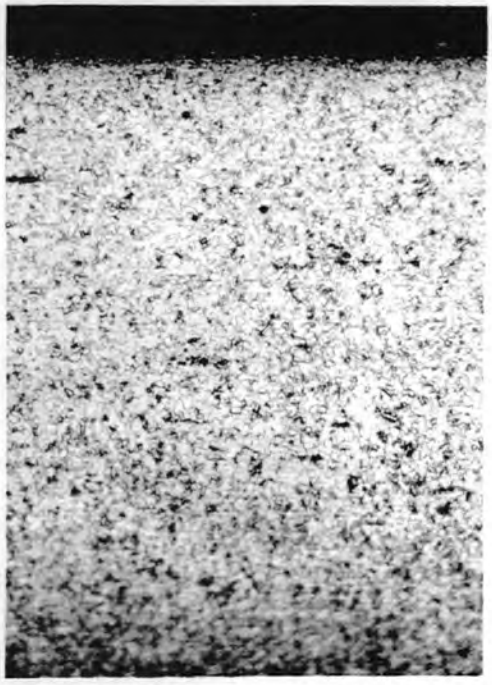

FIGURE 22 – AS RECEIVED KANTHAL+

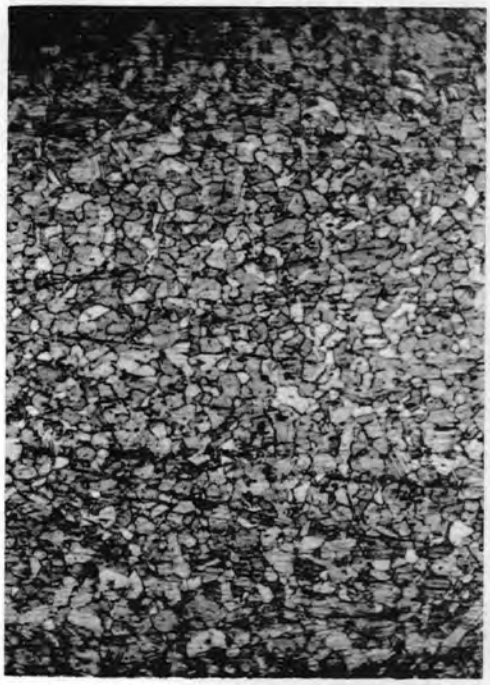

FIGURE 23 – AS RECEIVED KANTHAL–

than that of the Hoskins product.

Figure 24 is a microstructure of Chromel which had been exposed (unprotected) in air for 5000 hours at 1800°F in the Oak Ridge National Laboratory drift test facility. Two other samples were included in this test, one at 1600°F for 5000 hours and one at 1300°F for 5000 hours. The microstructures for all three are typified by Figure 24. Comparison to the as-received chromel shows that considerable grain growth has occurred, but that the amount of oxidation (as evidenced by scale on the surface) is very slight. The alumel which was exposed for 5000 hours at 1300°, 1600° and 1800°F is shown in Figures 25, 26, and 27. At 1300°F (Figure 25) a large amount of grain growth has occurred. In addition the oxidation of the outer portions of the wire is seen as a black and white mottled structure on the sides of the wire. Oxides are also seen which have penetrated along the grain boundaries to the central portions of the alumel wire. The 1600°F sample (Figure 26) is completely oxidized after 5000 hours. There is no metal structure as in the 1300°F sample. Two types of oxide appear to be present in the sample. The outer oxide is a porous oxide and the central oxide is a dense one. The alumel sample exposed at 1800°F (Figure 27) again shows that no metal structure remains after 5000 hours. The outer oxide which was also present in the 1600°F sample has continued to grow and has consumed more of the denser oxide at the central portion. It would appear that the "central" oxide can be oxidized to a higher oxide with exposure at higher temperatures. In Figures 26 and 27 the wire could not be removed from the refractory beads and so the beads were also mounted and polished. These can be seen as the outer regions of the photomicrographs and contains large voids.

Swaging thermocouples of chromel and alumel which were exposed for 5000 hours at 1300°F, 1600° and 1800°F are shown in Figures 28, 29, 30, 31, 32, and 33. These thermocouples were contained in inconel tubes and were tightly packed with MgO during the swaging process. The chromel microstructures 28, 29, and 30 illustrate the large amount

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FIGURE 24 – CHROMEL, HOSKINS, EXPOSED 5000 HOURS AT 1800°F

FIGURE 25 – ALUMEL, HOSKINS, EXPOSED 5000 HOURS AT 1300°F

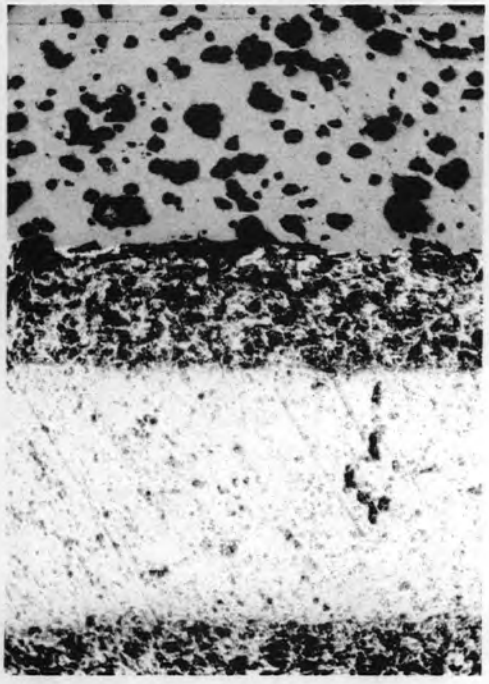

FIGURE 26 – ALUMEL, HOSKINS, EXPOSED 5000 HOURS AT 1600°F

FIGURE 27 – ALUMEL, HOSKINS, EXPOSED 5000 HOURS AT 1800°F

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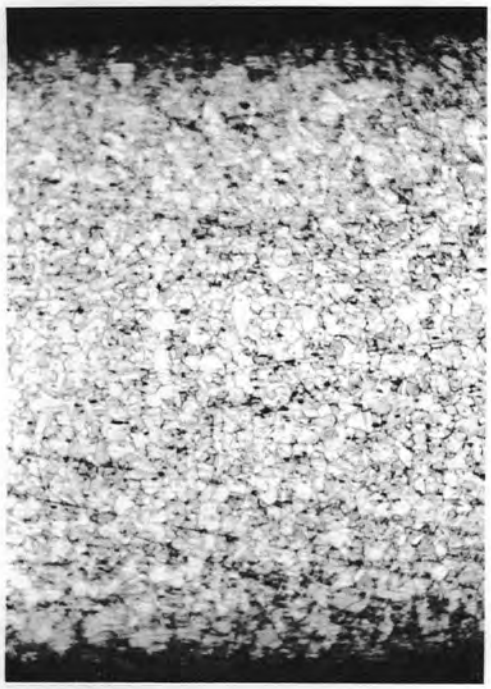

FIGURE 28 – CHROMEL IN SWAGED MgO ASSEMBLY – 5000 HOURS AT 1300°F

FIGURE 29 – CHROMEL IN SWAGED MgO ASSEMBLY – 5000 HOURS AT 1600°F

FIGURE 30 – CHROMEL IN SWAGED MgO ASSEMBLY – 5000 HOURS AT 1800°F

FIGURE 31 – ALUMEL IN SWAGED MgO ASSEMBLY – 5000 HOURS AT 1300°F

of grain growth which has occurred during the 5000 hours of exposure; virtually no oxidation of the chromel is visible.

The alumel structures show appreciably larger grains than for the chromel. Despite the MgO-Inconel protective envelop around the alumel wire; oxidation of this wire does occur. At 1300°F (Figure 31) the oxide is seen only on the edge of the wire and penetration appears to be uniform, whereas at 1600°F (Figure 32) the oxidation occurred on the edge of the wire and along the grain boundaries throughout the wire. At 1800°F (Figure 33) the grains have grown very large, however there is no real evidence of extensive oxidation as in the 1600°F sample. A duplicate sample of this wire is being prepared to investigate the apparent anomaly in microstructure at 1800°F.

A. C. Scott wires which were exposed at 1800°F, failed in less than 500 hours. Metallographic samples along the wire revealed that the most serious oxidation has occurred approximately 5 inches behind the hot junction for this particular test. The NiCr (+) "wire" is shown unetched in Figure 34 and the NiAl (-) is shown in Figure 35. Oxidation is extensive in the NiCr (+), occurring on the edge, in the grain and in the grain boundaries. In the NiAl (-) the oxidation appears to have occurred from one side only, but is very serious, leaving less than one tenth the original wire unattached.

Microstructures of a number of chromel-alumel type alloys have been prepared, but were not included due to the similarity of structures. Future metallographic studies are expected to yield very useful infomration about the stability of chromel-alumel thermocouple. As can be seen from the above microstructures, the alumel in the weaker component in the chromel-alumel thermocouple.

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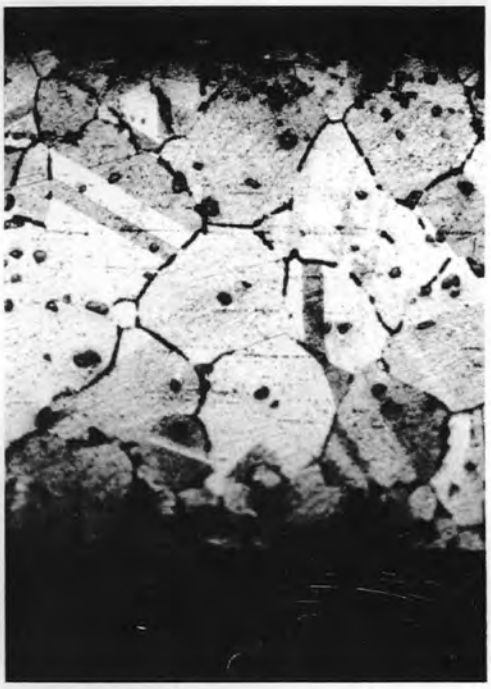

FIGURE 32 – ALUMEL IN SWAGED MgO ASSEMBLY – 5000 HOURS AT 1600°F

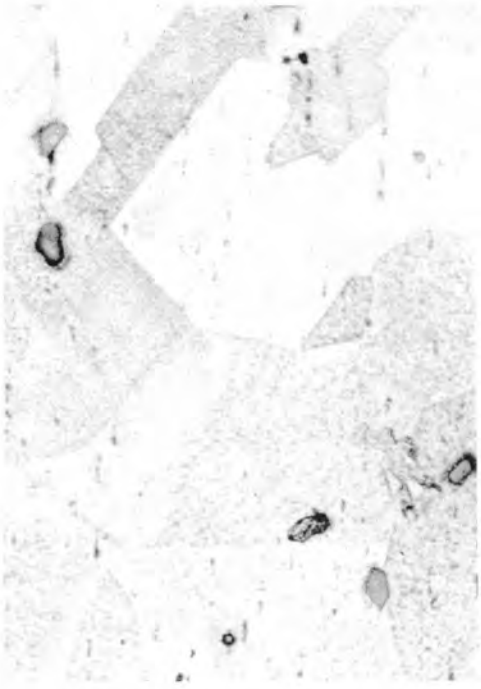

FIGURE 33 – ALUMEL IN SWAGED MgO ASSEMBLY – 5000 HOURS AT 1800°F

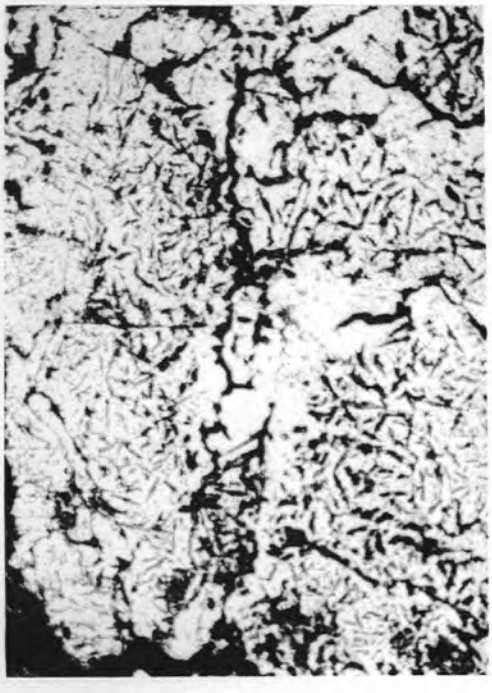

FIGURE 34 – SCOTT NiCr+, 1800°F FOR 500 HOURS, 5 INCHES FROM HOT JUNCTION

FIGURE 35 – SCOTT NiAl (–), 1800°F FOR 500 HOURS, 5 INCHES FROM HOT JUNCTION

Drift Tests

The justification of determining the drift in thermal emf of various thermocouples of the chromel-alumel type has been given. The test geometry has been described and from comparative results at Oak Ridge National Laboratory and the data of Spooner and Thomas (13), the drift systems being used are somewhat oxidizing in nature. This is due to the particular L/D ratio for the thermocouple hot junction wells in the copper blocks. A statistical analysis of the number of test thermocouples to be most advantageous, revealed that 6 thermocouples would closely approach the average result of a larger number of thermocouples. Accordingly six thermocouples of each of the following materials were prepared for prolonged testing at 600°, 800°, and 1000°C:

1. Hoskins Chromel P-Alumel 22 gauge, dull oxide finish
2. Hoskins Chromel P-Alumel 22 gauge, bright anneal finish
3. A. C. Scott NiCr(+)NiAl(−) 22 gauge, bright finish
4. Kanthal(+) : Kanthal(−), 22 gauge, bright finish

These wires were strung in six hole one inch long porcelain beads such that the entire assembly was approximately 18 inches long from the hot junction to the cold junction. In practice one would not use 22 gauge chromel-alumel thermocouples at 1000°C, but would use a larger diameter wire. However to gain insight into general thermocouple drift and failure characteristics, experiments involving the finer wire size should be less time consuming and yield useful information for an extrapolation to wire size effects.

Figures 36, 37, and 38 show the plot of time at temperature versus the deviation of the indicated temperature of the average emf of the six test thermocouples from the true temperature as determined by a Pt:Pt10Rh working thermocouple. The 600°C drift data show that all the thermocouples have a negative drift of between 3° and 4°C in 1000 hours. However in each case these data show an initial rise in thermal emf of about 5°C and then the negative drift which accounts for the net observed drift from the original emf. Because the behavior at 600°C is slightly different from that at 800°C (i. e. positive drift, followed by negative drift), duplicate experiments are to be run at both temperatures. There appears to be little difference in the Hoskins dull oxide finish and the bright anneal finish at 600° in 1000 hours. The A. C. Scott thermocouples have emfs slightly less than expected at 600°C and the Kanthal thermocouples are also slightly higher than expected.

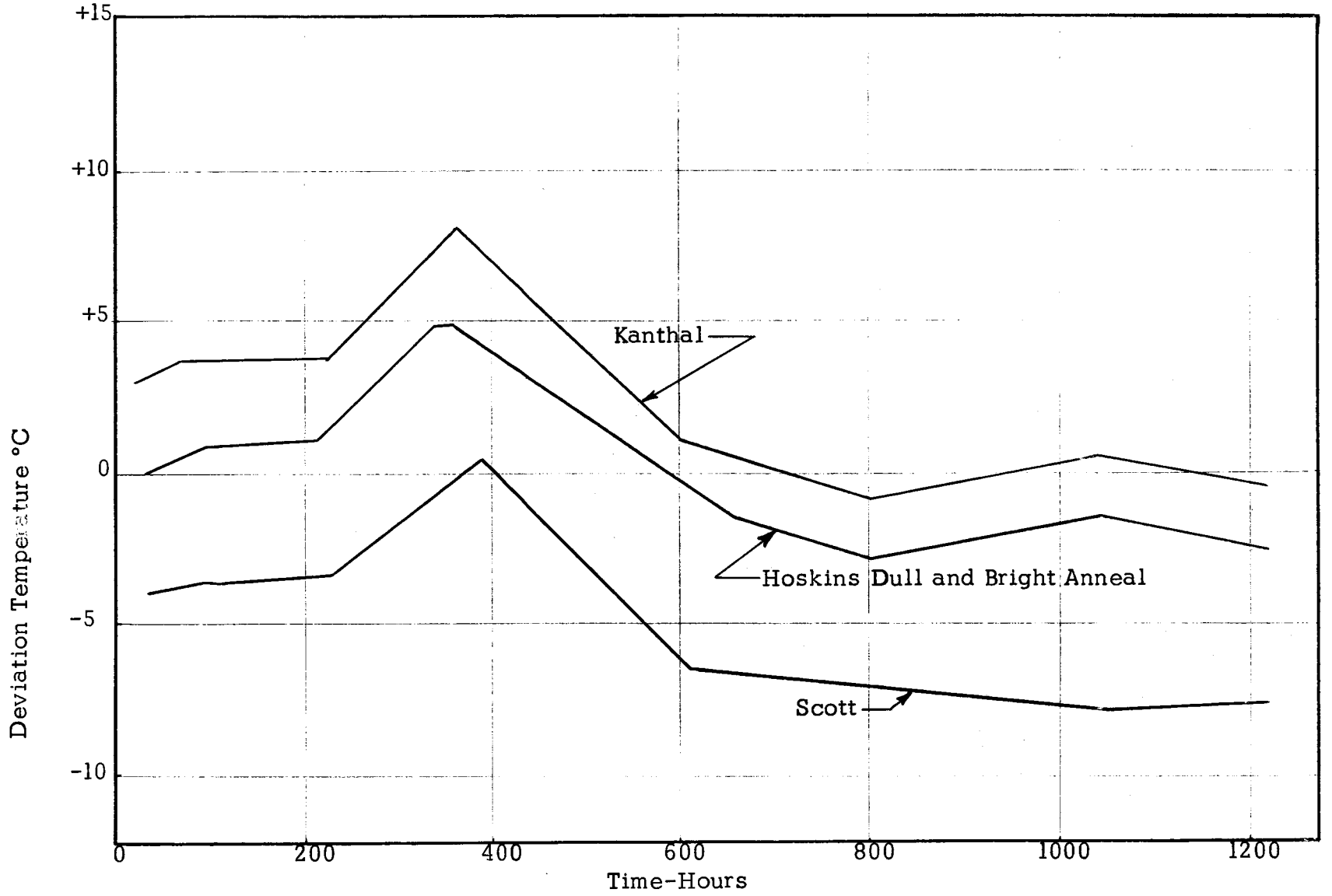

FIGURE 36 - DRIFT RESULTS FOR CHROMEL/ALUMEL THERMOCOUPLES AT 600°C

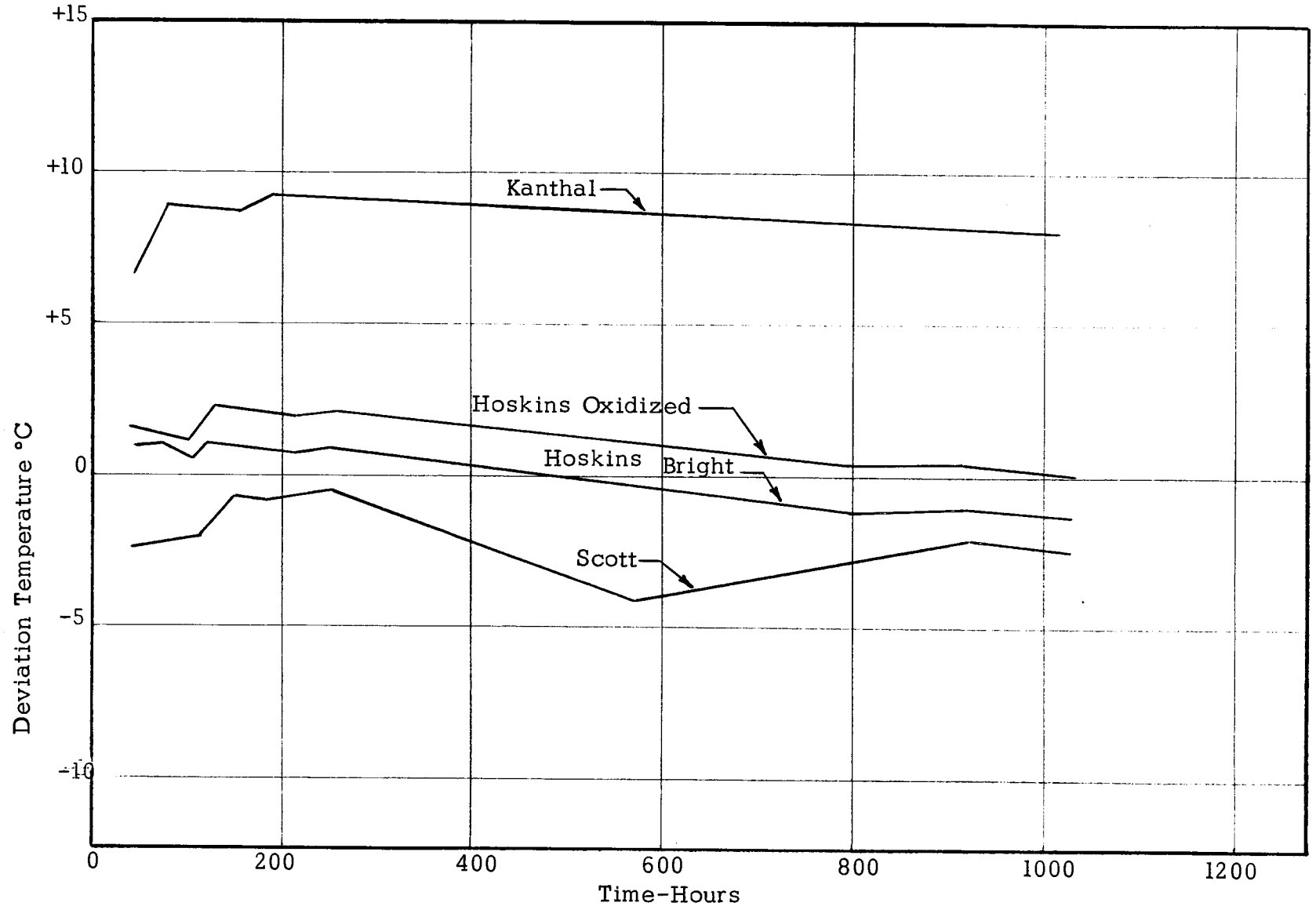

FIGURE 37 - DRIFT RESULTS FOR CHROMEL/ALUMEL THERMOCOUPLES AT 800°C

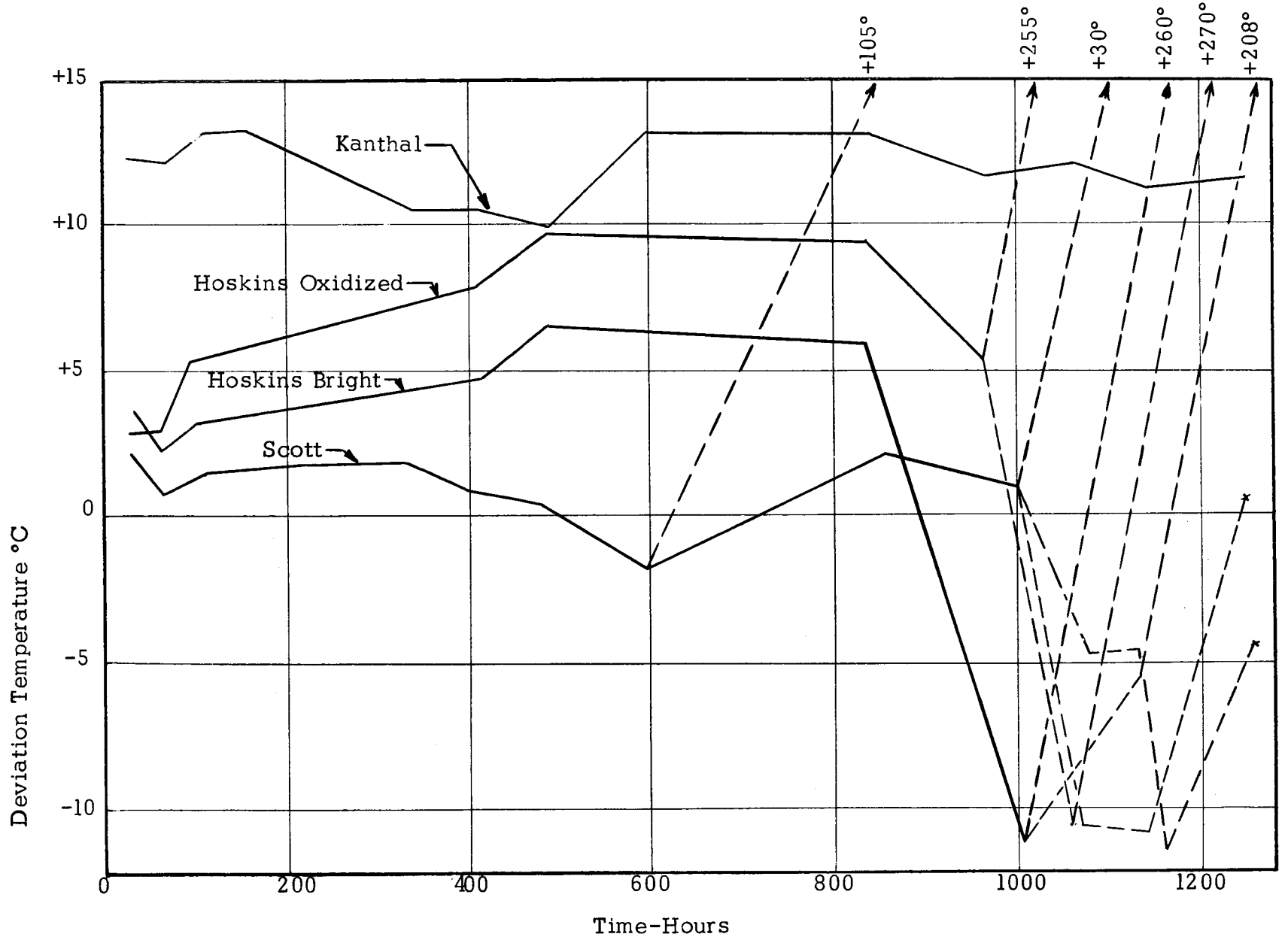

FIGURE 38 - DRIFT RESULTS FOR CHROMEL/ALUMEL THERMOCOUPLES AT 1000°C

At 800°C the average drifts of the thermocouples is slightly less than at 600°C. The net negative drift is between 1° and 3°C in 1000 hours. The averages of the two Hoskins products appear to be separated by approximately 1°C in 1000 hours although this variation may be within the temperature variation in the copper block. The A. C. Scott wire has a slightly greater fluctuation at this temperature than do the other systems. The Kanthal thermocouples appear to be equally as good as the Hoskins products at this temperature. The initial rise of the Kanthal thermocouples is thought to be significant and is a general characteristic found for almost all chromel-alumel type thermocouples placed in service in the as-received condition. The tests at 600° and 800°C are continuing to run at the present time, and nearly 1600 hours have been logged. The Hoskins Products have a slightly larger deviation from the table value at 800°C than at 600°C. The A. C. Scott wire appears to be nearer calibration at this temperature than at 600°C. The Kanthal thermocouple has a slightly greater deviation at this temperature than at 600°C.

At 1000°C the average drifts of the thermocouple systems must be individually considered for major changes are observed at long times. The Hoskins dull oxide wire drifts in a positive direction for nearly 500 hours with a net change of about 8°C. Then this thermocouple drifts in a negative direction for the next 400 hours and has an average negative deviation of about 20°C from the peak positive deviation. Between 850 and 1000 hours the thermocouples drift in a positive direction and give quite large positive deviations. Individual thermocouples have read as much as 250°C too hot. The spread in the emf of the six thermocouples is much greater at 1000°C than at the lower temperatures, and thermocouples fail at a surprisingly high rate.

The general behavior described for the Hoskins dull oxide finish applies to the Hoskins bright anneal thermocouples, with the major positive drift and the negative drift occurring in about 100 hours less time. Individual bright thermocouples have positive deviations between 200° and 260°C in 1200 hours. The bright anneal thermocouples appear to be closer to the reference table than the full oxide thermocouples at 1000°C, although the spread in the thermal emfs of the two types is approximately the same.

The A. C. Scott thermocouples at 1000°C drift in a negative direction (-5°C) for about 900 hours and then have a sudden shift to a negative deviation

of -12°C. This is followed by a sudden positive drift in 1100 hours to +25°C. Thus the same general trend is followed in the Scott thermocouples as in the Hoskins thermocouples. The Scott thermocouple appears to be more subject to individual thermocouple failure than any of the other systems. The initial thermal emfs of the Scott wire is slightly greater than expected from the reference table.

The Kanthal wire has a larger positive deviation from the reference table at 1000°C than at 600° or 800°C. However this wire is surprisingly stable at this temperature and in 1000 hours has a net change in thermal emf of less than 2°C. No intrinsic positive deviation has occurred in 1000 hours, the emf of the individual thermocouples are very close, and only one thermocouple was observed to have failed.

To explain these results is difficult, but the following is proposed as a possible explanation. It has been observed that the initial electrical resistance of all of the thermocouple systems is near 4 or 5 ohms, however the electrical resistance of the Hoskins products, and the A. C. Scott thermocouples has reached a value of 20,000 to 25,000 ohms in 1100 hours. This high resistance is due to virtually complete oxidation of the thermocouple wire which results in a portion of what was formerly wire becoming a metal oxide. The oxide can be seen in Figure 34 where it is consuming the wire. Thus the chromel-alumel thermocouple has changed to an alumel wire to "alumel" oxide to "chromel" oxide to chromel wire circuit. This is used to explain the excessive drifts observed at 1000°C.

Several hypotheses must be drawn on to explain the general shape of the curves. For clarity the general shape at the three temperatures is schematically shown in Figure 39. The slight initial rise observed in the short time of drift is due to the removal of mechanical strains and the adjustment of the wire to the temperature gradient. The differences in the drift observed up to 400 hours can be accounted for by the preferrential oxidation of the alloying elements in the wires and the resulting change in thermal emf associated with this loss. If one supposes (and experimental verification of this is needed) that the emf versus composition function changes with temperature in the manner shown qualitatively in Figure 40 for chromel and Figure 41 for alumel, and if one realizes that there is a difference in rate of removal of the alloying elements

due to the temperature differences in the three systems, then a change in

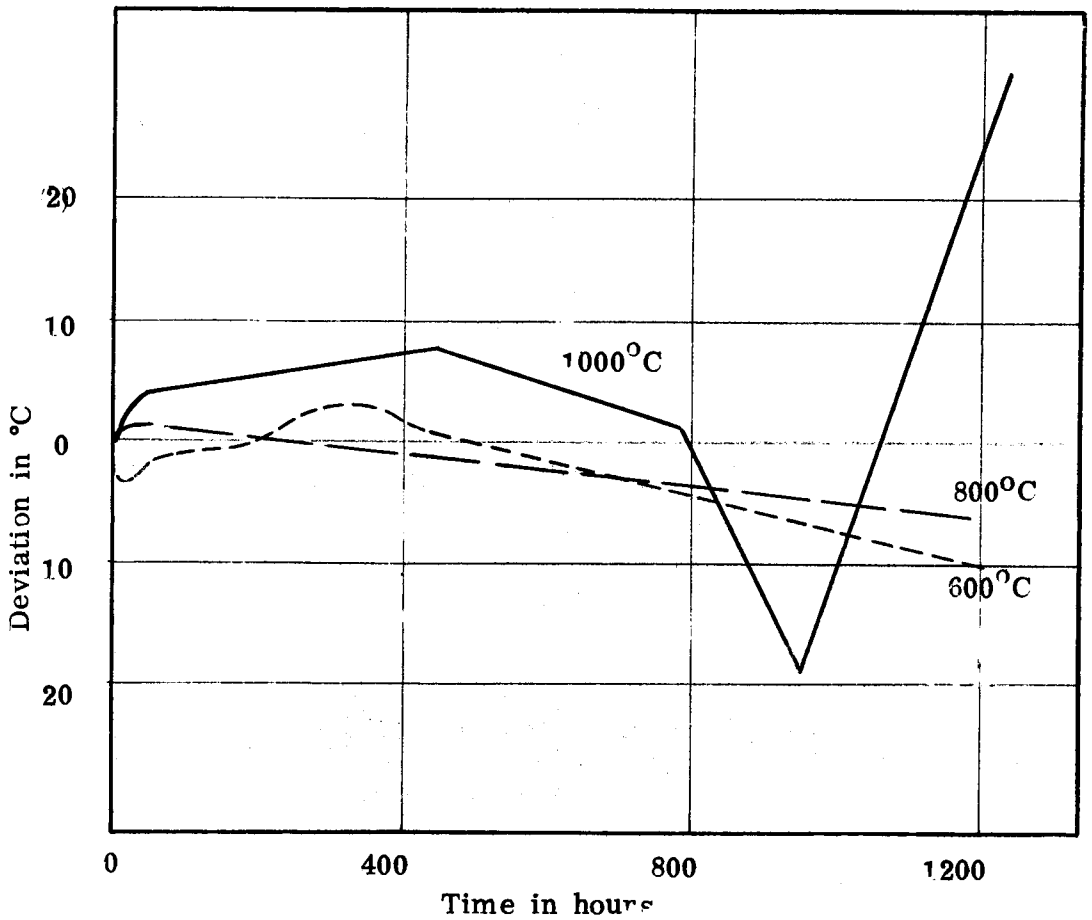

FIGURE 39 - SCHEMATIC DRAWING OF DRIFTS AT 600, 800, AND 1000°C

composition at one temperature may cause a significant difference in the thermal emf depending on the drift test temperature. The apparent drift can be due to changes either in the chromel wire, the alumel wire, or both. To illustrate the argument, changes in the chromel will be used, although the metallographic studies indicate that the changes in the alumel may be more serious. If one a unit of composition (ΔC) of chromium is lost from the chromel in a given time (Δt) at the drift temperatures, then the effect at 600°C would be to slightly increase the thermal emf of chromel to platinum and a net positive drift would be observed. But if still more chromium is lost the shift would be on the plateau of the curve (low $\Delta E/\Delta C$) and little change

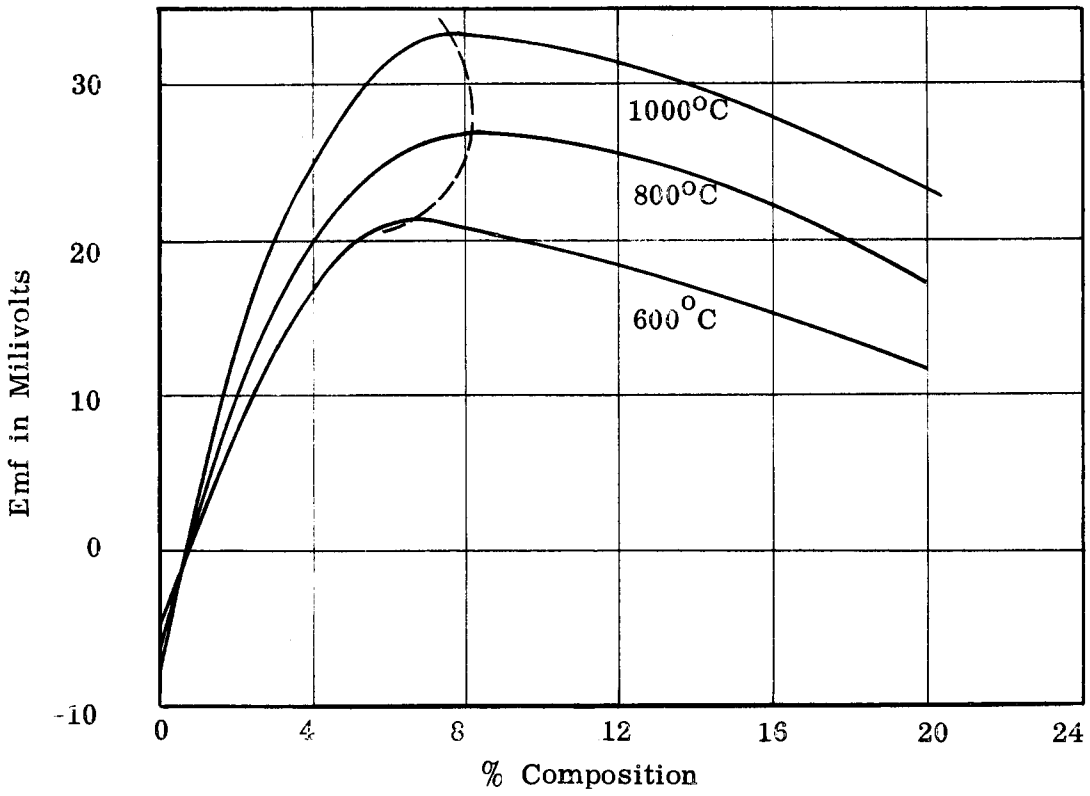

FIGURE 40 - EMF VERSUS COMPOSITION AT SEVERAL TEMPERATURES FOR "CHROMEL"

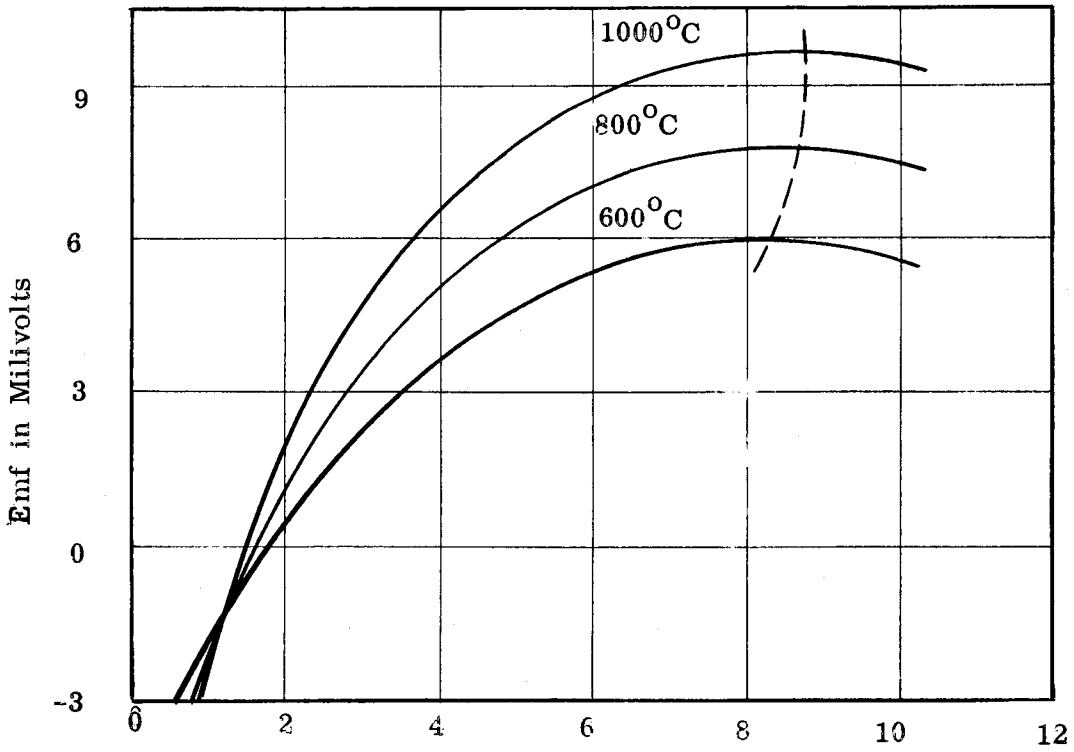

FIGURE 41- EMF VERSUS COMPOSITION AT SEVERAL TEMPERATURES FOR "ALUMEL"

would be observed. If still more chromium is lost then the emf would start to drop (Negative $\Delta E/\Delta C$) and would continue to do so as more and more chromium is lost and the resultant drift would become more and more negative. Likewise if one is at 800°C and the curve exists as it is drawn, then any loss in chromium would cause a net lowering of the thermal emf of chromium to platinum and the thermocouple would drift in the negative direction from the start. The situation at 1000°C can be explained exactly as that at 600°C, except at 1000°C the rate of chromium lost is greater and the observed drift is greater.

If one choses to argue the above for alumel then one can consider the three major elements as one with the proper ratio between them, and the argument is the same as above. Admittedly this is a naive approach since it is highly unlikely that the oxidation rate for the three are identical and so one should use individual plots, as illustrated for silicon, but with the other two elements considered. (This latter is not illustrated).

It is most probable that losses are occurring from both wires and that the chromel with such a large percentage of chromium used in getting such a large thermal emf, suffers just as badly as does the alumel which has only a small amount of alloying element.

The above drift argument can be used to explain the large differences observed between the Kanthal thermocouples and the Scott thermocouples. From the chemical analysis and from a private communication with Dr. Bjorn Edwin, the major differences in the two thermocouples is in the alumel wire, with the chromels being almost the same except for Mn. The Scott alumel contains principally 1.1 to 1.5 percent silicon, whereas the Kanthal (-) contains between 2 and 3 percent silicon, alone. Thus if Figure 42 represents the emf composition curve for silicon in nickel at various temperatures, then losses of silicon would be less detrimental to the Kanthal (-) than to Scott NiAl-. This is observed in the drift curves at the various temperatures, in which the drifts are greater for the Scott thermocouple than for the Kanthal thermocouple, and this is especially true at 1000°C.

Thus for the drift curves only the sudden increase in thermal emf is left to be explained. This is believed to be due to the nature of the thermocouple system shifting from one of a metal:metal couple to one of a metal/metal

oxide:metal oxide/metal couple. The exact identity of the two oxides are not known, but if one glibly calls one the "alumel" oxide and the other the "chromel"

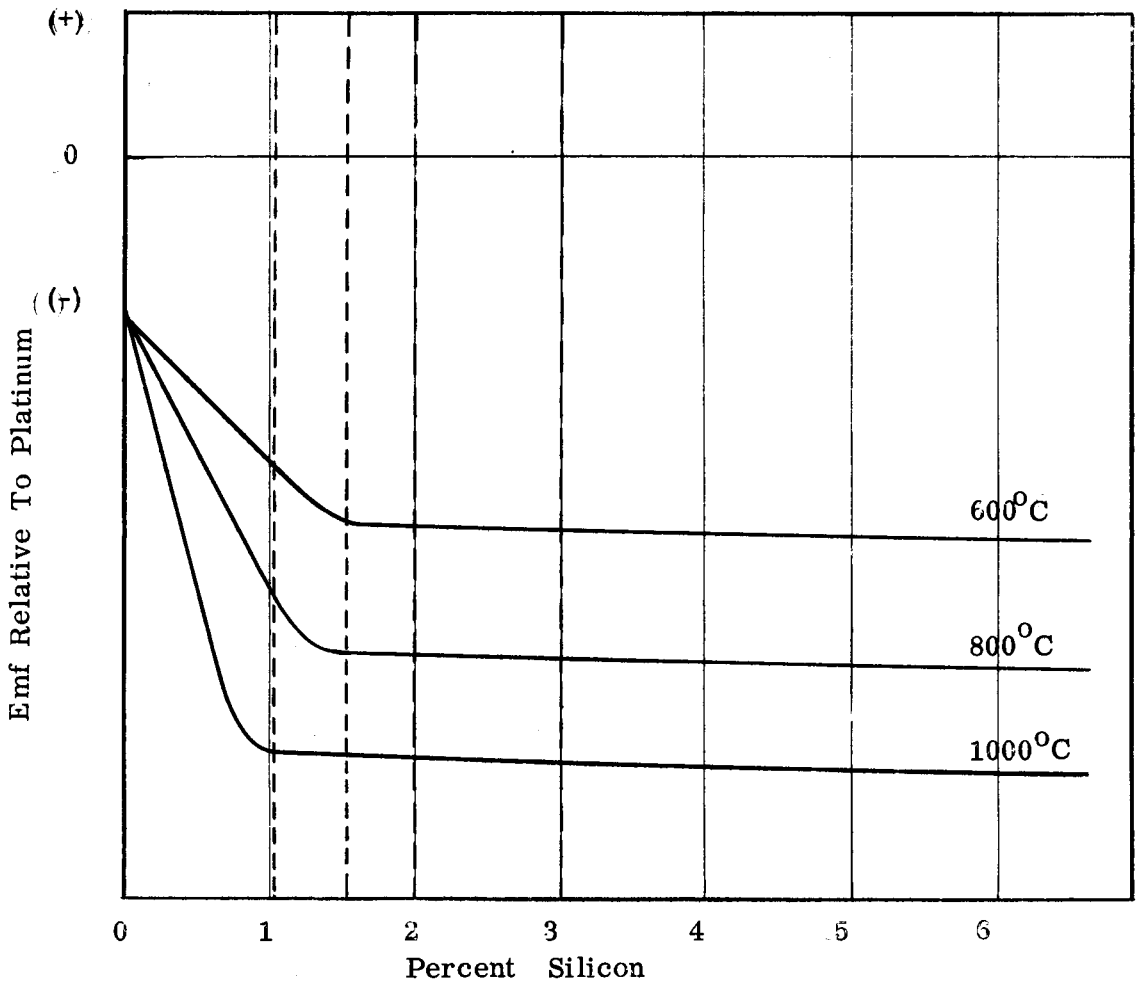

FIGURE 42 - EMF VERSUS COMPOSITION AT SEVERAL TEMPERATURES FOR NICKEL-SILICON ALLOYS

oxide then the resulting increase is readily explained. The change in resistance of the thermocouple system with time seems to verify that the above is correct. That is, as long as the resistance is in the neighborhood of 3 to 10 ohms the thermocouple is not deviating appreciable, but as the resistance climbs to values of 300 to 400 ohms, the net thermal emf appears to drop and

then as the resistance reaches values of 20,000 and 30,000 ohms, indicating large amounts of oxide present, then the "thermocouple emf" is in serious error. Figure ~~58~~ 43 shows the emf generated between NiO and platinum, and Cr_2O_3 and platinum.

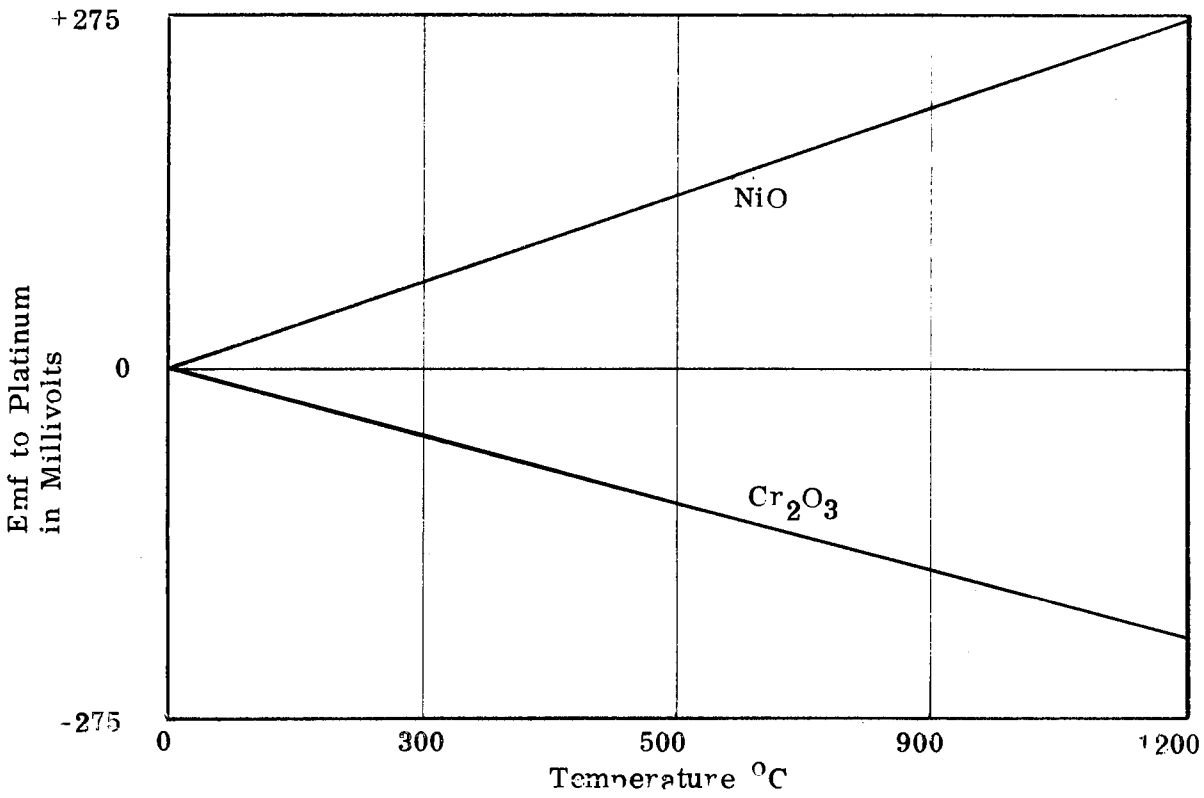

FIGURE 43- EMF VERSUS TEMPERATURE FOR NiO/PLATINUM AND Cr_2O_3/PLATINUM

Thus if the hot junction is composed of materials approaching these two compounds, and certainly there is some approach, then the resultant emf is tremendously increased over that of a normal chromel:alumel thermocouple and a large apparent error is observed.

From this proposed hypothesis for the explanation of the drift curves, a number of verifying experiments are suggested, as well as a number of precautionary measures which could be taken to indicate the beginning of serious thermocouple drift. In addition to the above tests under one type

geometry which has a fixed L/D ratio, it would be desirable to investigate the above hypothesis in view of various L/D ratios. This is to suggest a long-time Spooner-Thomas experiment on the chromel-alumel thermocouples and possible on other thermocouples.

All of the above tests have been run on as-received thermocouples, and with the present knowledge of their behavior, it would be informative to run experiments on thermocouples which have been treated in various ways. This is proposed, well-realizing that the long times at temperature are in a sense giving the wire a treatment which could swamp the effects of other treatments.

Calibration Results

Calibrations have been run in two manners: (1) by a comparison to a standard platinum:90 platinum10rhodium thermocouple: (2) by the fixed point method. Measurements by both methods are invaluable, in calibrating thermocouples and interpreting the results of treatments given to the wires of thermocouples in trying to evaluate their performance. Only a few runs have been made. However, a number of interesting points have been revealed and are under investigation.

Perhaps the most interesting and the most serious phenomenon being investigated is that there is an apparent difference in the calibration of certain thermocouples on heating and cooling. This phenomenon was first hinted at by one of the vendors visited on the previously mentioned trip. Figure 44 shows the results on a piece of chromel wire which is particularly sensitive to this effect in the as received condition. The width of the loop is nearly 3 degrees Centigrade at its broadest point. This is of particular importance because if one uses an as-received thermocouple which has a known calibration on heating, and a different but unknown calibration on cooling, then serious variations in operation may result. With data of this type one starts to question the meaning of any calibration which was taken on heating only, if very close tolerances are needed in a particular experiment. For work involving ±3/4% accuracy limits this effect does not appear to be too serious. However it is the purpose of this research to establish the accuracy class of the data so that proper considerations are made of the phenomena. It does appear that this situation can be improved for most of the materials

thus far checked. If the chromel shown in Figure 44 is annealed for 24 hours

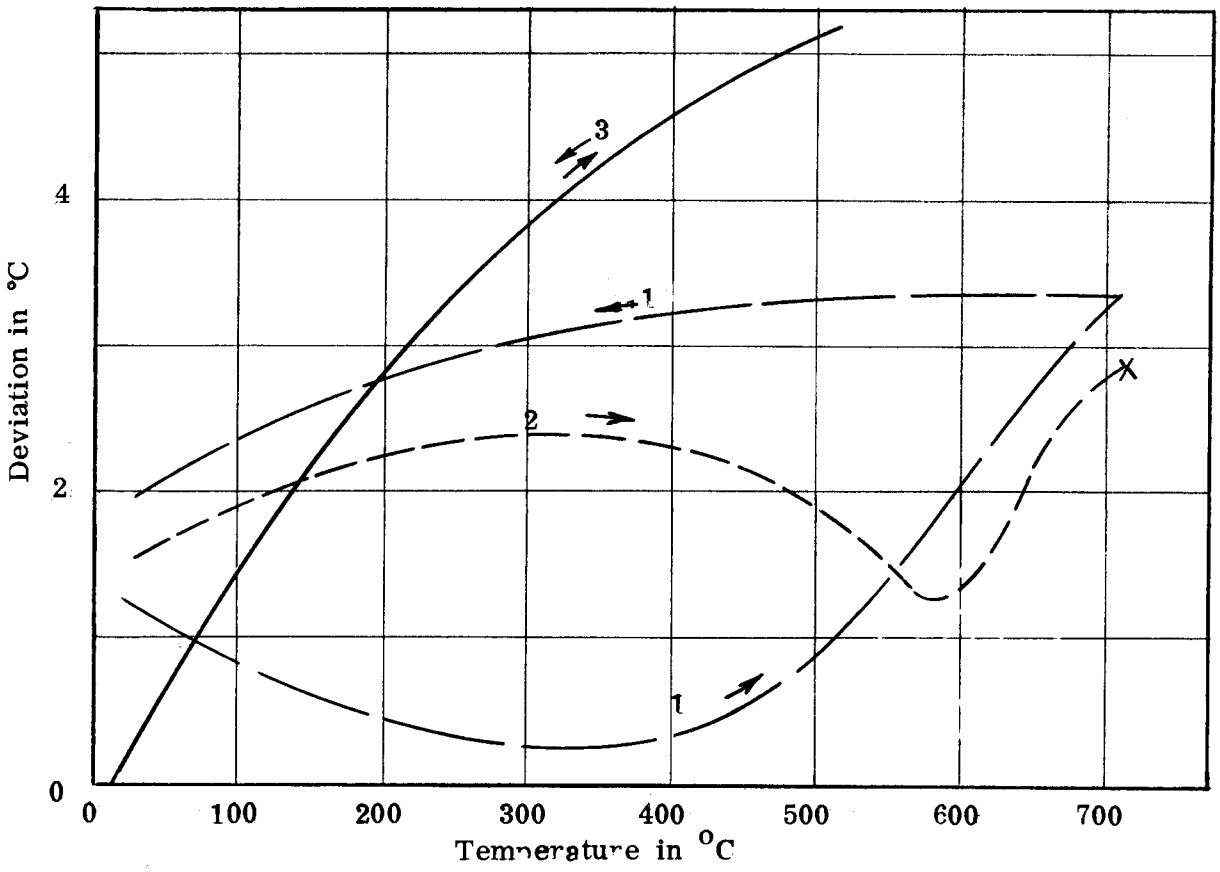

FIGURE 44 - CHROMEL/PLATINUM CALIBRATION LOOP ON AS-RECEIVED CHROMEL

at 600°C one obtains the calibration as shown in Figure 45. If the chromel wire is annealed at 950°C one obtains the calibrations shown in Figure 46. There is still a loop existing between the first heating and first cooling calibration, but subsequent calibrations appear to be remarkably close together. However if one changes the position of the temperature gradient on the wire, i.e. increases or decreases the depth of immersion of the hot junction, then still other calibrations exist for the wire, as shown in Figure 47. However, it will be noted that these calibrations are extremely close to one another on heating and cooling. This implies that on the first heating of a

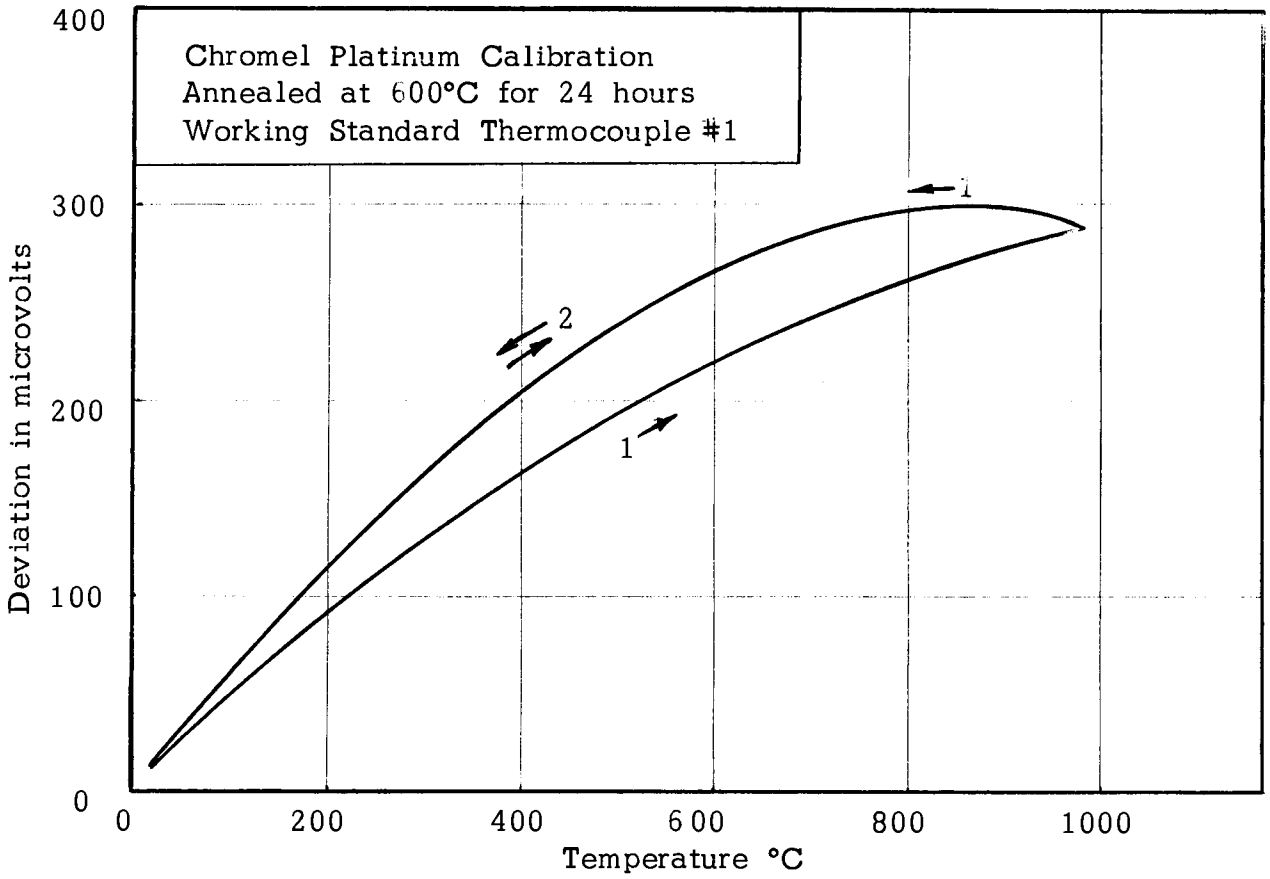

FIGURE 45 - CHROMEL/PLATINUM CALIBRATION FOR 600°C ANNEALED CHROMEL

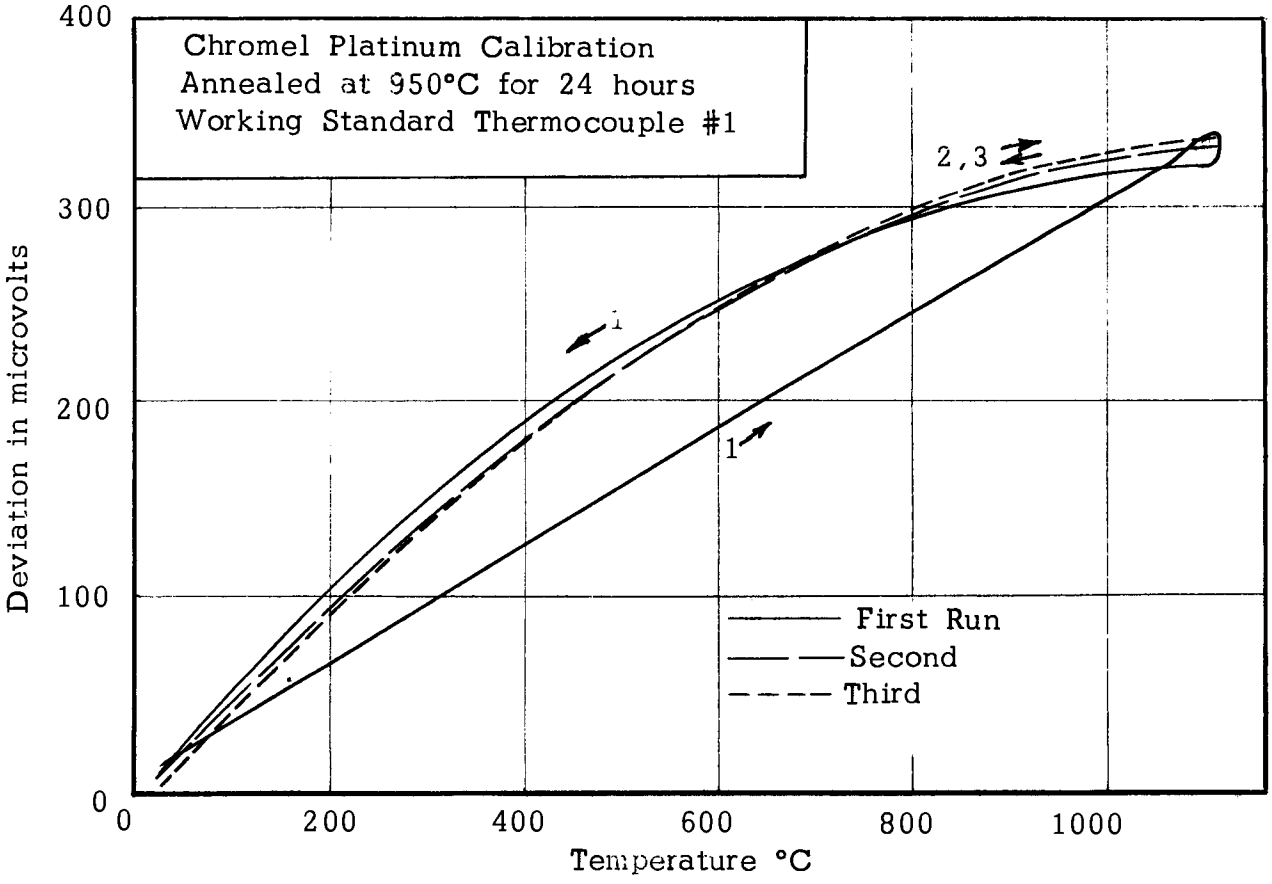

FIGURE 46 - CHROMEL/PLATINUM CALIBRATION FOR 950°C ANNEALED CHROMEL

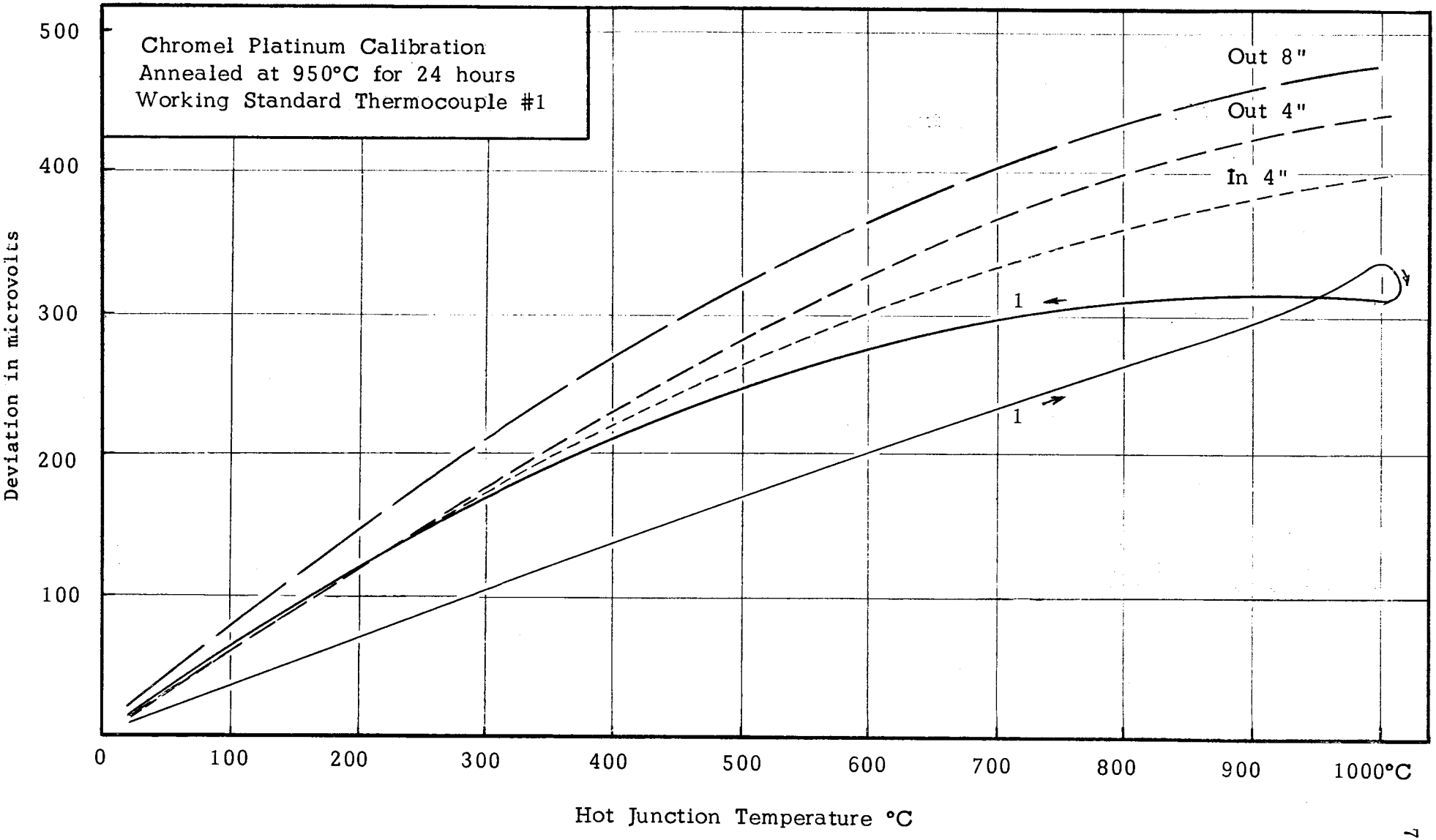

FIGURE 47 - CHROMEL/PLATINUM CALIBRATION AS INFLUENCED BY DEPTH OF IMMERSION

newly prepared thermocouple hot junction, some changes are occurring. Thus an experiment is in progress to produce the thermocouple hot junction of the treated wire, prior to treatment, and then to perform the heat treatment on the entire assembly. If no differences are observed in the heating and cooling calibrations, then an estimate can be made of the magnitude of the original changes which were occurring in the wire. Initial calibrations have been run on wires treated in the following manner:

1. A. C. Scott NiCr+:NiAl Annealed at 500°C for 1200 hours in CO_2
2. Hoskins Chromel and Alumel, vacuum annealed at 1600°F for 10 and 135 hours.
3. Hoskins Chromel and Alumel, as-received, but pickled.

The results of these calibrations are not included because calibration data on the as-received alloys is needed but have not yet been obtained to allow a proper interpretation of the results.

It is believed that the above mentioned calibrations and the proper interpretation of the calibration loop being detected will allow one to use calibrations as a real analytical tool in the interpretation of many phenomena.

Finally Figure 48 is included to show the calibration of totally heating undisturbed chromel-alumel thermocouples at 500°C for 18 hours as compared to the calibration of as-received chromel-alumel thermocouples. The primary comparison temperature measurement was a platinum resistance thermometer. As can be seen, up to 400°C the calibrations for the two are significantly different by increasing amounts as the temperature increases (approximately a 0.9% of the temperature change). This further points out that the calibration can be shifted by heat treatment. In both cases the calibration on heating differs slightly from that on cooling, however there is less difference in the heat-treated wire. Attention is called to the fact that the as-received wire actually receives non-isothermal heat treatment in being calibrated and thus the large shift in this wire is not too surprising, though it is disturbing that this is occurring in as-received wires. This experiment points out an interesting fact that the as-received wire is within the ±3/4% tolerance for the reference calibration curve, but that after several heatings the thermocouple may be outside this calibration limit. To the thermocouple user it would appear that a more satisfactory thermocouple would be the one which had been heat treated. The

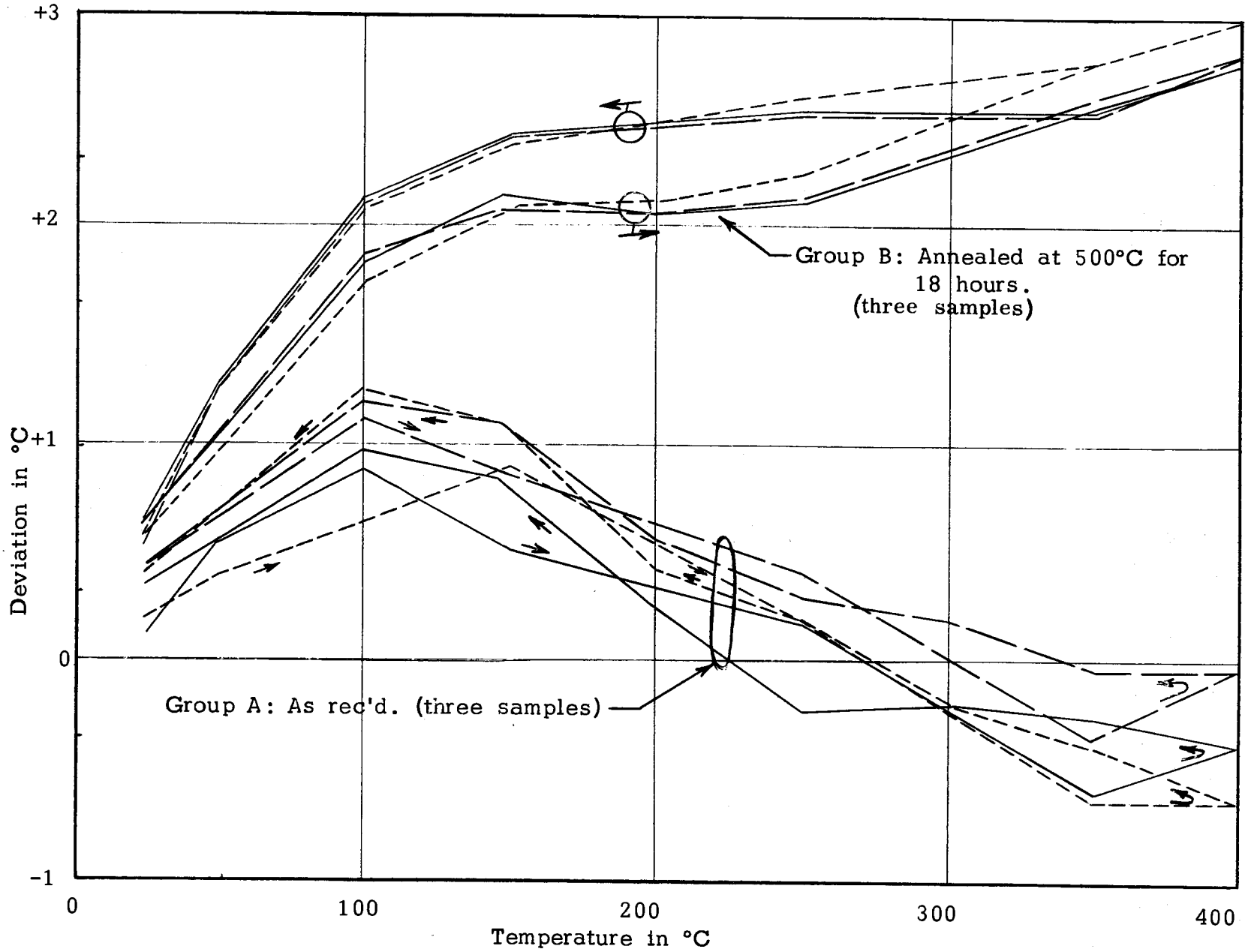

FIGURE 48 - CHROMEL ALUMEL CALIBRATION VS. PLATINUM RESISTANCE THERMOMETER

general similarity of the deviation curves, near 100°-200°C is considered significant and is thought to be due to the particular chromel and alumel compositions being different from the average materials. But if these materials are "typical" then there is a need for a readjustment of the emf-temperature table in the region (see Figure 10).

CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS

In this report the general characteristics of thermocouples have been reviewed, and particular reference has been made to available information on the Chromel-Alumel type alloys. The equipment which has been constructed and operated for this study on Chromel and Alumel alloys has been described, and the operational characteristics of this equipment have been detailed. The following conclusions have been drawn from the experimental results:

1. LITERATURE: Considerable information exists in the literature on temperature measurement. However, the fundamental reasons for observed thermocouple performance in temperature measurement are not clearly defined in the literature.

2. CHEMICAL ANALYSIS: The Chromel-and Alumel-type alloys being used for thermocouples are nickel-base alloys which contain appreciable amounts of which are varied from alloy to alloy in order to facilitate fabrication and to match a reference calibration curve. However, variations in the amounts of these materials in the alloys as revealed in the chemical analyses obtained are a number of wires, can cause calibration differences from the accepted emf-temperature relations for the average alloys.

3. REFERENCE JUNCTION: With proper precautions a mercury U-tube reference-junction connection located in the geometrical center of a Dewar flask is a convenient connection which will limit reference-junction errors to less than 0.1_0C.

4. HOT JUNCTION: The emf generated by a thermocouple is not influenced by the method of hot-junction preparation if the hot junction has adequate electrical continuity and mechanical strength.

5. INHOMOGENEITIES: Large errors in thermal emf have been observed in thermocouples containing inhomogeneities which vary from wire to wire and from producer to producer. As-received Chromel and Alumel alloys contain mechanical inhomogeneities which are removed to a certain extent by short-time heatings. Continued annealing at high temperatures will produce marked inhomogeneities in both Chromel and Alumel. Pickling of annealed Chromel and Alumel can reduce the emf which results from inhomogeneities. This may indicate that

surface oxide can cause inhomogeneities. Vacuum annealing does not remove inhomogeneities in Chromel and Alumel.

6. RECRYSTALLIZATION: The recrystallization temperature for Chromel is 1160°F for 70 percent cold work, and for Alumel it is 1100°F.

7. MICROSTRUCTURE: Chromel and Alumel can be polished and etched to resolve the microstructure of the metal; however, variation in composition of both types of alloy and the variation in condition of the alloys necessitates considerable variation in the etchants for both materials. Chromel and Alumel are single-phase alloys and the microstructure varies somewhat from vendor to vendor. Chromel is extremely resistant to oxidation, as evidenced by the microstructure of exposed material. In contrast, Alumel undergoes appreciable oxidation in similar situations; this is seen in the microstructure. Grain growth is quite evident in Chromel and Alumel exposed for long times at high temperatures.

8. DRIFT: The emf generated by Chromel-Alumel thermocouples does change with time at temperature in the range 500°C to 1100°C. In general the magnitude and direction of the drift depend on the test temperature and environment, and are most serious at the high temperatures. The hypothesis which was presented to explain the variations in the emf's with time at temperature, based on composition changes, is basically sound.

9. CALIBRATIONS: Accurate calibrations have been performed on Chromel and Alumel wires. They indicate that, on the first heating of an as-received material, the calibration differs from the calibration on cooling and from that of subsequent heatings and coolings. Studies of the effect of changing the depth of immersion of a thermocouple indicate that this may cause a change in its calibration.

Stated in the original proposal....."Results of this research will be correlated with data in the literature and presented so that quantitative estimates of the performance of a thermocouple in a given application can be made along with recommendations which will permit maximum utilization of the thermocouple...." The aforementioned thermocouple might be one of current issue and now under study, or conceivably, an entirely new thermocouple.

The current work has suggested treatments to presently available thermocouples to give improved performance. However, the exact criteria for judging the performance of a particular thermocouple (stability, consistency, costs, etc.) are still not precisely known, although they are more clearly understood now than at the beginning of this study. In any case, these criteria will be conditional, depending upon the accuracy desired and the environment encountered.

This indicates the need for further study to delineate the fundamental causes for the behavior of thermocouples from their behavior as influenced by extraneous factors. In order to accomplish this, the following recommendations are made:

1. More complete correlation of the current work with that of the literature is needed and this will be annotated in the forthcoming bibliography publication.

2. A more systematic appraisal of the influence of the alloying components on calibration is needed.

3. Critical experiments are needed to verify the proposed explanation of observed thermocouple drifts in emf at various temperatures.

4. Studies are needed to resolve the variations in calibration caused by wire condition (aside from composition variations).

5. In addition, experiments are needed to (1) obtain exact calibration curves for various Chromel-Alumel thermocouples, (2) identify oxides formed on the thermocouples during drift tests, (3) determine the master curves for the effect of composition on thermal emf in nickel-base alloys, and (4) analyze the meaning of dE/dT and d^2E/dT^2 versus T relations and thus lead to a smoother and more meaningful reference calibration table.

Finally, attention is called to the fact that this document describes the progress of the first year of investigation on thermocouple thermometry. Some of the conclusions presented may need further consideration at a later date, however, it is strongly felt that most of the conclusions which have been reached from the above reported experiments are fundamentally sound and will remain essentially unchanged.

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APPENDICES

APPENDIX A

The following samples were sent to Lucius Pitkin Company for Qualitative Spectrographic Analysis and Quantitative Chemical Analysis.

A. Chromel: Hoskins coil 2816: Date 8-9-56

B. Chromel: Hoskins coil 2816: Date 8-9-56

C. Alumel: Hoskins coil 6774: Date 7-13-56

D. Chromel: Leeds and Northrup Spool No. 61378-4 D. O. 242155 Date 12-10-56

E. Alumel: Leeds and Northrup Spool No. 25294-11 D. O. 238141 Date 9-17-56

F. Chromel: A.C. Scott Reel No.: None: Date 3-11-57

G. Alumel: A.C. Scott Reel NO.: None: Date 3-11-57

The following samples were sent to Oak Ridge National Laboratory for Qualitative Spectrographic Analysis and Quantitative Chemical Analysis.

H. Chromel: Hoskins coil 2816: Date 8-9-56

I. Alumel: Hoskins coil 6774: Date 7-13-56

J. Chromel: A.C. Scott Reel No.: None: Date 3-11-57

K. Alumel: A.C. Scott Reel No.: None: Date 3-11-57

L. Alumel: Hoskins coil 6774: Date 7-13-56

M. Chromel: Leeds and Northrup Spool No. 61378-4 D. O. 242155 Date 12-10-56

N. Alumel: Leeds and Northrup Spool No. 25294-11 D. O. 238141 Date 9-17-56

APPENDIX B

Major Nickel Base Thermoelements, excluding Copper alloys

Company	Material	Chief Constituents Cr	Si	Al	Mn	Balance	Millivolts at T°C # 100	400	700	1000°C
Hoskins Manuf. Co.	Chromel-P	9.5	0.4	---	.05	Nickel*	4.01	16.40	29.14	41.31
	Alumel	----	1.2	1.6	1.8	Nickel				
Driver Harris Co.	Geminol P (242)	18.0	0.7	---	---	1.0Cb, Ni*	2.4	8.9	20.65	31.9
	Geminol N (33)	----	2.7	---	---	Nickel*				
General Electric Co.	Nickel	----	---	---	---	Nickel	5.4	20.0	33.8	48.0
	Nickel-Moly.	18% Molybdenum		--	---	Nickel				
A. C. Scott Ltd.	NiCr (+)	9.0	0.3	2.1	.01	Nickel	4.01	16.40	29.14	41.31
	NiAl (-)	----	1.5	0.2	.5	Nickel				
A. B. Kanthal Corp.	Kanthal (+)	9.1	0.4	.04	--	Nickel*	4.01	16.40	29.14	41.31
	Kanthal (-)	---	2.4	--	.04	Nickel*				
Vacuumschmelze A. G.	Vacoplus (Ni-Cr)	10.0	---	---	---	Nickel	4.04	16.38	29.15	41.32
	Vacominus (Ni-Al)	---	---	---	---	Nickel				
	Heraeus Plus	10	---	---	---	Nickel	3.22	15.56	28.33	40.50
	Heraeus Minus	----	---	---	---	Nickel				
	Chromnickel B	18.0	---	---	---	60Ni, BalFe	1.75	9.15	17.95	28.50
	Heraeus Minus	----	---	---	---	Nickel				

* Author's Analysis

ISA and DIN Tolerances are not shown.