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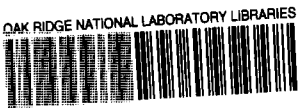


ABSTRACT

After annealed, type K (Chromel vs Alumel) thermocouples were heated above 200°C (392°F), their temperature measurements were in error up to 1.7%, as determined by comparison calibrations to working standard 90% Pt-10% Rh vs Pt thermocouples or platinum resistance thermometers. Reannealing the type K thermocouples removed the errors. The errors were due to changes in the thermal emf vs temperature relationship of the type K thermocouples, which from previous work of others can be attributed to short-ranged ordering of the Chromel thermoelements. Reannealing the thermocouples removed the errors because the order-disorder transformation is reversible; that is, short-ranged ordering of the Ni and Cr atoms of the Chromel alloy occurs between 200 and 600°C and disordering occurs above 600°C (1112°F). The traveling gradient method was used to determine the effects of heat treatment on the thermal emf of type K thermocouples, to investigate the kinetics of ordering of Chromel, and to determine the amount of order produced by heat treatments. Though the order-disorder transformation could not be stopped, our results demonstrate that there exists an optimum amount of order in the Chromel thermoelement to yield a repeatable thermal emf vs temperature relationship for a type K thermocouple in a specific application. When the experimental conditions of the application were controlled carefully, heat treatment to produce the optimum order in the Chromel thermoelements and calibration of the type K thermocouples prior to use essentially eliminated the temperature measurement errors due to order. The optimum amount of order depended on the application and was determined experimentally. Variations from the optimized heating or cooling cycles, changes in the depth of thermocouple immersion during use, or modification of the temperature gradient on the thermocouple caused temperature measurement errors of up to 1% with ordered and calibrated type K thermocouples.

CONTENTS

1. INTRODUCTION

Annealed, type K (Chromel vs Alumel) thermocouples are specified by the manufacturer to generate a thermal emf vs temperature (E:T) relationship within ±3/8% (special grade) or ±3/4% (standard grade) of the E:T relationship of ASTM E-230.[1] However, during use at temperatures above about 200°C (392°F), the Chromel thermoelement of the type K thermocouple undergoes a solid-state transformation that causes deviations of up to 1.7% from the ASTM E:T relationship. Because this transformation is reversible and cannot be prevented, temperature measurement errors of up to 1.7% are inherent in type K thermocouples when used above 200°C with the ASTM E-230 E:T relationship.

The temperature measurement limitations of type K thermocouples, first recognized at ORNL in 1956, were studied by McElroy,[2] Potts,[3] and others.[4-10] At that time, for many applications an error of less than 2% was not detrimental. Within the past few years, however, greater accuracy of temperature measurement using these thermocouples was sought by several programs at ORNL. Therefore, a series of experiments were planned at ORNL to study the solid-state transformation responsible for the temperature measurement errors; that is, the short-ranged, order-disorder transformation in which the Ni and Cr atoms occupy specific (ordered) sites in the Chromel alloy crystal lattice. The goal was to find a heat treatment that would optimize the state of short-ranged order in the Chromel thermoelement so that a reproducible E:T relationship would be achieved for the type K thermocouple during a given application. Calibration of the heat treated thermocouple was necessary to correct for the 1% deviations of the E:T relationship from ASTM E-230 caused by the partially ordered Chromel thermoelement. Commercial, sheathed, type K thermocouples were employed in these studies.[11]

2. THEORETICAL BACKGROUND

It is well established[2-10] that the thermal emf of an annealed, type K thermocouple increases when portions of the thermocouple are held between 200 and 600°C (392 and 1112°F). However, it has not been proved that the

order-disorder transformation is responsible for this increase in thermal emf. Therefore, in this section we present evidence from crystallographic measurements that short-ranged order does occur in Ni-Cr alloys similar to Chromel. Also, other supporting evidence is given and is based on measured changes in physical properties of Chromel-like alloys which are consistent with the existence of the order-disorder transformation. Finally, the effects of order on the thermal emf of a type K thermocouple are described. First, however, to aid in the understanding of the phenomena involved, the basic theory of thermoelectric thermometry is discussed and the metallurgical aspects of the order-disorder transformation are presented.

2.1 Thermal EMF of a Thermocouple

The thermal emf E of a thermcouple is given by the line integral along the path ℓ from the positive to the negative terminal of the thermocouple:

$$E = \int_{\ell} S \, \vec{\nabla} T \cdot d\vec{x} \, , \tag{1}$$

where S is the absolute thermoelectric power (Seebeck coefficient) of the thermoelements, and $\vec{\nabla} T$ is the temperature gradient at any position $\vec{x}$ along the thermoelements. For a homogeneous thermocouple, S is a function only of T for each thermoelement. However, some thermocouples are inhomogeneous, and S is then a function of both the position $\vec{x}$ and the temperature T along the thermocouple. Inhomogeneities in a thermocouple are caused by metallurgical factors. Of particular interest are inhomogeneities due to variations in the amount of short-ranged order along the length of a Chromel thermoelement of a type K thermocouple. Because S of Chromel increases with increased short-ranged order,[5] the contribution to E of an ordered section of a Chromel thermoelement is larger than if it were disordered.

Equation (1) implies that electric field gradients are larger in sections of thermocouples that are in steep temperature gradients. Or stated another way, there is no contribution to the total E from isothermal zones of a thermocouple. Therefore, the effect of inhomogeneities in a thermocouple is greatest where the thermocouple passes through a steep tempera-

ture gradient, which in many applications is where it exits a furnace to the ambience. Note, however, that changes in E need not result solely from inhomogeneities in a thermocouple. For example, if a section of a Chromel thermoelement were ordered homogeneously, S of the thermoelement would increase[5] uniformly. By Eq. (1), E would increase if the homogeneously ordered section were placed in a temperature gradient.

2.2 Order-Disorder Transformation

An understanding of the order-disorder transformation in solids is essential to the interpretation of the results presented herein. Therefore, because of the diverse background of those expected to read this report, a brief description of the metallurgical aspects of the order-disorder transformation in solids is included. In particular, we explain what ordering of a binary alloy means and why ordering occurs at low temperatures and disordering at high temperatures, and we discuss the kinetics of the order-disorder transformation.

2.2.1 Explanation of Ordering

When viewed in three dimensions, the atoms of a solid are arranged in a repeating geometric pattern that constitutes the crystalline lattice of the solid. The smallest group of lattice points whose translation in three dimensions will reproduce the crystal lattice is called the "unit cell" of the lattice.

Many different types of lattices occur in solids, and they are classified by the symmetry of the lattice points to each other. Most metals have lattices with either cubic or hexagonal symmetry. Of particular interest herein is the *face-centered-cubic* (*fcc*) lattice, because both Chromel and Alumel alloys are of this type. The *fcc* unit cell is shown in Fig. 1a. This cell has one lattice point at each corner of a cube and one at the center of each face.

In a pure metal, each lattice point is "occupied" by the same type of atom (A atoms in Fig. 1a). However, in a substitutional binary alloy some lattice points are occupied by the solute (B) atoms and others by the solvent (A) atoms. In most alloys, the A and B atoms are arranged

randomly on the lattice points, but some binary alloys have an ordered arrangement. For example, in the *fcc* system, an ordered unit cell would have only B atoms on the corner points and only A atoms on the face-centered points. This ordered *fcc* unit cell is shown in Fig. 1b. If the ordered arrangement extends over many adjacent unit cells, the binary alloy is said to be "long-ranged ordered." If the arrangement is limited to near-neighbor unit cells, the alloy is said to be "short-ranged ordered."

The percentage of the unit cells of an alloy that can be long-ranged ordered depends on the chemical composition of the alloy. For example, each face-centered atom and each corner atom of the *fcc* lattice is shared between two and eight unit cells, respectively. Thus, on the average, an *fcc* unit cell consists of four atoms: three are face-centered atoms, and one is a corner atom (6 atoms in faces x 1/2 = 3; 8 atoms on corners x 1/8 = 1). Therefore, the theoretical chemical composition is 75% A and 25% B to obtain a completely ordered lattice with the atoms of all unit cells arranged as shown in Fig. 1b. This type of order is designated as A_3B.

It is possible for a nonstoichiometric alloy to be long-ranged ordered; that is, for an *fcc* alloy not having 75% A and 25% B atoms to be A_3B type long-ranged ordered. For example, the Ni_3Fe structure occurs[12] in alloys containing 60 to 85% Ni. Many unit cells would have Fe atoms (B atoms) on face-centered lattice points for the 60% Ni (A atom) alloy.

To obtain a quantitative expression of the amount of long-ranged order in any binary alloy, Bragg and Williams[13] defined a long-ranged order parameter S. For an *fcc* alloy, S is related to the fraction of face-centered lattice sites occupied by B atoms. The range of values for S is from zero for complete disorder (random number of B atoms on face-centered points) to one for complete long-ranged order (no B atoms on face-centered lattice points, and possible only for the stoichiometric alloy A_3B).

As for long-ranged order, the extent of short-ranged order in an alloy is represented quantitatively by Bethe's[14] short-ranged order parameter σ. The range of values for σ is from zero for a random distribution of A and B atoms to one for complete short-ranged order. Obviously, if σ is one, then S is one, also. However, it does not follow that if S is

zero, then σ is zero because:

1. Short-ranged order can exist for alloy compositions for which long-ranged order is not possible; for example, Ni-Fe alloys having 90% Ni.[15]
2. Short-ranged order occurs in some binary alloys for which long-ranged order has not been found; for example, in Cu-rich, Cu-Al alloys.[16]
3. Short-ranged order will exist at higher temperatures than long-ranged order for any alloy. This is demonstrated in Fig. 2 in which S and σ are plotted vs temperature for A_3B type order in an *fcc* alloy.[14,17]

Thus, long-ranged order may be considered as the limiting case of short-ranged order.

2.2.2 Temperature Dependence of Order in an Alloy

Swalin[18] explained the temperature dependence of order, using the quasichemical theory of thermodynamics, as follows:

1. At absolute zero temperature, a completely ordered alloy is theoretically possible; that is, S is one and σ is one for a stoichiometric alloy.
2. As the temperature is raised, the values of S and σ decrease, slowly at first, then more rapidly.
3. Above a critical temperature T_c, S is zero. At T_c, S is either step-wise discontinuous, as for the *fcc* A_3B type long-ranged order shown in Fig. 2, or monotonically approaches zero, as for the *body-centered-cubic* (*bcc*), AB type long-ranged order.
4. The T_c for a nonstoichiometric alloy is always less than that for a stoichiometric alloy.
5. Short-ranged order occurs above T_c. At T_c, σ is step-wise discontinuous for the *fcc*, A_3B type short-ranged order (Fig. 2), but it is continuous and monotonic for the AB type short-ranged order in *bcc* alloys, as shown by the theoretical curve of Fig. 3.

2.2.3 Kinetics of the Order-Disorder Transformation

The order-disorder transformation is a nucleation and growth type process. Nucleation can be thought of as the formation of an ordered unit

cell, and growth as the spreading of the ordered arrangement of atoms to adjacent unit cells. The nucleation rate increases as the temperature is lowered; but because growth depends on diffusion of atoms, its rate decreases exponentially with decreasing temperature. The result is that the amount of order achieved in an alloy is less than the theoretical amount and depends on the time-temperature treatment of the alloy.

Figure 3 is a parametric plot of σ vs T for isothermal heat treatments for 1 hr, 1 day, 1 week, and 1 month at temperature for AB type short-ranged order. At low temperatures, σ increases with time at a fixed temperature, but is less than theoretical; at high temperatures, σ is essentially equal to the theoretical value. The theoretical curve would be achieved after an infinite length of time. Also shown in Fig. 3 is the σ vs T curve obtained on rapid cooling, called "quenching." Quenching to low temperature, usually room temperature, results in complete retention of the disordered state of the alloy.

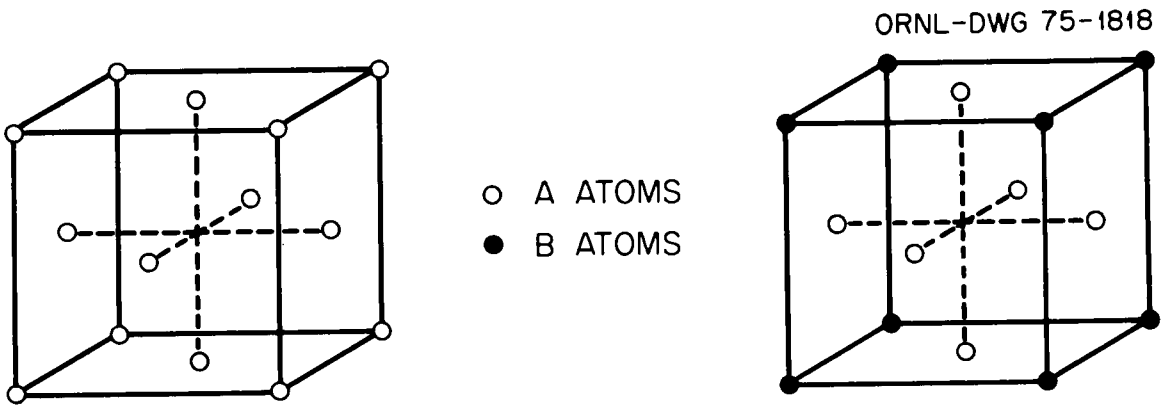
2.3 Evidence of Order In Ni-Rich, Ni-Cr Alloys (Chromel)

2.3.1 Crystallographic Evidence

Analytical techniques of crystallography provide the only certain method of detecting order in an alloy. The most common crystallographic methods are x-ray, neutron, and electron diffraction. Extra lines, called "superlattice lines," in the diffraction pattern are produced by long-ranged order. Diffuse scattering spectra in the diffraction pattern are employed to detect short-ranged order.

Chromel is a Ni-based alloy containing about 9% Cr.[1] Because the neutron, x-ray, and, to a lesser extent, electron atomic scattering factors for Ni and Cr atoms are about equal, detection of order in Ni-Cr alloys is difficult. Some diffraction experiments[19] did not show ordering, probably because the method employed lacked sufficient sensitivity.

To the authors' knowledge and according to Hansen,[12] Elliott,[20] and Shunk,[21] diffraction measurements have not revealed order of the type Ni_3Cr in Ni-Cr alloys. However, x-ray,[22,23] neutron,[24-26] and electron diffraction[27,28] measurements have established the existence of the long-ranged



a. Pure metal A

b. Ordered A_3B alloy

Fig. 1. The *face-centered-cubic* (*fcc*) unit cell.

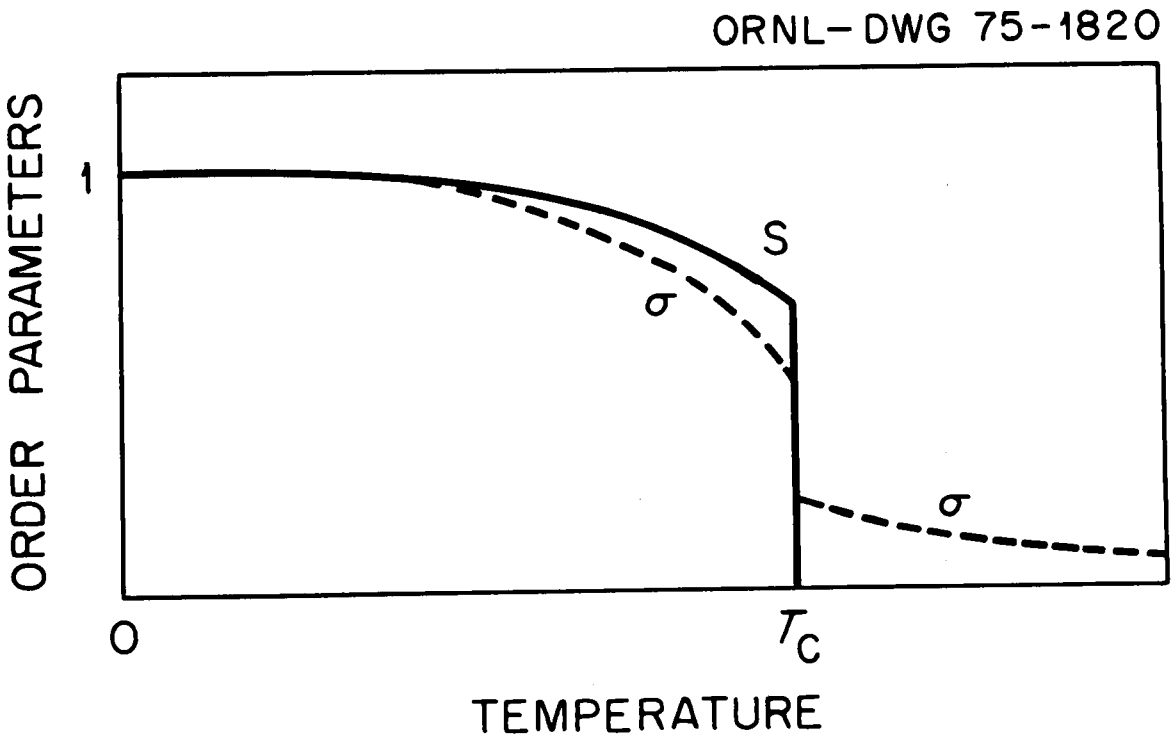


Fig. 2. The theoretical temperature dependence of the long- and short-ranged order parameters for A_3B type order in a stoichiometric *fcc* alloy (sources: refs. 14 and 17).

ordered structure Ni_2Cr (66.6% Ni, 33.3% Cr). Figure 4 shows the relationship of the ordered Ni_2Cr unit cell to the *fcc* lattice. The Ni_2Cr unit cell is *body-centered orthorhombic*.

Baer[23] has shown that long-ranged order of the type Ni_2Cr occurs in nonstoichiometric Ni-Cr alloys having compositions between 25 and 36% Cr. Bagaristskii[22] proved that Ni_2Cr short-ranged order is present in 28 and 35% Cr alloys. Burley reported[4] that neutron diffraction studies by Sabine[29] "have produced evidence of super-lattice formation in powder patterns of polycrystalline samples of a Ni-10% Cr" alloy. However, to the authors' knowledge, diffuse scattering measurements have not established the existence of Ni_2Cr short-ranged order in dilute Ni-based, Ni-Cr alloys with compositions similar to Chromel. Nonetheless, it is reasonable to assume on theoretical grounds that Ni_2Cr type short-ranged order does occur in Chromel, even though it has not been detected by crystallographic techniques.

2.3.2 Evidence Due to Changes in Physical Properties

It is well established that the physical properties of an ordered alloy differ from those of a disordered alloy.[30] Properties such as electrical resistivity and heat capacity have been used to study the mechanisms and kinetics of ordering by measuring the change of these properties as ordering proceeds. However, an otherwise unexplained change in the physical properties of an alloy cannot be attributed to atomic ordering unless there is crystallographic evidence, such as there now is for Ni-Cr alloys, that ordering exists in the alloy system.

Due to the similarities of the atomic scattering factors of Ni and Cr, ordering in Ni-rich, Ni-Cr alloys was not detected until the late 1950's, confirmatory results were not available until the 1960's, and short-ranged ordering in dilute alloys such as Chromel is yet to be detected. Thus, many seemingly anomalous changes in physical properties of these alloys were obtained in the past. These anomalies were attributed by Thomas[31] to formation of a peculiar structural state, which he called the "K-state." Guy[32] believed that precipitation of a second phase was responsible. However, more recent interpretations of the property changes are consistent with long- and short-ranged order-disorder transformations in Ni-Cr alloys.[33]

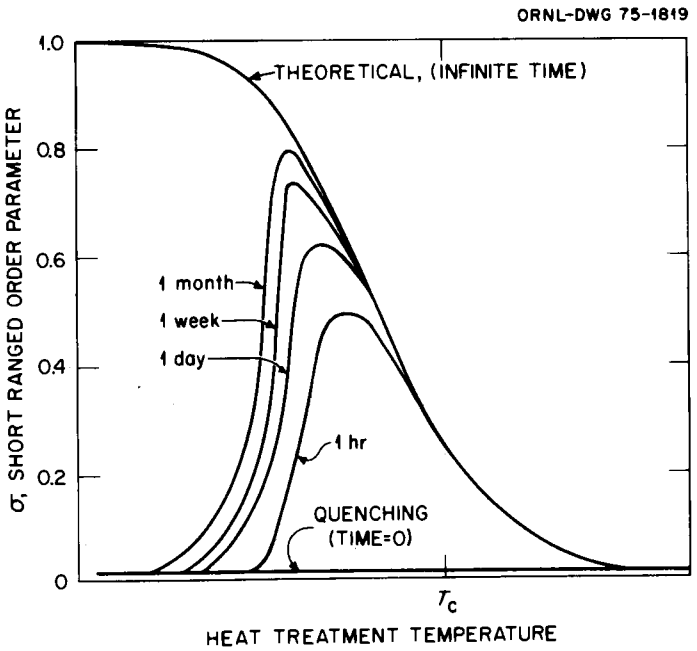


Fig. 3. Short-ranged order parameter for AB type *bcc* alloy vs temperature, showing theoretical curve (infinite time) and curves for quenching and isothermal heat treatments for 1 hour, 1 day, 1 week, and 1 month.

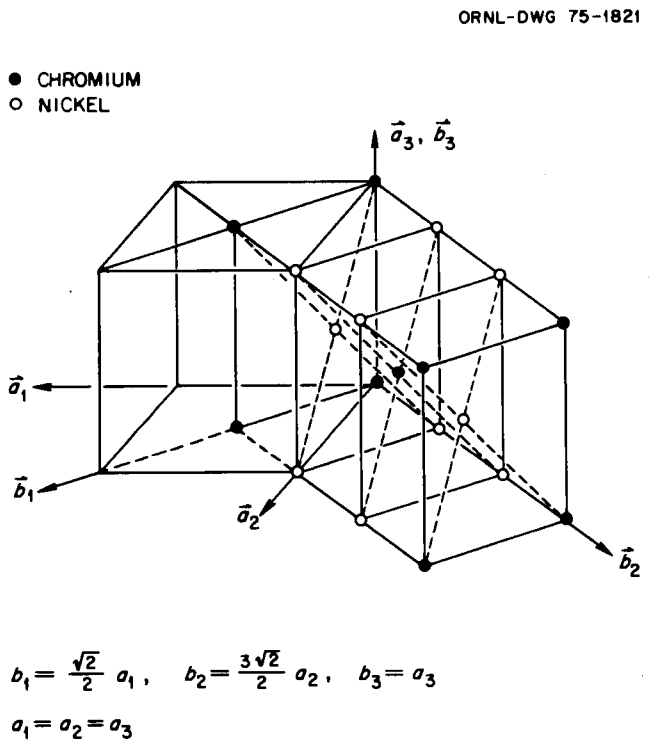


Fig. 4. Relationship of the ordered Ni_2Cr unit cell to the *fcc* lattice. Symbols $\vec{a}_1$, $\vec{a}_2$, and $\vec{a}_3$ are lattice vectors of the *fcc* cell, and $\vec{b}_1$, $\vec{b}_2$, and $\vec{b}_3$ are lattice vectors of the *orthorhombic* cell (sources: refs. 23 and 28).

The electrical resistivity, heat capacity, Seebeck coefficient, Hall coefficients, thermal expansion, and various mechanical properties of Ni-Cr alloys have been measured for various states of order as well as during ordering and disordering.[34] The conclusions from the results of these measurements for alloys similar to Chromel (9% Cr) are as follows:

1. Rapid quenching to room temperature retains completely the disordered structure of this alloy.
2. A quenched alloy orders between about 300 and 600°C (572 and 1112°F) if quenched from below 1000°C (1832°F).
3. Quenching from above 1000°C retains high-temperature defects (vacancies, dislocations, etc.) in the alloy. Because the defects have a high mobility, they increase the kinetics of the order-disorder transformation and lower the temperature at which ordering occurs to about 200°C (392°F).
4. Cold working produces high-mobility defects in the alloy and similarly lowers the ordering temperature.
5. The alloy is disordered above 600°C.
6. The energy absorbed or released during the order-disorder transformation (300 to 400 J/mole) is the same order of magnitude as that associated with short-ranged order in other alloys in which short-ranged order was observed by crystallographic techniques (This energy is about an order of magnitude lower than that for long-ranged order.)

2.4 Effect of Order on the Thermal EMF of Type K Thermocouples

The Seebeck coefficient S is a physical property of a solid that is usually different for an ordered or disordered alloy. Fenton's[5] measurements of the change in S of Chromel as a function of temperature for various heat treatments are shown in Fig. 5. (The change in S with time at temperature is similar to the change in the short-ranged order parameter σ vs time at temperature during ordering shown in Fig. 3.) Thus, because the Chromel thermoelement of a type K thermocouple can be either short-ranged ordered or disordered below 600°C, the thermal emf of a type K thermocouple at a particular temperature depends on the state of order of Chromel.

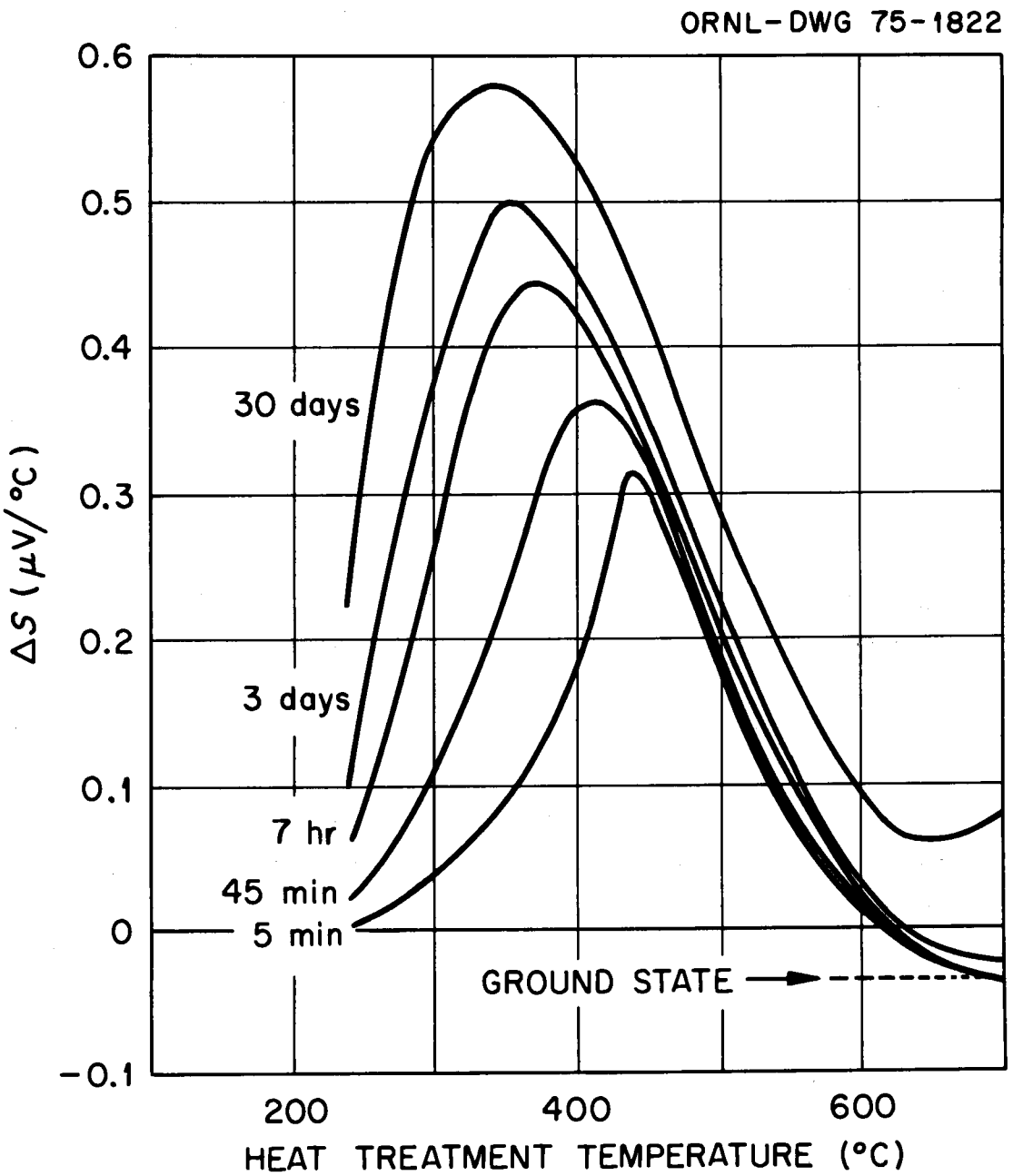


Fig. 5. Change in Seebeck coefficient of Chromel as a function of time at temperature (source: ref. 5).

The last step in the manufacture of type K sheathed thermocouples is the annealing procedure, which involves heating the thermocouple to about 1000°C for several minutes, followed by cooling in ambient air to room temperature. This procedure results in the retention of the high-temperature disordered crystal structure of Chromel. It was for this state of order that the ASTM E-230[1] E:T relationship was established. During use, some portion of the annealed thermocouple is usually at a temperature at which ordering in Chromel can occur. As the Chromel thermoelement orders, the thermal emf of the type K thermocouple changes, resulting in temperature measurement errors. Fenton's measurements[5] (Fig. 5) show that the maximum deviation from ASTM E-230 could be as large as +1.5% at 330°C (626°F). In addition, the temperature of a thermocouple usually varies along its length, from room temperature at its cold end to that of the hot junction. Consequently, the amount of order in the Chromel thermoelement varies along its length; that is, the thermoelement is inhomogeneous. If the inhomogeneous thermocouple is moved in the temperature gradient or if the hot-junction temperature is changed, the distribution of order changes in the Chromel thermoelement. As the order changes, so does S and E, and the temperature measured by the thermocouple changes erroneously.

The net effect of ordering in Chromel is that it limits the accuracy of temperature measurements with type K thermocouples. Unfortunately, no means exists for preventing the order-disorder transformation in Chromel. Burley[4,35] has observed, however, that short-ranged ordering does not affect S if the Cr content of the positive thermoelement (Chromel) is raised from 9 to about 14% Cr, and he has named this alloy "Nicrosil II." Presumably at a concentration of 14% Cr, the d- and s-bands of the electrons are full, and this concentration is the cross over from ferromagnetism to paramagnetism in the alloy.[36] Of course, the change in the Cr concentration yields a thermal emf vs temperature relationship different from that of a type K thermocouple. Therefore, a change from a type K thermocouple to the new thermocouple proposed by Burley, that is, Nicrosil vs Nisil, would require recalibration of all instrumentation designed for a type K thermocouple to be compatible with the Nicrosil vs Nisil thermocouple. (Nisil is

the new negative thermoelement developed by Burley, which has an oxidation resistance superior to Alumel.)

3. EXPERIMENTAL APPARATUS

The experimental apparatus employed in this investigation consisted of three devices: (1) the amount of order in the Chromel thermoelement was measured semiquantitatively using the sheathed-thermocouple inhomogeneity test facility, (2) the repeatability of the temperature-thermal emf relationship was determined using the thermocouple calibration facilities of the standards laboratory, or (3) of the temperature measurement development laboratory.

3.1 Sheathed Thermocouple Inhomogeneity Test Facility

In the experiment illustrated in Fig. 6, the cold and hot junctions of a thermocouple are held at temperatures T_1 and T_2, respectively, and a thermal gradient with a temperature maximum T_3 is impressed over portions of the thermocouple. If the thermoelements are homogeneous, the Seebeck coefficients of the thermoelements are functions only of temperature; that is, for a given temperature S is single-valued along the length of the thermoelements. Under this condition, the integral of Eq. (1) is independent of the path, and E is the same for gradients 1 or 2 of Fig. 6. Thus, E remains constant as the gradient is passed along the length of the thermocouple, as shown in Fig. 7. However, if one of the thermoelements is inhomogeneous, the S of this thermoelement is a function of both temperature and position, and thus is double-valued (S has different values at the same temperature but at different positions along the thermocouple). Therefore, E is different for paths 1 and 2, and as the temperature gradient is passed over the inhomogeneous section of the thermocouple, E changes as in Fig. 7. (See ref. 37 for a discussion of line integrals and when they are independent of their path.)

The preceding reasoning is the basis of the traveling gradient method for study of thermocouple inhomogeneities as described by Fenton,[5] Carr,[6] and Moffett.[7] Because short-ranged ordering in Chromel caused inhomogeneities in type K thermocouples, the traveling gradient method was em-

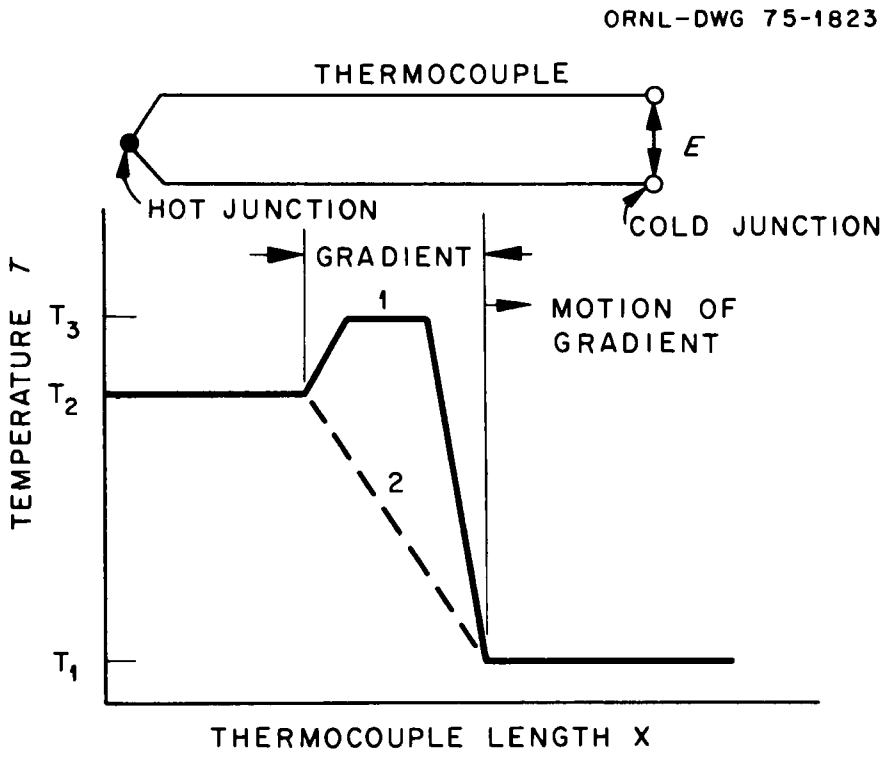


Fig. 6. Moving temperature gradient, with maximum temperature T_3 impressed on thermocouple having cold- and hot-junction temperatures of T_1 and T_2, respectively.

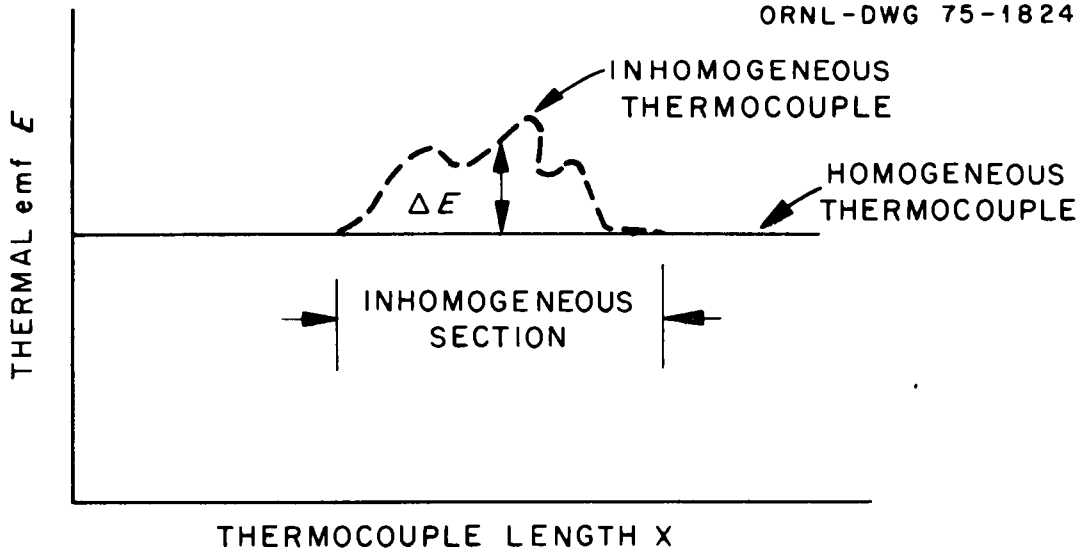


Fig. 7. Thermal emf vs thermocouple length as thermal gradient of Fig. 6 is pressed along a homogeneous and an inhomogeneous thermocouple.

ployed in this study. The sheathed thermocouple inhomogeneity test facility at ORNL (Fig. 8) consists of a thermostat controlled, stirred salt bath into which a test thermocouple is lowered automatically by the drive mechamism. An X-Y plotter records simultaneously the position of the thermocouple and its output. To obtain high resolution, the output terminals of the thermocouple are placed in series opposition with a stable suppression voltage supply, and the resulting differential signal is amplified and fed to the Y-axis of the plotter.[38] [The thermocouple experiences a steep temperature gradient at the surface of the salt bath (Fig. 9a), which was measured by a specially designed sheathed thermocouple (Fig. 9b). The gradient measured was not the true gradient, but rather it is the "effective" gradient impressed on a sheathed thermocouple during testing.] The bath temperature is about 150°C (about 300°F), which is below the temperature at which Chromel could order.

Between 25 and 150°C (77 and 300°F), which is the temperature range experienced by a thermocouple tested in the inhomogeneity test facility, the Seebeck coefficient S_k of a type K thermocouple is about constant at 40 μV/°C. The change ΔS_k in S_k due to ordering of the Chromel thermoelement is calculated by dividing the measured change in emf, ΔE of Fig. 7, by the temperature gradient, 125°C, of the facility:

$$\Delta S_k \approx \Delta E/125 \ . \tag{2}$$

Because S_k is approximately constant above room temperature, the temperature measurement error in percent due to ΔS_k is

$$\Delta T(\%) \approx \frac{\Delta S_k}{40} \times 100 = 2.5 \times \Delta S_k \ . \tag{3}$$

3.2 Thermocouple Calibration Facilities

The repeatability of the E:T relationship of a type K thermocouple was determined using the thermocouple calibration facilities of the standards laboratory and of the temperature measurement development laboratory at ORNL. In both facilities, the thermocouples to be calibrated are inserted to a depth of 10 in. in an Inconel-clad, copper block in a tube

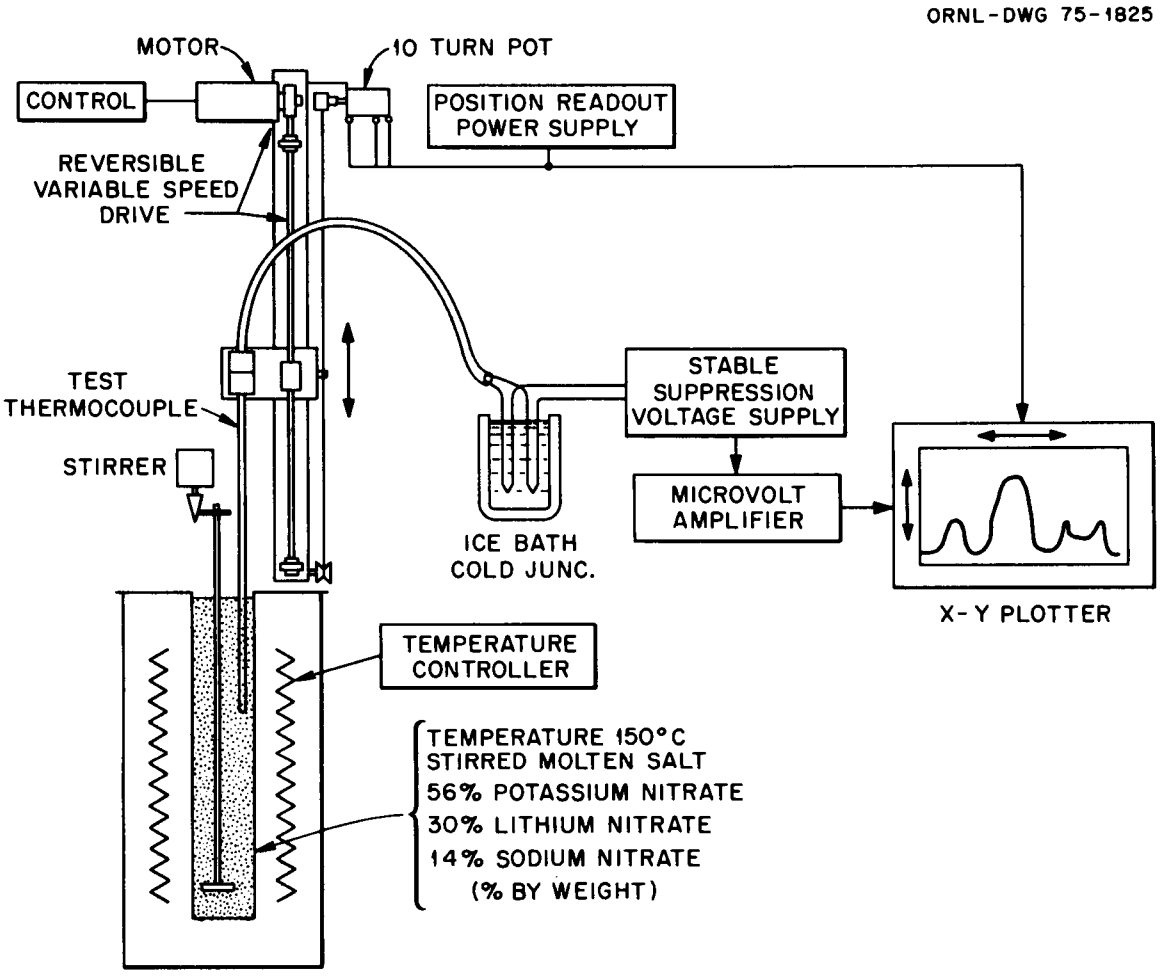
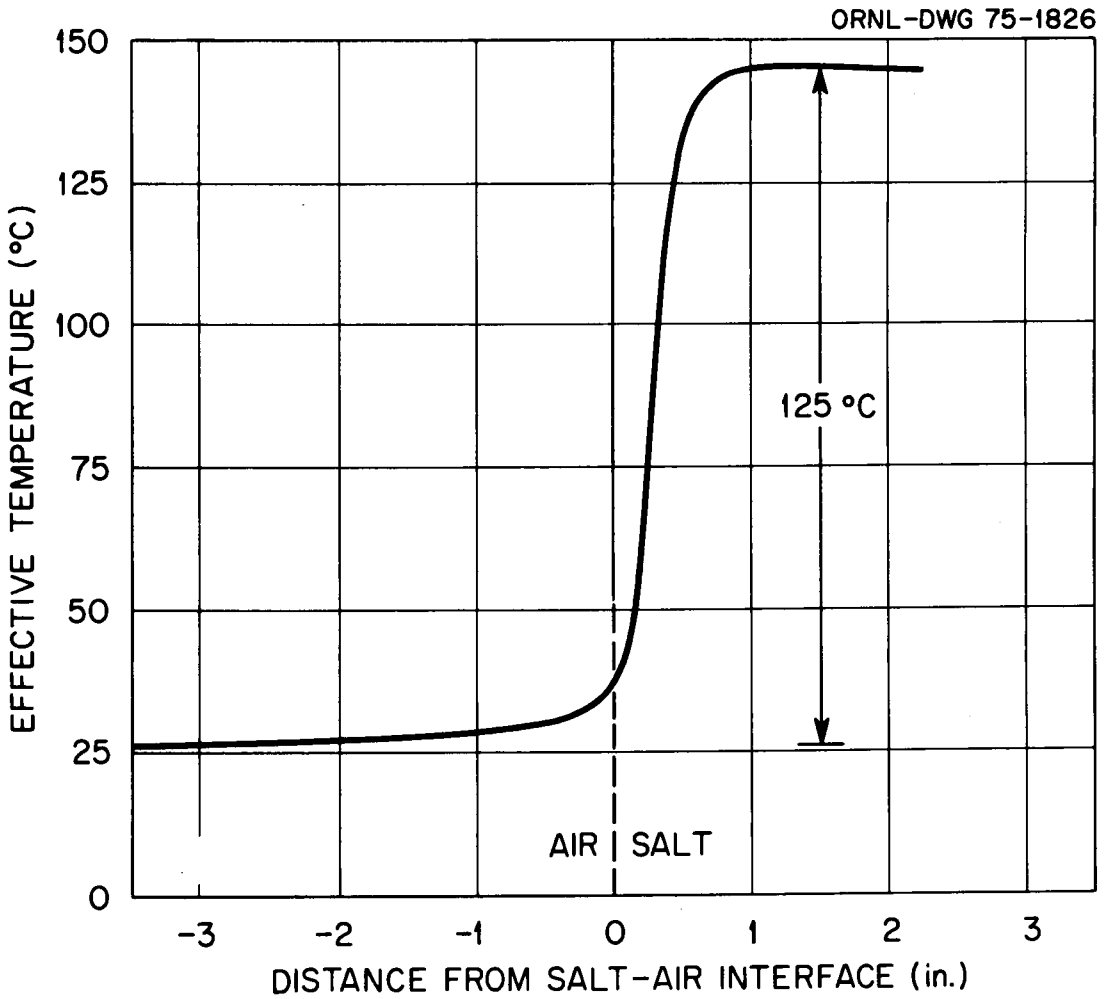
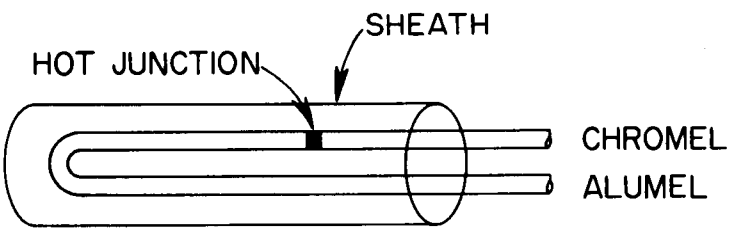


Fig. 8. Sheathed-thermocouple inhomogeneity test facility.



a. Effective temperature vs distance from salt-air interface



b. Specially designed sheathed thermocouple used to measure the temperature

Fig. 9. Temperature gradient of the inhomogeneity test facility.

furnace.[39] In the standards laboratory, the thermocouples are calibrated by comparing their E:T with a working-standard 90% Pt-10% Rh vs Pt thermocouple at five temperatures, both during heating and cooling. The furnace is heated and cooled at a rate of about 1°C/min, and ∿0.5 hr is allowed for the apparatus to reach thermal equilibrium at each data point. Figure 10 illustrates the calibration facility and the effective temperature profile imposed on the thermocouple at a furnace temperature of 750°C (1382°F).

The temperature measurement development laboratory facility is controlled by a computer, and a thermocouple is calibrated by comparing its E:T relationship with a working-standard platinum resistance thermometer. The furnace is heated or cooled at a rate of 0.3°C/min, and the calibration data are printed on-line by the computer. Due to the low temperature-change rates, the temperature gradients impressed on the thermocouple are approximately those illustrated in Fig. 10.

4. RESULTS AND DISCUSSION

All results were obtained on several lots of commercial, type K thermocouples—1/16 in. OD, 3 ft long, stainless steel sheathed, and insulated with MgO. Calibrations obtained before and after use of one lot of thermocouples showed the magnitude of the temperature measurement errors caused by the order-disorder transformation in Chromel and that calibrations alone could not correct these errors. Experiments were performed to increase our understanding of the ordering phenomenon, and the results showed that (1) ordering occurs only in the Chromel and not the Alumel thermoelement of a sheathed thermocouple, (2) ordering occurs in the bare Chromel wire as well as in sheathed wire, (3) changes in the thermal emf due to ordering of Chromel are completely reversible with proper heat treatments, and (4) the kinetics of ordering of the Chromel thermoelement of a sheathed thermocouple are in agreement with theory. From repeatabilities of calibrations for different heat-treated thermocouples, the results show that the optimum heat treatment is dependent on the heating and cooling rates. Finally, movement of a sheathed type K thermocouple in a temperature gradient is shown to vary the state of order in the Chromel thermoelement.

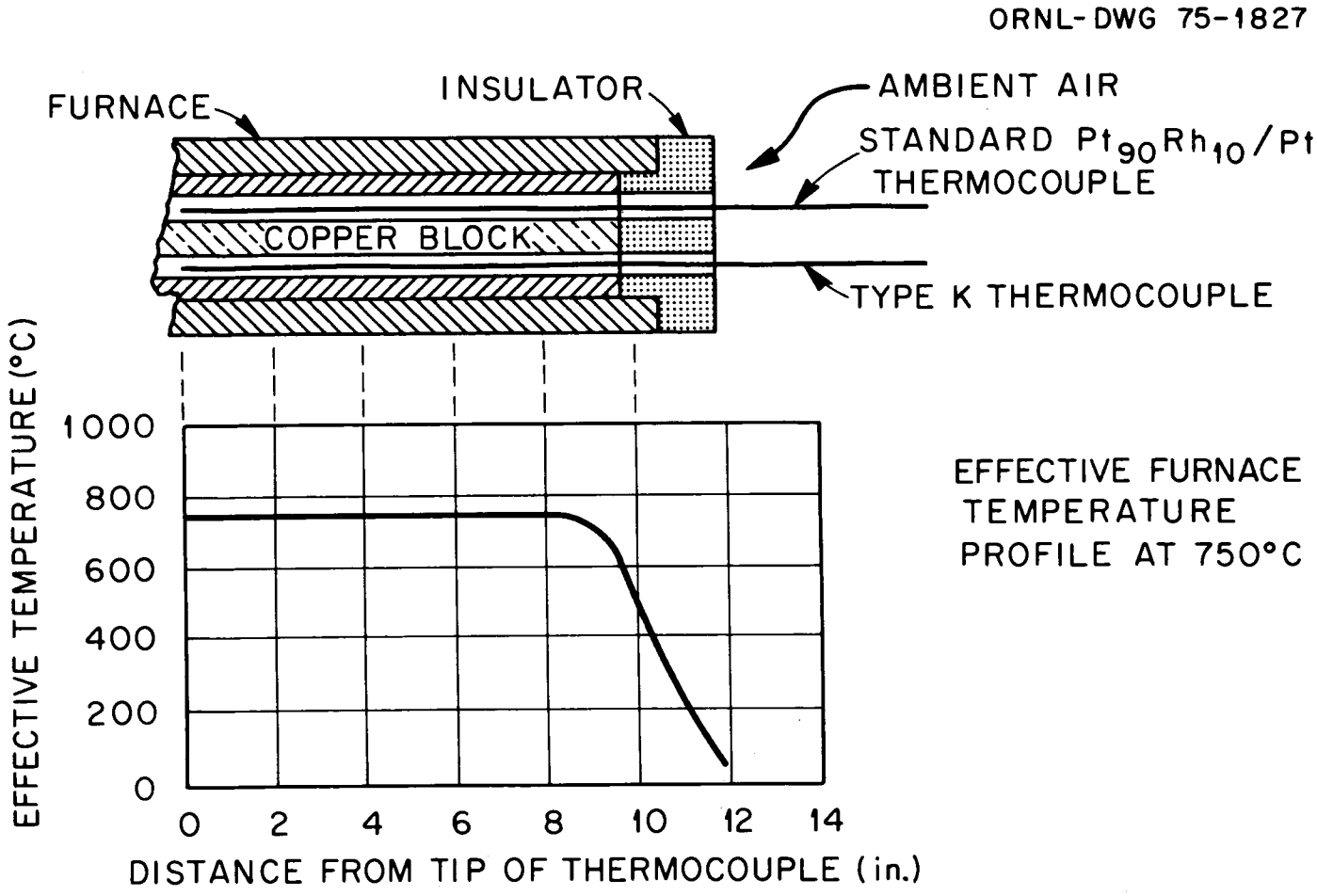


Fig. 10. Thermocouple calibration facility, showing the effective temperature profile of furnace at 750°C (1382°F).

4.1 Magnitude of the Measurement Error

The magnitude of measurement errors caused by the order-disorder transformation in type K thermocouples was determined by comparing calibration data from sixteen thermocouples from the same lot before and after use at 593°C (1100°F). Two thermocouples from the lot were calibrated during heating to 650°C (1202°F). Figure 11 is a plot of the difference in temperature measured between one of the type K thermocouples and a working-standard 90% Pt-10% Rh vs Pt thermocouple vs the true temperature. The E:T relationship of ASTM E-230[1] was used to convert the E output of the type K thermocouples to temperature. The calibration data are essentially within the ±3/8% error specification for special-grade, type K thermocouples. From the data of Fig. 11, a correction equation was derived for the lot, and the thermal emf's of all sixteen thermocouples were checked against this equation at 127 and 270°C (261 and 518°F). Figure 12 shows that all the deviations from the correction equation were less than ±0.5°C (±0.9°F), which is well within specifications.

After calibration, the thermocouples were placed in a furnace and held at a temperature of 593°C (1100°F) for 400 hr. Therefore, a section of each thermocouple was at temperatures between 300 and 600°C (572 and 1112°F), the temperature range for short-ranged ordering of Chromel. After use, the calibrations of all sixteen thermocouples were rechecked with respect to the calibration equations. Figure 13 shows the errors determined for thermocouples that had been immersed in the hot zone of the furnace to depths of 9.5, 13.5, and 16 in. The maximum errors (about 6°C, or 10°F) are in thermocouples immersed 13.5 in. because the sections of these thermocouples having the maximum short-ranged order were in the steep part of the gradient of the calibration furnace (9 to 12 in., see Fig. 10). These data show that measurement errors up to about 1.1% occurred in the measured furnace temperatures, even though the thermocouples had been calibrated. This result demonstrated that calibration alone cannot correct measurement errors in type K thermocouples due to short-ranged ordering in Chromel.

4.2 Preliminary Experiments

Because sheathed, type K thermocouples were employed throughout this investigation, we first determined whether changes in the thermal emf's

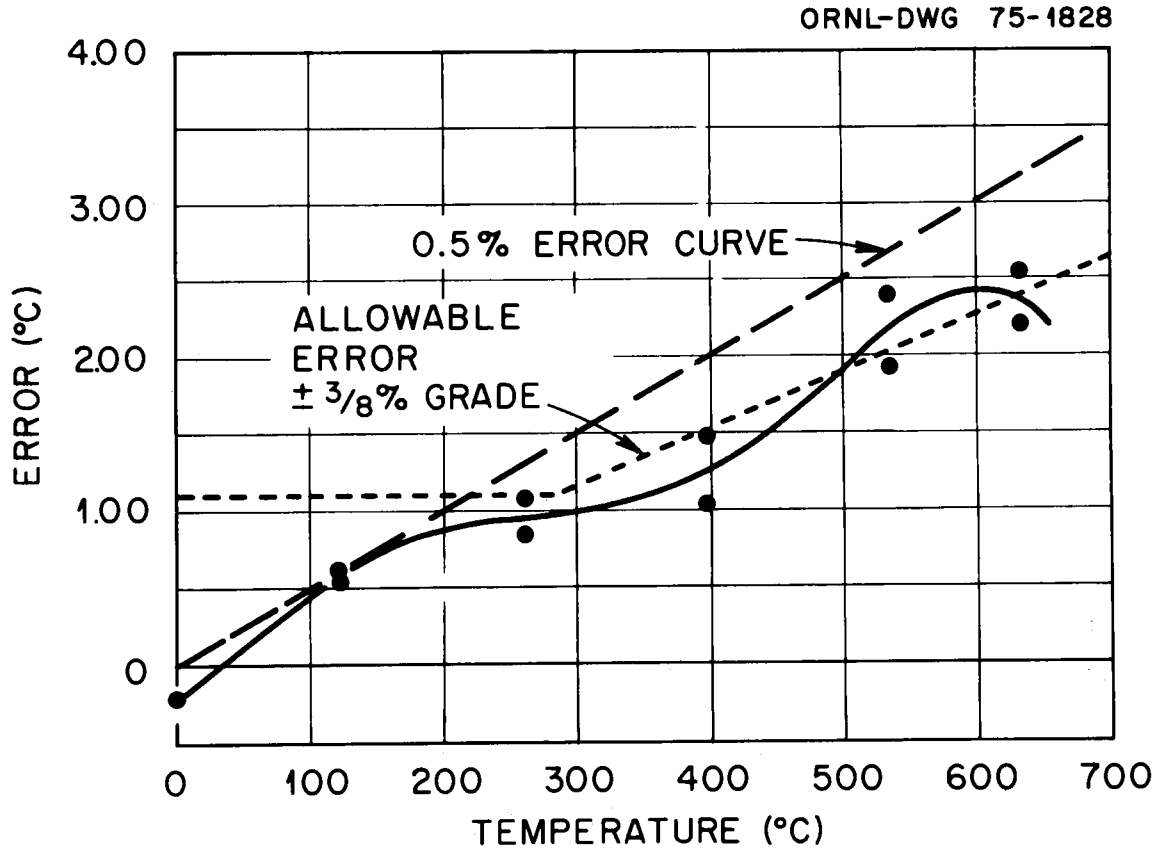


Fig. 11. Calibration data for two thermocouples prior to use in the the furnace.

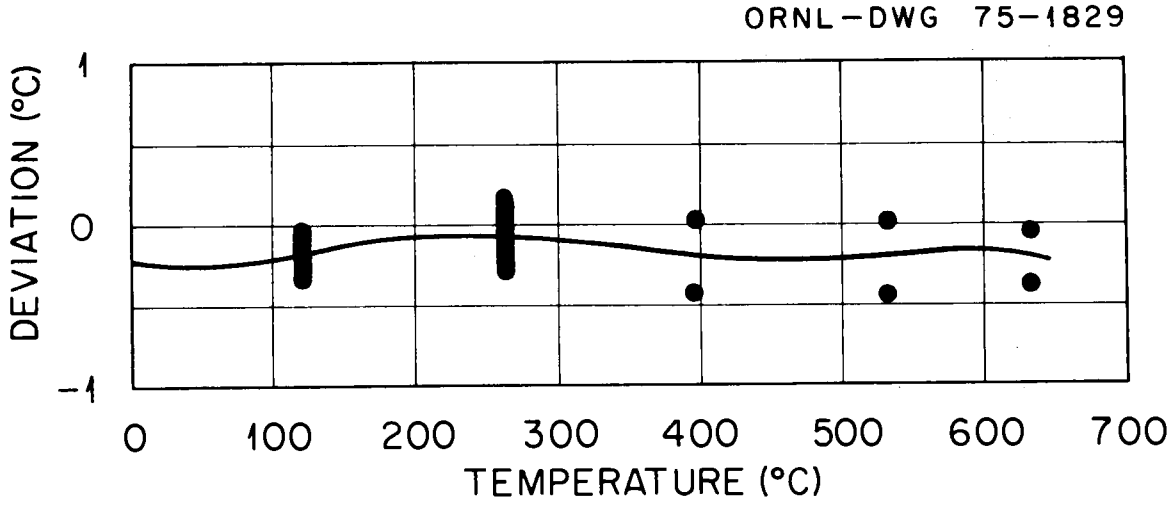


Fig. 12. Deviation at 127 and 270°C (261 and 518°F) of 16 thermocouples from the correction equation obtained from data of Fig. 11.

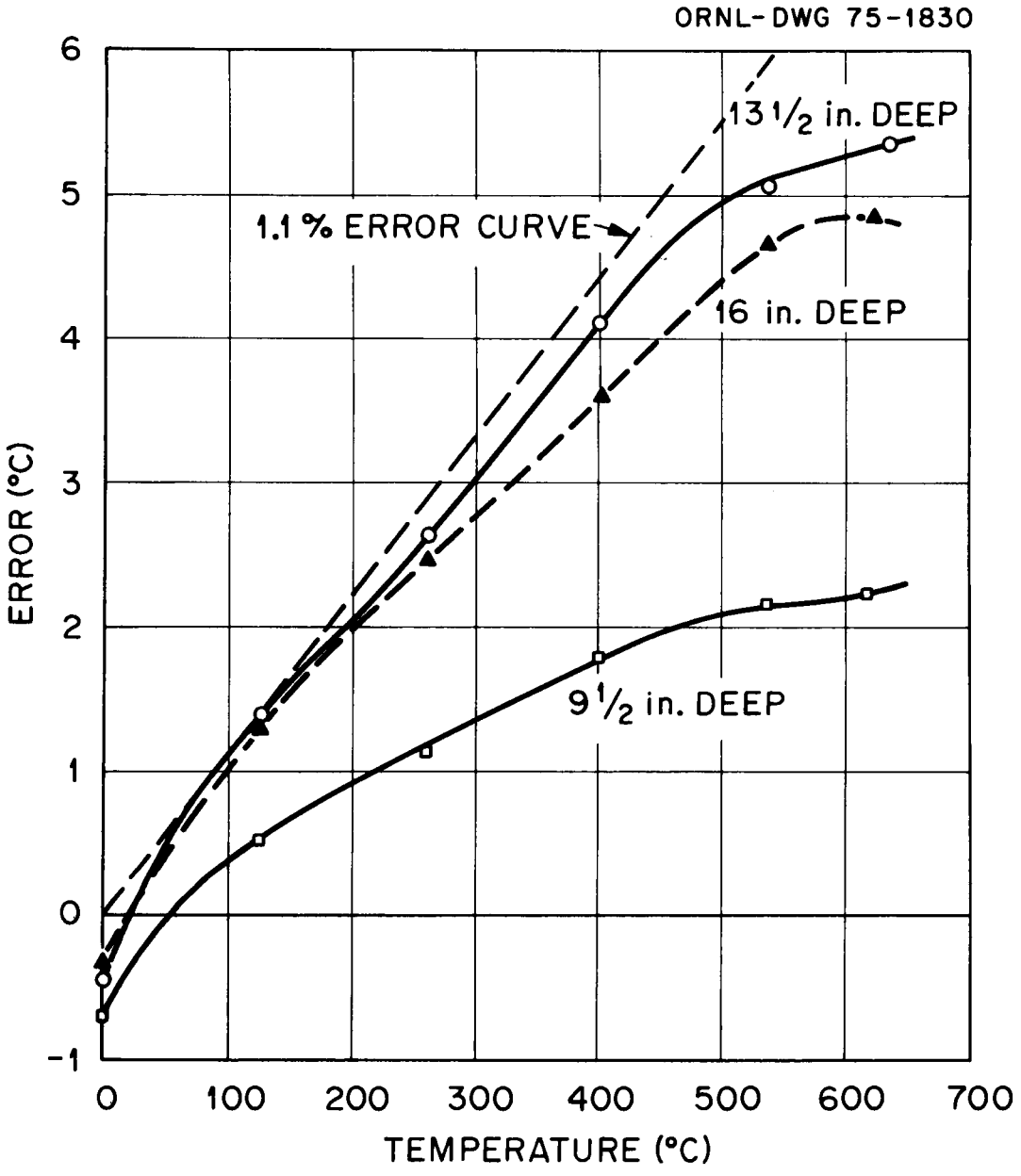


Fig. 13. Temperature measurement error vs temperature determined during recalibration of thermocouples immersed to various depths in the furnace.

of the sheathed thermocouples were due to the Chromel thermoelements. Thus, we performed the following two sets of experiments, using the inhomogeneity test facility (ITF).

First, we fabricated an open (U-shaped) loop of wires from sheathed thermocouple cable (Fig. 14a) to compare the ΔEs measured between two Chromel thermoelements or two Alumel thermoelements as the loop was immersed in the salt bath. By heat treating only side 1 of the loop, we could determine the effect of the heat treatment on ΔE of the Chromel and Alumel thermoelements, using those of side 2 as a reference.

Before this test, the entire loop was heated in air to 905°C (1661°F) for 10 min by passing a current through the stainless steel sheath of the cable, and then it was cooled in air to room temperature. During cooling, the temperature of the sheath decreased from 595 to 315°C (1103 to 599°F) in about 20 sec. This heat treatment is referred to as the "annealed condition" because it produces an essentially disordered state in the thermoelements.

After this heat treatment, the Chromel and Alumel thermoelements of both sides of the loop were in the same metallurgical state. Consequently, the differential voltage ΔE was small, as shown in the X-Y recorder traces for Alumel 1 vs Alumel 2 (Fig. 14b) and for Chromel 1 vs Chromel 2 (Fig. 14c). Both traces show differences of less than 5 μV over the first 20 in. of the loop. If each side of the loop were made into a thermocouple, the ΔEs of Fig. 14b and c would result in temperature measurement differences of about 0.1% or less. [By Eqs. (2) and (3), $\Delta T \approx 2.5 \times \Delta E/125 = 2.5 \times 5/125 \approx 0.1\%$.]

Sections of side 1 of the loop, each 2 in. long, were heat treated at temperatures below 600°C (1112°F) and retested. The temperatures and times of these heat treatments are shown in Fig. 14e, which is an X-Y recorder trace that shows ΔE measured between Chromel 1 and Chromel 2 after heat treatment of side 1. Similarly, Fig. 14d is the ΔE measured between Alumel 1 and Alumel 2. Heat treatment of side 1 below 600°C substantially increased ΔE between Chromel 1 and Chromel 2 but had little effect between Alumel 1 and Alumel 2. For example, the ΔE of 50 μV measured between the Chromel thermoelements after side 1 was slowly cooled from 600°C would result in temperature measurement differences of about 1% if

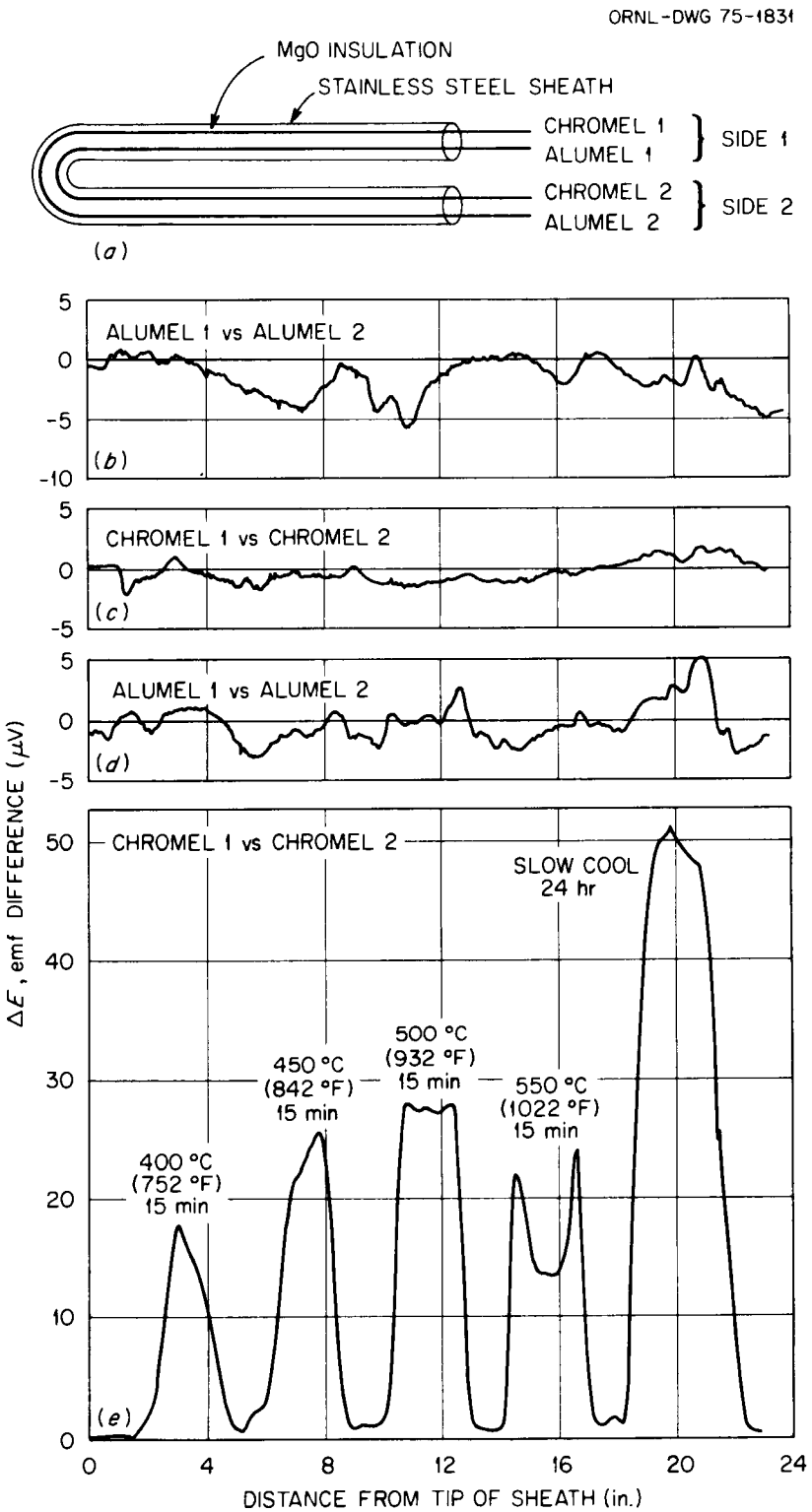


Fig. 14. EMF difference, ΔE, vs distance from tip of loop of thermoelement wire measured in the inhomogeneity test facility: (a) design of thermoelement loop; (b) Alumel 1 vs Alumel 2, both in annealed condition; (c) Chromel 1 vs Chromel 2, both in annealed condition; (d) Alumel 1 (heat-treated) vs Alumel 2 (annealed); and (e) Chromel 1 (heat-treated) vs Chromel 2 (annealed).

each side of the loop were made into a type K thermocouple. These results demonstrate that the measured changes in a type K, sheathed thermocouple are due only to effects of heat treatment on the Chromel thermoelement.

The second set of experiments was performed on 32-mil diameter, bare, Chromel wire. Because the salt bath of the ITF was an electrical conductor, it was replaced for these tests by an oil bath operated at about 200°C (392°F). As before, a loop of Chromel wire was annealed, and then two adjacent 4-in.-long sections of one side of the loop were heated in a furnace for 40 min at 399°C (750°F) and 454°C (850°F), respectively. Figure 15 is a plot of the ΔE measured between the annealed and heat treated sides of the loop during immersion of the loop in the oil bath. If each side of the Chromel loop were matched with an identical Alumel thermoelement to form a type K thermocouple, the ΔEs of Fig. 15 would result in temperature measurement differences of about 1.0 and 1.2%. These results demonstrate that heat treatments below 600°C cause changes in the thermal emf of sheathed or bare Chromel wire.

4.3 Reversibility of the Transformation

The reversibility of the order-disorder transformation was studied using three sheathed thermocouples from the same lot. Figure 16a shows the differential voltage ΔE recorded as one of the as-received thermocouples was immersed in the salt bath of the ITF. Although the heat treatment of these thermocouples during manufacture is proprietary information, it possibly consisted of about 3 min at 1000°C (1832°F), followed by cooling to ambient temperature, which was probably significantly above 25°C (77°F). It is likely that short-ranged ordering of the Chromel thermoelement occurred during this treatment, but the amount of the order was reduced near the hot junction during subsequent welding of the hot junction and closure of the sheath. This reasoning explains the results shown in Fig. 16a in which the measured ΔE is between 15 and 20 μV in the interval between 4 to 24 in. from the thermocouple tip but is about half as large and irregular from 0 to in. from the tip.

Figure 17a shows the calibration errors for the three as-received thermocouples measured at 231 and 370°C (346 and 698°F) in the standards

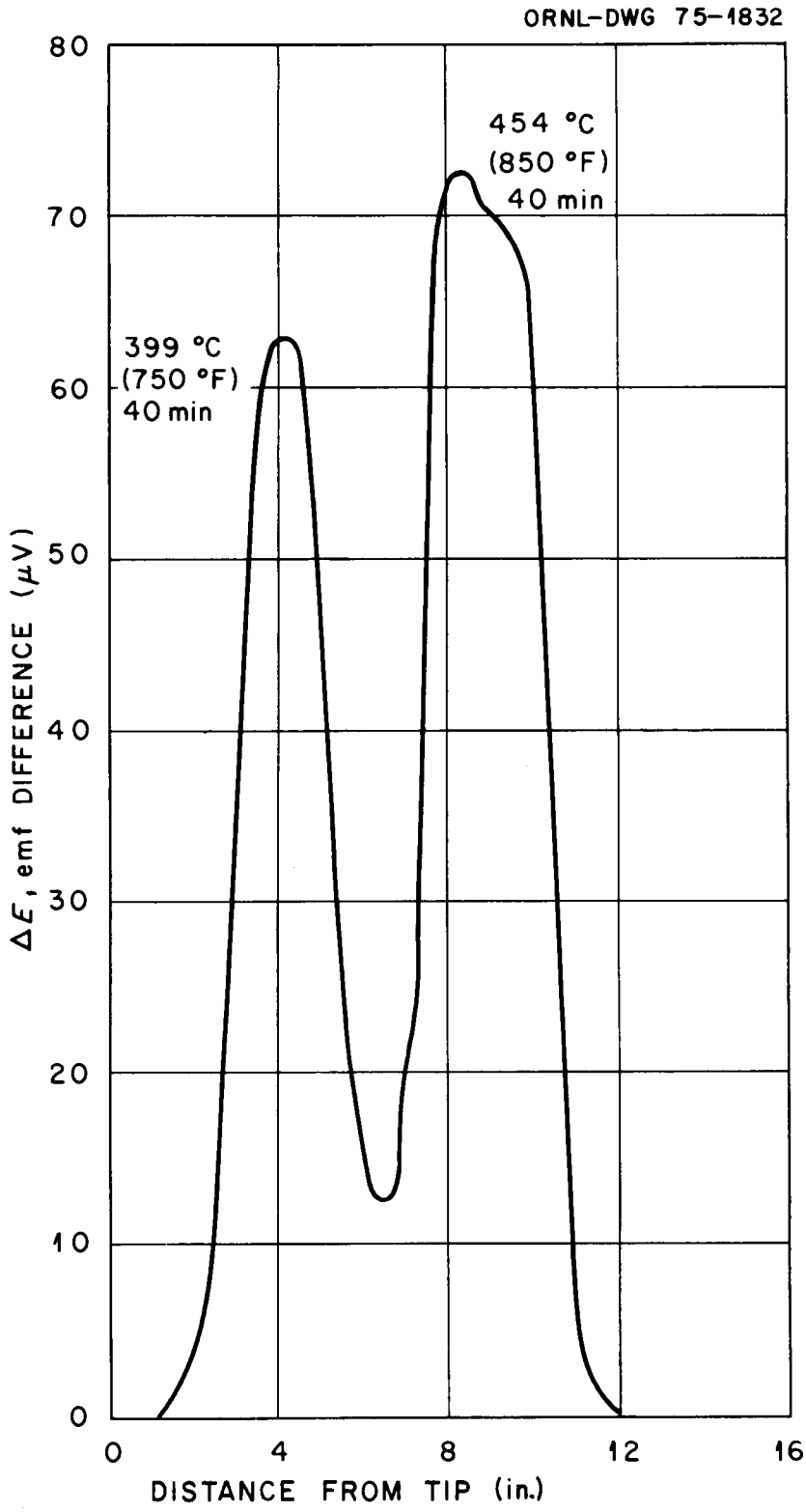


Fig. 15. EMF difference, ΔE, vs distance from tip of loop of bare Chromel wire measured in the inhomogeneity test facility. One side of the loop was annealed, and the other was heat treated. (Oil bath temperature was 200°C, with ΔT = 175°C.)

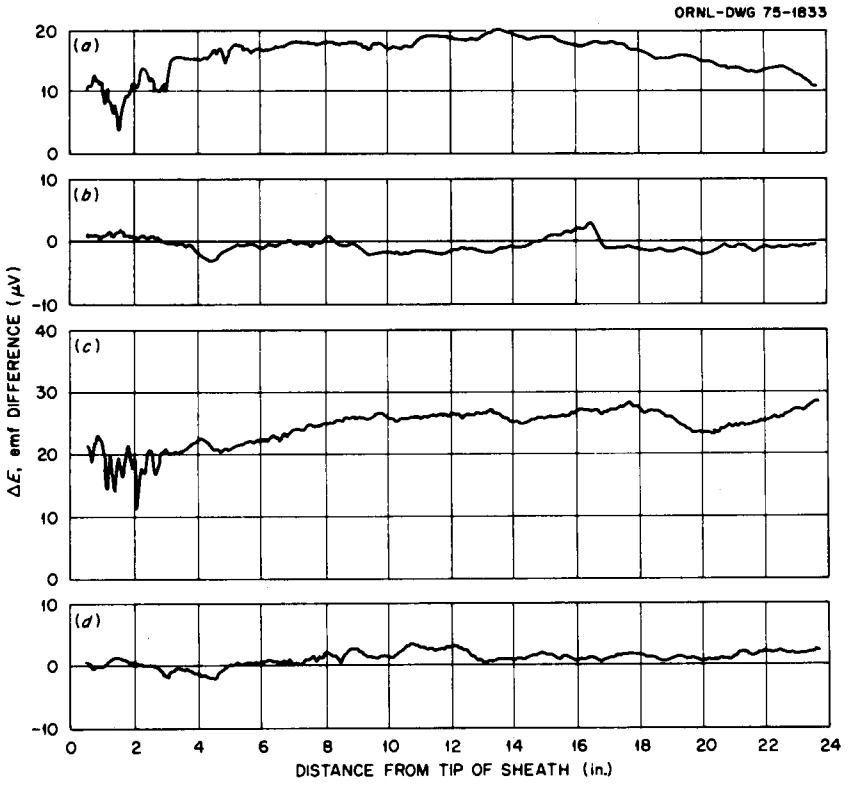


Fig. 16. EMF difference, ΔE, vs distance from sheath of type K thermocouple measured in the inhomogeneity test facility: (a) as-received; (b) 905°C (1661°F) for 10 min, air quench; (c) 482°C (900°F) for 15 min, air quench; and (d) 905°C (1661°F) for 10 min, air quench.

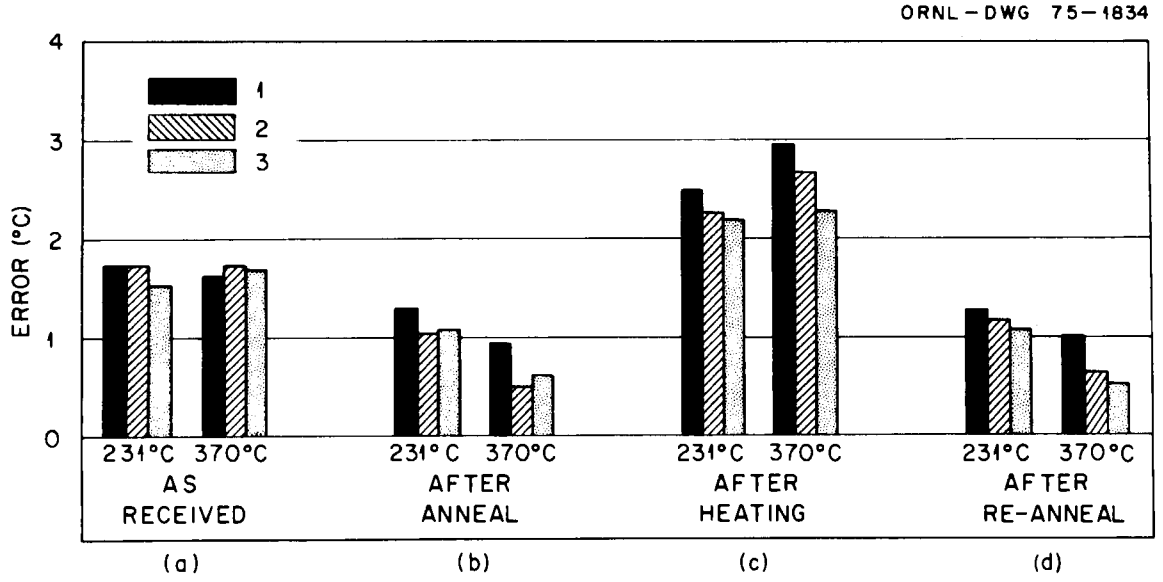


Fig. 17. Calibration error of three thermocouples at 231 and 370°C (346 and 698°F): (a) as-received; (b) 905°C (1661°F) for 10 min, air quench; (c) 482°C (900°F) for 15 min, air quench; and (d) 905°C (1661°F) for 10 min, air quench.

laboratory. The errors of about +1.7°C at both temperatures exceed the limits of the specification[1] for these thermocouples, namely, ±1.1°C at 231°C and ±1.4°C at 370°C. The ΔE (Fig. 16a) accounts for errors of between +0.7 and +0.9°C at 231°C, and between +1.1 and +1.5°C at 370°C.

The ΔE shown in Fig. 16b was determined after the thermocouples had been annealed. This annealing yielded a disordered Chromel thermoelement, and the ΔE was reduced from between +15 and +20 μV (Fig. 16a) to between ±3 μV. The calibration errors (Fig. 17b) of the annealed thermocouples were about half those of the thermocouples in their as-received condition and were within the specified error limits.[1]

The thermocouples were short-ranged ordered by resistively heating their sheaths to 482°C (900°F) for 15 min, followed by cooling in ambient air. Figures 16c and 17c show ΔE and the calibration errors for this heat treatment. The short-ranged order in the Chromel thermoelements produced a ΔE of about +25 μV and calibration errors approximately triple those of the annealed condition. The calibration errors were +2.3°C (+1.0%) and +2.6°C (+0.7%) at 231 and 370°C (346 and 698°F), respectively, and exceeded the specified[1] error. Subtraction of the calibration errors of the annealed condition (Fig. 17b) from these preceding errors yields differential errors of +1.1°C (+0.5%) at 231°C, and +1.9°C (+0.5%) at 370°C. Because the ΔE of 25 μV accounts for errors of +0.5% by Eqs. (2) and (3), the change in the calibration errors due to order is predictable from the value of ΔE. These results are summarized in Table 1.

Table 1. Summary of results shown in Figs. 16 and 17

Calibration Errors (°C)				Calibration Change Due to Order (°C)			
Heat-Treated Condition (°C)		Annealed Condition (°C)		Measured (°C)		Calulated[(a)] (°C)	
231	370	231	370	231	370	231	370
2.3 (1.1%)	2.6 (0.7%)	1.2 (0.5%)	0.7 (0.2%)	1.1 (0.5%)	1.9 (0.5%)	1.1 (0.5%)	1.9 (0.5%)

[a] ΔE = 25 μV.

After the thermocouples were reannealed, ΔE and the calibration errors shown in Figs. 16d and 17d were essentially the same as those after the first annealing (Figs. 16b and 17b). These results (Figs. 16 and 17, b through d) verify the reversibility of the order-disorder transformation and the resulting reversible effects on the thermal emf of type K thermocouples.

4.4 Ordering Kinetics

The kinetics of the order-disorder transformation in Chromel was investigated by heat treating type K thermocouples for periods of times between 1 min and 30 days at temperatures between 400 and 600°C (752 and 1112°F). The amount of order formed during these heat treatments was assumed proportional to the ΔE measured in the ITF. For example, Figs. 18 and 19 show the ΔEs of two thermocouples, sections of which were heated for 15 or 30 min at the temperatures shown. These data show that for times between 15 and 30 min short-ranged order (that is, ΔE) is maximized at a temperature between 482 and 500°C (900 and 932°F). Also, after 15 min at 427°C (800°F) there is approximately half the amount of order as after 30 min at 400°C (752°F), and after 30 min at 600°C (1112°F) there is little order. The "rabbit ear" shapes of the ΔE vs distance data at 510 and especially 600°C are attributed to temperature gradients in the sheath during heat treatment; that is, the "ears" were produced by ordering that occurred at temperatures below 600°C.

All ΔE data obtained from ITF measurements for the various heat treatments are summarized in Table 2 and plotted parametrically in Fig. 20b as a function of time at a given temperature. Figure 20a is a plot of the maximum ΔE measured vs temperature; that is, the ΔEs measured at the longest times shown in Table 2 for each temperature. The ΔE vs T relationship of Fig. 20a is approximately that shown in Fig. 3 for the theoretical value of the short-ranged order parameter σ as a function of temperature. The parametric curves drawn in Fig. 20b are based on the data of Table 2 as well as the previously discussed principles of kinetics of diffusion controlled processes. In general, these results demonstrate that at low temperatures the maximum possible amount of order is higher,

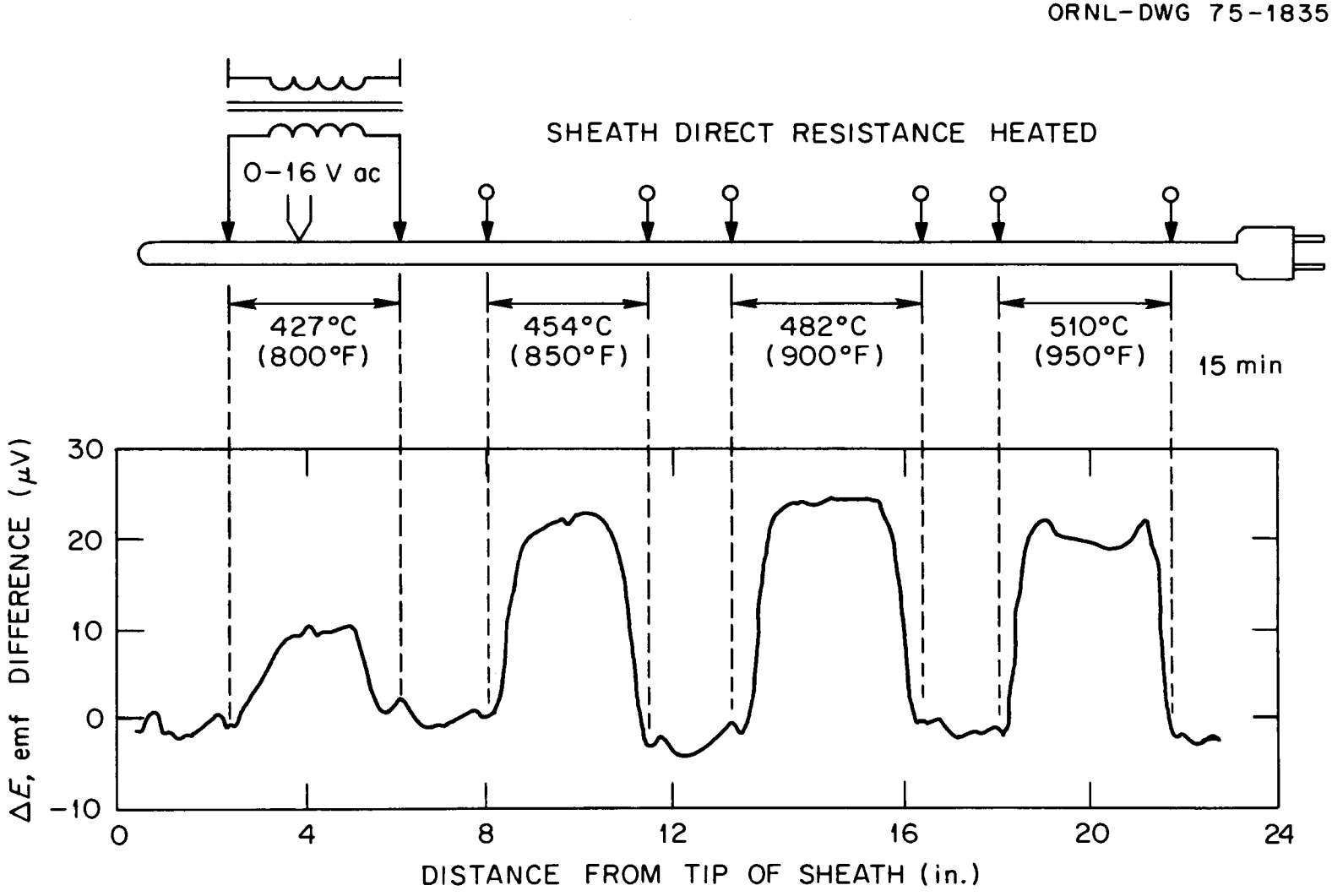


Fig. 18. EMF difference, ΔE, vs distance from tip of thermocouple that was heated in 2-in. segments for 15 min at 426°C (800°F), 454°C (850°F), 482°C (900°F), and 510°C (950°F).

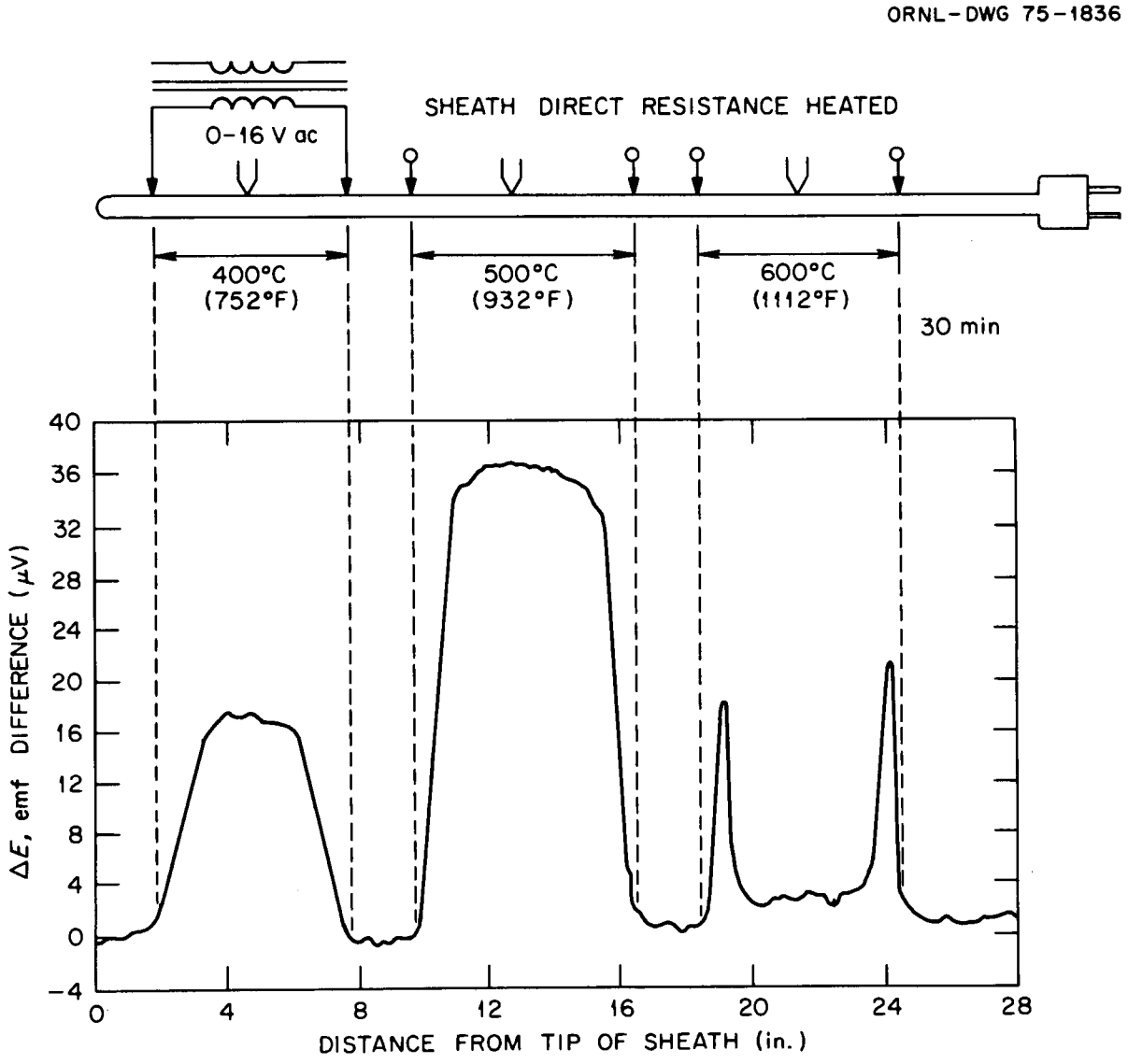


Fig. 19. EMF difference, ΔE, vs distance from tip of thermocouple that was heated in 4-in. segments for 30 min at 400°C (752°F), 500°C (932°F), and 600°C (1112°F).

Table 2. ΔE measured in the ITF after heat treatment

Heat Treatment Time	ΔE(μV)							
	Heat Treatment Temperature (°C)[a]							
	399 (750)	427 (800)	454 (850)	482 (900)	500 (932)	510 (950)	600 (1112)	550 (1022)
1 min	-	-	15	9	-	-	-	-
10	3	8	21	26	-	-	-	-
15	-	10	22	24	-	20	2	12
30	17	-	-	-	36	-	-	-
100	16	33	34	40	-	-	-	-
7 hr	19	40	-	-	-	-	-	-
18	-	-	49	45	-	-	-	-
24	35	48	-	-	-	-	-	-
42	-	-	50	46	-	-	-	-
72	46	52	-	-	-	-	-	-
144	52	52	-	-	-	-	-	-
216	53	52	-	-	-	-	-	-
720	66[b]	-	-	-	-	-	-	-

[a] °C are upper numbers and the corresponding °F are in parentheses.

[b] This is the maximum ΔE measured and corresponds to a temperature measurement error of 1.7% by Eq. (3).

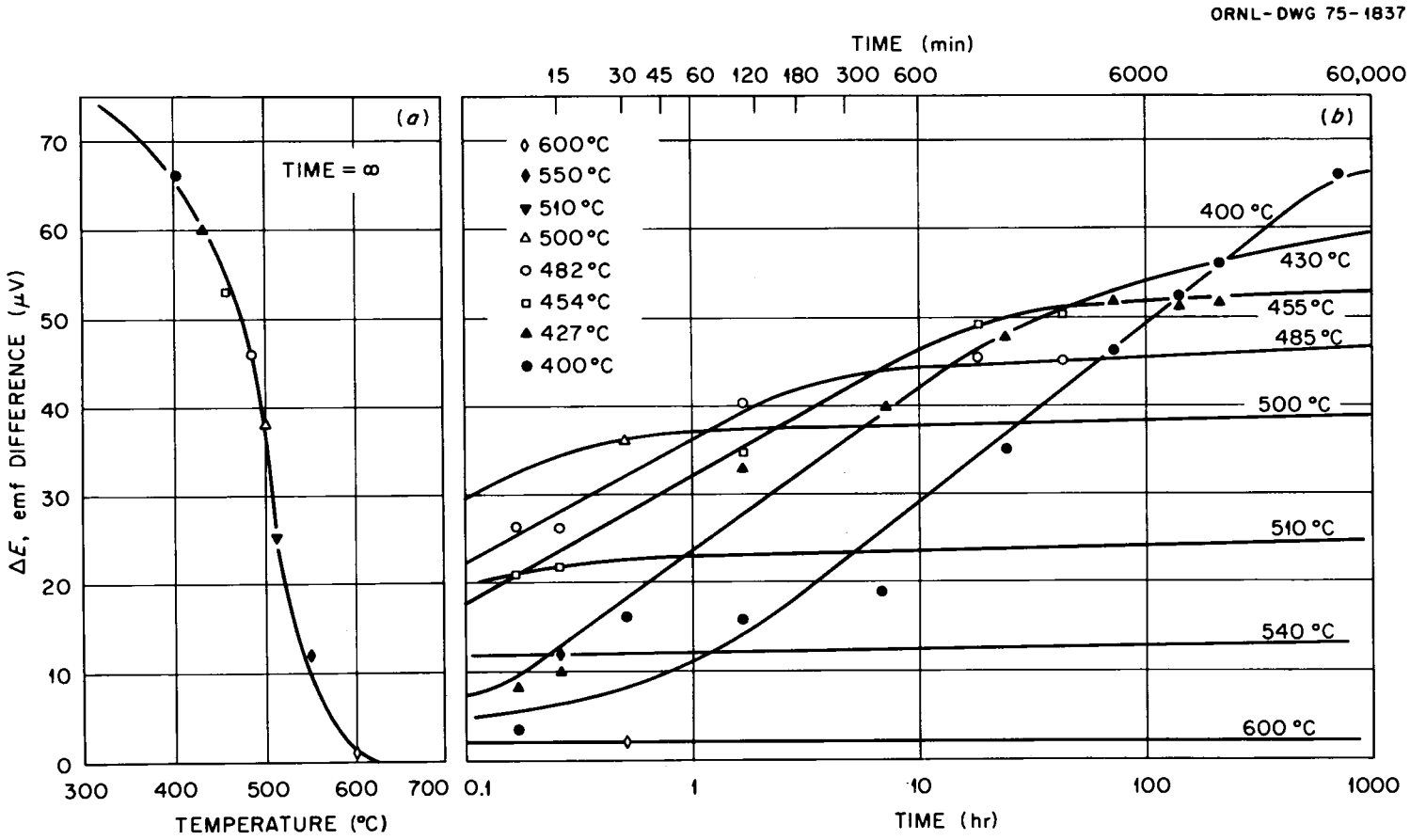


Fig. 20. Short-ranged order (ΔE) in Chromel as a function of temperature and time: (a) short-ranged order vs temperature at time equal to infinity; (b) short-ranged order vs time at temperatures of 400°C (752°F), 430°C (806°C), 455°C (851°F), 485°C (905°F), 500°C (932°F), 510°C (950°F), 540°C (1004°F), and 600°C (1112°F).

but it takes a longer time to achieve the maximum order. Figure 20 is a pictorial representation of the ordering kinetics for the Chromel thermoelement of a type K thermocouple.

The parametric curves of Fig. 20b were used to minimize the time required to obtain a desired state of order in the calibration repeatabilty studies. For example, the same state of order can be achieved within 0.5 hr at 500°C (932°F), 1.2 hr at 485°C (905°F), 2.5 hr at 455°C (851°F), 6 hr at 430°C (806°F), or 30 hr at 400°C (752°F).

The maximum ΔE of 66 μV was measured after a heat treatment of 720 hr at 399°C; and, by Eq. (3), it corresponds to a temperature measurement error of 1.7%. Extrapolation of the curve of Fig. 20a to lower temperatures predicts even larger ΔEs and, thus, temperature measurement errors.

4.5 Calibration Repeatability of Annealed and Ordered Thermocouples

Two, sheathed, type K thermocouples from the same lot were annealed; 12 in. nearest the hot junction of one of these two thermocouples was heated to 482°C (900°F) for 27 hr, followed by cooling in air. Figure 21 shows ΔE for both thermocouples measured in the ITF; thermocouple A was in the annealed condition and B in the heat treated condition. Comparison of ΔE for thermocouple B with Fig. 20 indicates that this heat treatment produces the equilibrium amount of short-ranged order at 482°C. The data also show that thermocouple A was essentially disordered.

Figure 22 is the calibration data for these thermocouples determined in the standards laboratory. As the annealed thermocouple A cooled, its errors increased to twice those observed on heating, and most values exceeded the ±3/8% error limits for special-grade type K thermocouples.[1] Before the calibration, however, thermocouple A was within specification limits. As ordered thermocouple B cooled, its calibration also deviated from its heating calibration, but the error decreased (instead of increasing, as did the annealed thermocouple). A second heating and cooling cycle (not shown in Fig. 22) further increased the error of annealed thermocouple A and decreased the error of ordered thermocouple B. These results suggest that after repeated heatings in the calibration furnace both thermocouples would eventually produce identical calibration curves.

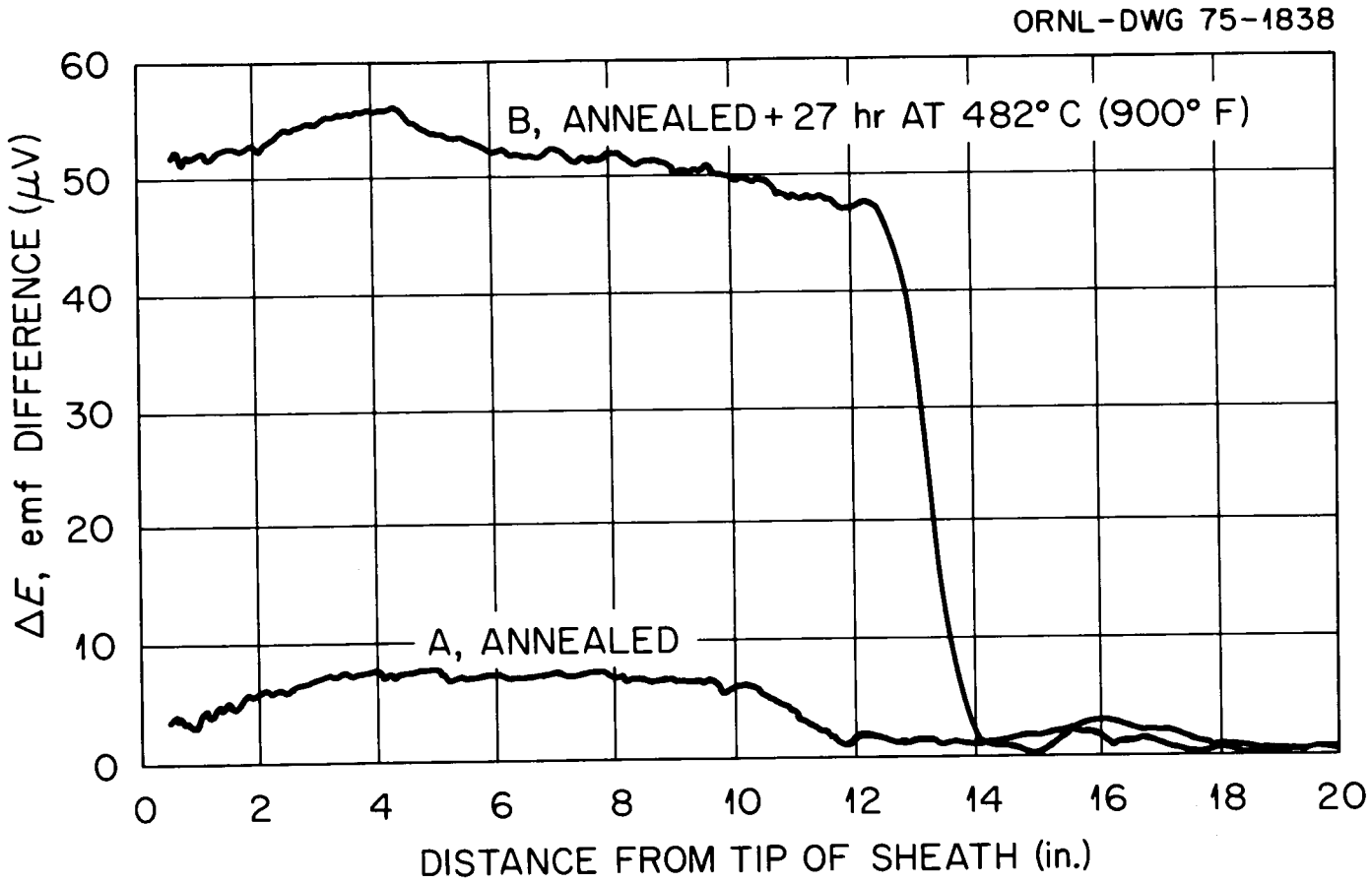


Fig. 21. EMF difference, ΔE, vs distance from tip of an annealed and a heat treated [27 hr at 482°C (900°F)] thermocouple.

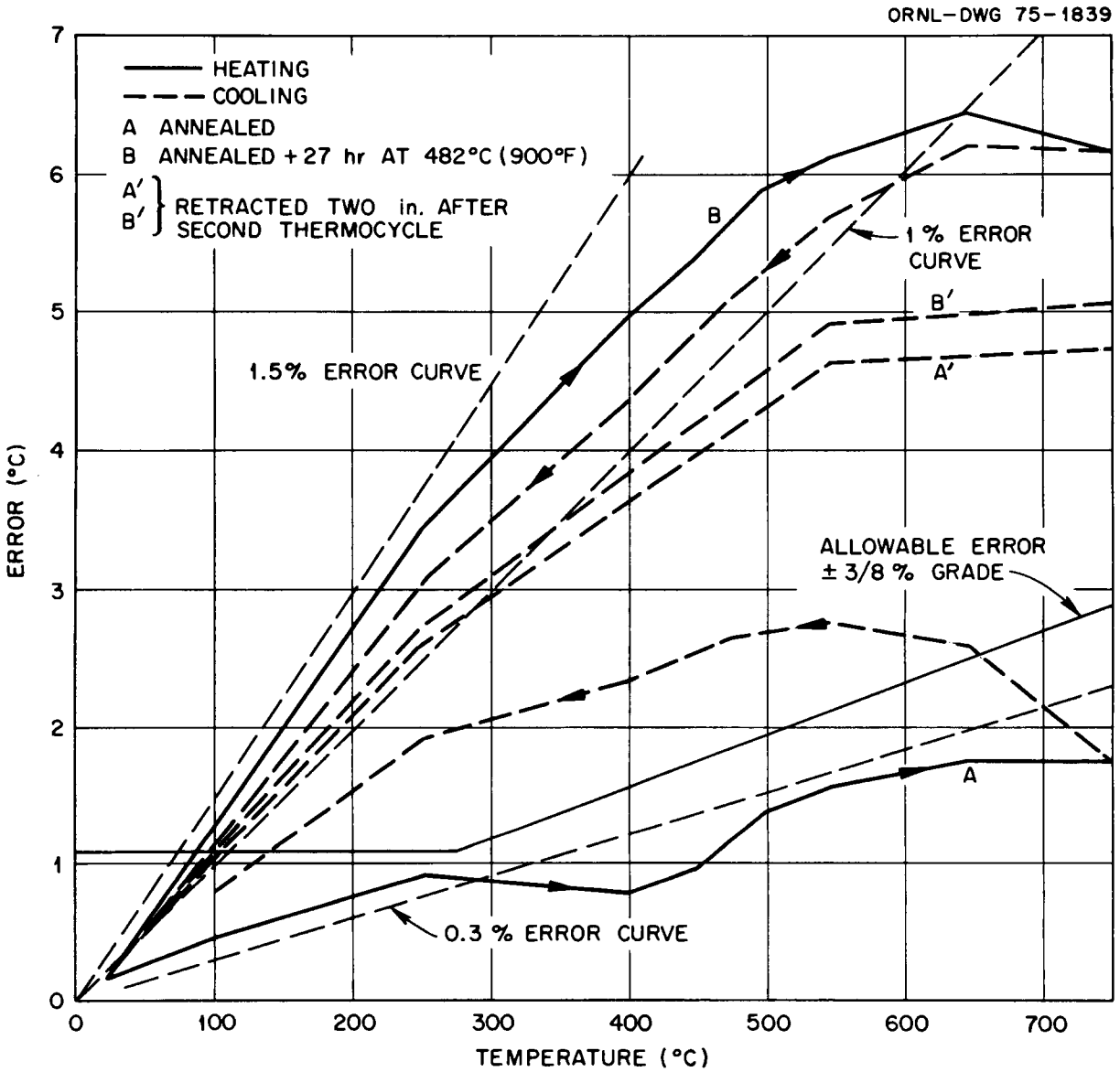


Fig. 22. Calibration curves on heating and cooling for an annealed and a heat treated [27 hr at 482°C (900°F)] thermocouple.

To hasten the process, the two thermocouples were retracted 2 in. from the calibration furnace. As shown in Fig. 22 (curves A' and B'), the errors were approximately the same during the third cycle because movement of the thermocouples placed similarly heat treated (in the calibration furnace) sections of the two thermocouples in the steep part of the temperature gradient of the calibration furnace. Calibration data recorded while thermocouples A' and B' were cooled (not shown in Fig. 22) were almost the same as when they were heated. These results suggest that there is an optimum amount of order, less than the equilibrium amount at 482°C, that would yield a repeatable calibration curve for the particular heating and cooling rates (≈1°C/min) and temperature gradient (Fig. 10) of the calibration furnace of the standards laboratory. (One can observe that movement of the thermocouple changed each calibration curve and that the calibration curves of thermocouples A' and B' differ about 1% from the ASTM E:T relationship. Therefore, movement of the partially ordered thermocouples A' and B' could result in temperature measurement errors up to +1%.)

4.6 Calibration Repeatability of a Partially Ordered Thermocouple

One of the goals of this study was to determine the heat treatment that would produce the optimum amount of short-ranged order in Chromel to yield a repeatable calibration curve (thermal emf-temperature relationship) for a type K thermocouple. Curves A' and B' of Fig. 22 were repeatable, but the heat treatment of the thermocouple was in situ during calibration of the thermocouple between 0 and 750°C (32 and 1382°F). We wished to determine what isothermal heat treatment would reproduce these calibration curves.

Between 0 and 500°C (32 and 932°F), calibration curves A' and B' of Fig. 22 are approximately the same as the 1% error curve, and calibration curve A for the annealed condition is approximately the same as the 0.3% error curve. Thus, the change in the calibration error was 0.7% due to the short-ranged order formed in situ during calibration. A temperature measurement error of 0.7% due to order corresponds to a Seebeck coefficient change of 0.28 μV/°C by Eq. (3) and to a ΔE, measured in the ITF, of 35

μV by Eq. (2). The data of Fig. 20 predict that isothermal treatment for ∿1 hr at 450°C (842°F) will produce a ΔE of 35 μV.

Twenty-inch segments of three thermocouples (A, B, and C) from the same lot were annealed. Subsequently, 15 in. of thermocouple A was heated for 80 min at 454°C (850°F) to produce the optimum amount of short-ranged order in the Chromel thermoelement. Also, 15 in. of thermocouple B was heated for 42 hr at 482°C (900°F) to produce the equilibrium amount of short-ranged order. Thermocouple C was left as annealed. Calibration data from thermocouples B and C were used to check the results of Fig. 22. The ΔE measured in the ITF and the calibration curves of these three thermocouples are shown in Figs. 23 and 24.

The same hysteresis effect after heating and cooling was measured in the calibration curves of the annealed thermocouple C and the higher-ordered thermocouple A, as shown in Fig. 24. However, the hysteresis effect for the optimum ordered thermocouple B is less than ±0.1°C. Withdrawal of the three thermocouples 2 in. from the calibration furnace appreciably altered calibration curves of C' (annealed) and A' (higher order) thermocouples but changed thermocouple B' (optimum order) less than 0.2°C.

The results shown in Fig. 24 demonstrate that proper heat treatment of a type K thermocouple yields a reproducible calibration curve and indicate that usage of annealed, type K thermocouples should be discontinued for applications with heating and cooling rates similar to those employed herein. However, an important observation is that the heat treatment of 80 min at 454°C is the optimum for the procedure employed in these calibrations performed in the standards laboratory furnace, namely, heating and cooling rates of ∿1°C/min and sufficient time (0.5 hr) to achieve equilibrium at a calibration temperature. The most important criterion is that the segment of the thermocouple in the temperature gradient, about 3 in. in our experiment (Fig. 10), should be cooled between 500 and 400°C (932 and 752°F) over a period of about 1 hr. If rates of 0.01°C/min are common to the application, the thermocouple should be more highly ordered; that is, it should be heat treated at a lower temperature for a longer time. The converse is true for higher heating rates.

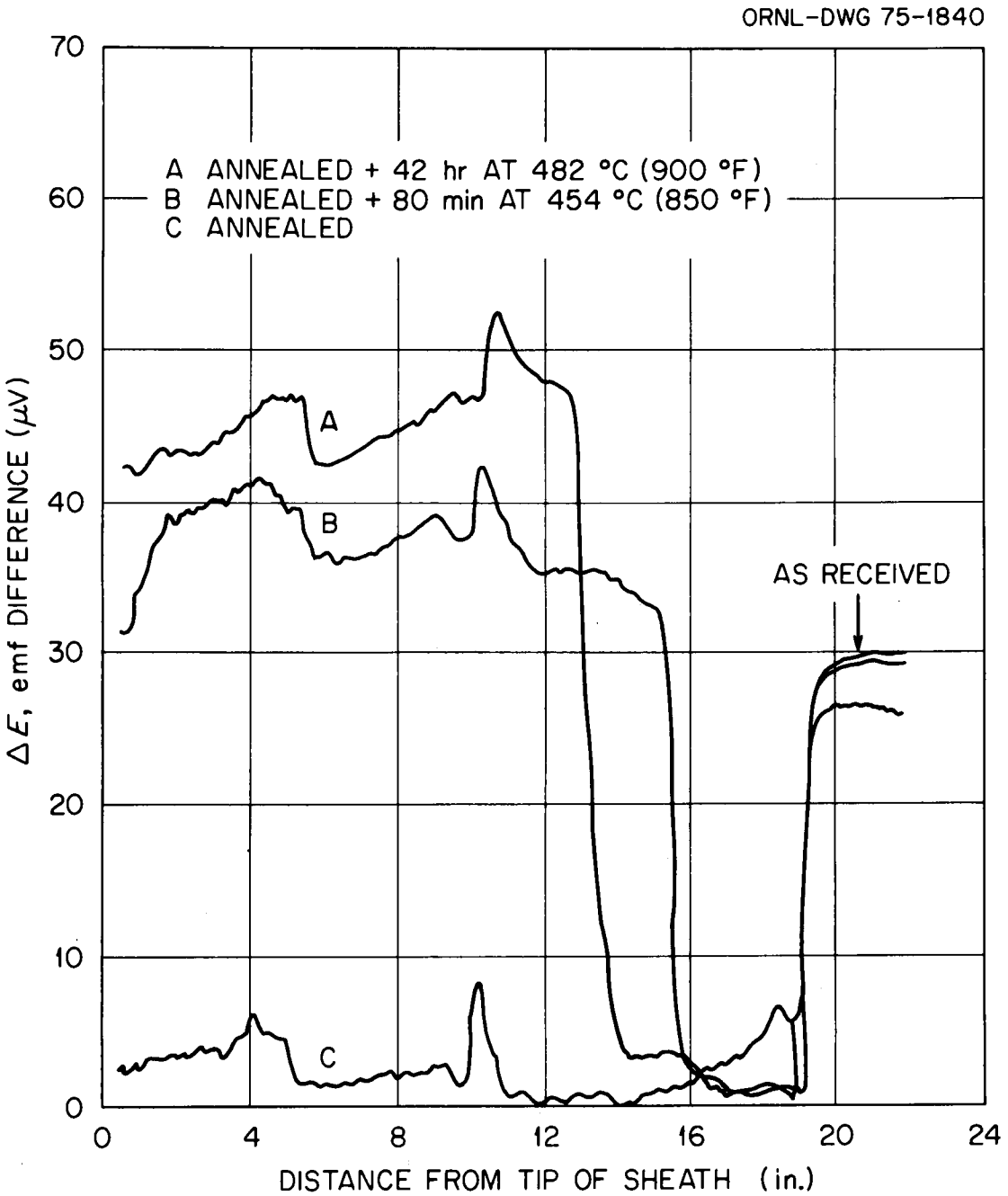


Fig. 23. EMF difference, ΔE, vs distance from tip of three thermocouples: A thermocouple held 42 hr at 482°C (900°F), B thermocouple held 80 min at 454°C (850°F), and C thermocouple annealed.

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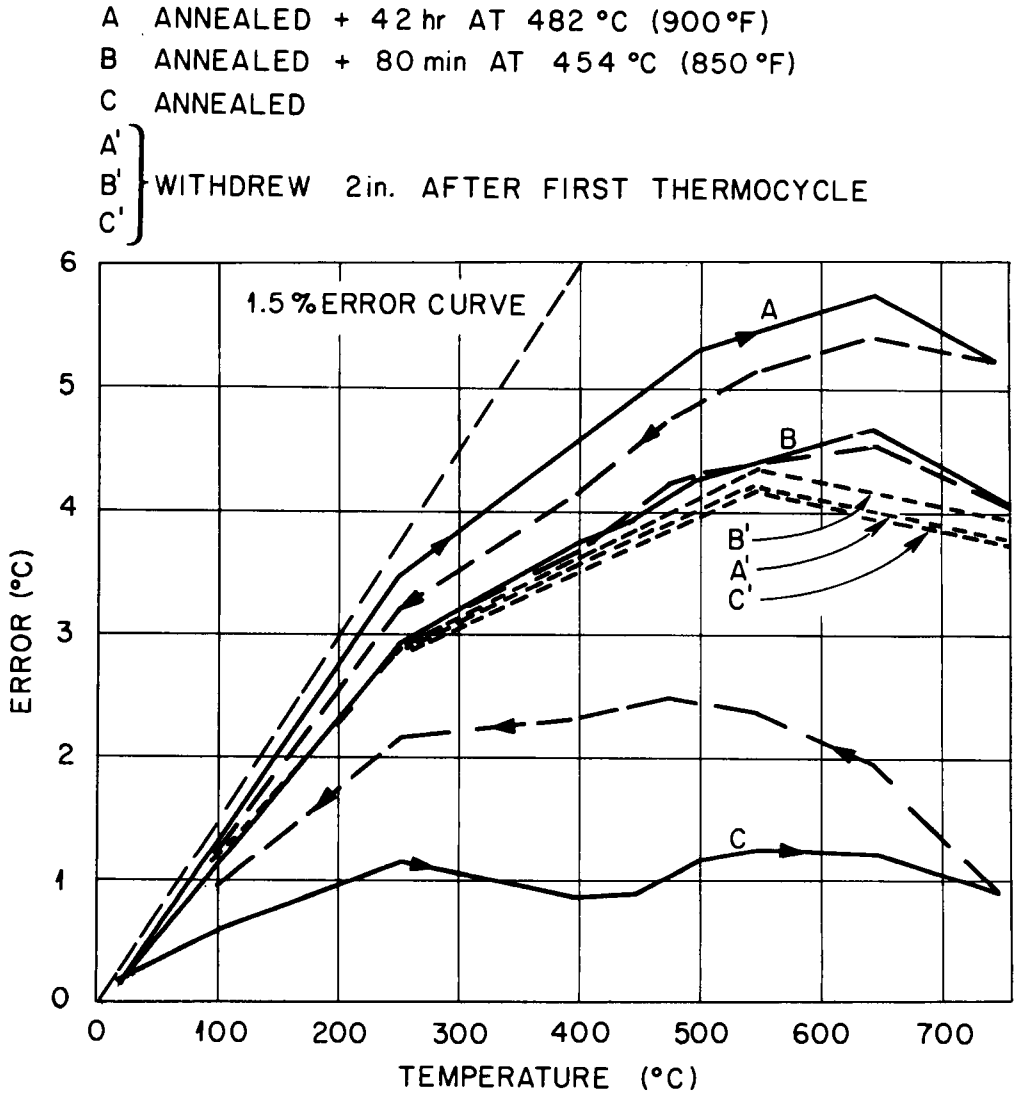

Fig. 24. Calibration data for three thermocouples: A thermocouple held 42 hr at 482°C (900°F), B thermocouple held 80 min at 454°C (850°F), and C thermocouple annealed.

Other observations are that a calibration was invalid unless the in-service application had heating and cooling rates similar to the calibration procedure, and that the temperature gradients in the application and the calibration furnace should be similar.

4.7 Calibration During a Temperature Ramp

The preceding observations prompted an experiment by the authors in which type K thermocouples were calibrated during a monotonic temperature ramp. A computer-operated thermocouple calibration facility was used to heat or cool thermocouples between room temperature and 650°C (1202°F) at a rate of 0.3°C/min. The computer system recorded the output of three, type K thermocouples and a platinum resistance thermometer, which had been placed in an Inconel-clad, copper block in the furnace.

Three, type K thermocouples from the same lot were annealed at 982°C (1800°F) for 30 min and air cooled to room temperature. Subsequently, two of the thermocouples were heated to 454°C (850°F), one for 1 hr (number 1) and another for 2 hr (number 2), followed by air cooling to room temperature. These heat treatments produced ΔEs measured in the ITF of 27 and 34 μV, respectively, the latter being that of the optimum ΔE for the standards laboratory calibration furnace. Figure 25 (a) is a plot of the calibration data for the three thermocouples on first heating; the results are as expected, that is, the larger the amount of initial short-ranged order in the Chromel thermoelement, the larger the temperature error. Figures 25 (b), (c), and (d) compare the results obtained from the first and second heating of these thermocouples. The calibration error of the annealed thermocouple increased a factor of two on second heating. However, thermocouple 2, which had the largest amount of initial order (ΔE = 34 μV), showed the smallest increase ($\approx$0.2°C) in calibration error on second heating. Because the calibration error of thermocouple 2 increased, the heat-treatment it received during calibration produced an increased order of the Chromel thermoelement [See Eqs. (2) and (3)]. Therefore, the optimum amount of order for a type K thermocouple subjected to a temperature ramp of 0.3°C/min is greater than that received by thermocouple 2, which was approximately the optimum order for the 1°C/min heating rates of the standards laboratory calibration furnace.

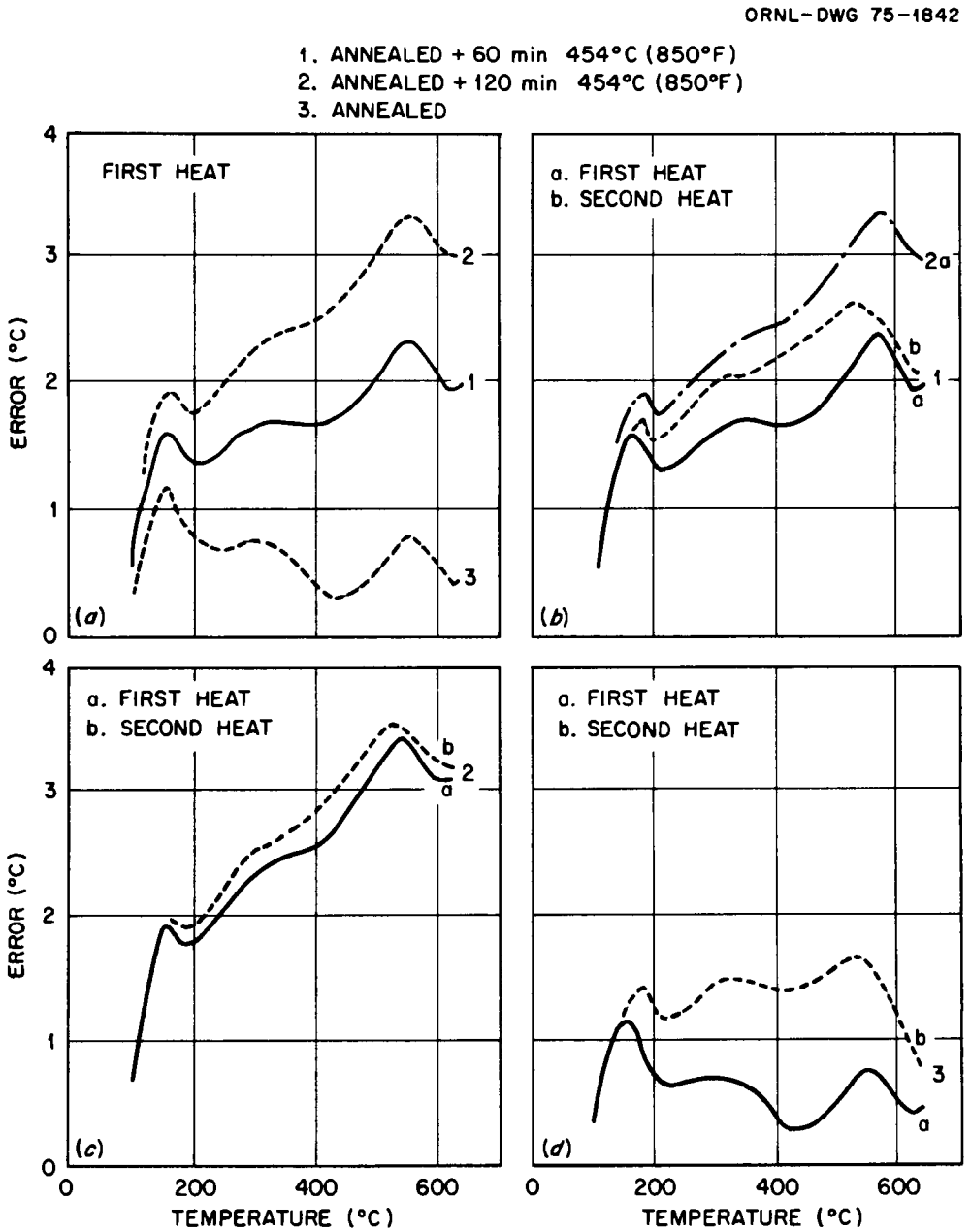

Fig. 25. Calibration data for three thermocouples: (a) first heating of all three thermocouples; (b) first and second heating of thermocouple 1 [1 hr at 454°C (850°F)] and also first heating of thermocouple 2; (c) first and second heating of thermocouple 2 [2 hr at 454°C (850°F)]; and (d) first and second heating of thermocouple 3 (annealed).

The data recorded during first and second cooling (Fig. 26) verified the data taken during heating.

4.8 Temperature Profile Thermocouple

During the measurement of the temperature profile of the calibration furnace (Fig. 10), a type K thermocouple was extracted in six 1-in. steps and then in six additional 1/2-in. steps. The temperature at the center of the furnace was 750°C (1382°F). At 9 in. from the center of the furnace, the temperature was 720°C (1328°F); and at the edge of the insulator, 11-1/4 in. from the center of the furnace, the temperature was 200°C (392°F). Thus, the segment of the thermocouple 9 to 11-1/4 in. from the center of the furnace was in a temperature gradient and in the temperature interval in which short-ranged order could form in Chromel. Because the kinetics of ordering is temperature dependent, an inhomogeneous state of order was formed in the Chromel theromoelement. Figure 27 depicts the results of the ΔE trace in the ITF for this thermocouple. Each movement of the thermocouple is indicated by a maximum and minimum value of the measured ΔE.

The results show that when a type K thermocouple was moved in a temperature gradient in the temperature interval of 400 to 600°C (752 to 1112°F), serious inhomogeneities were formed in the Chromel thermoelement by short-ranged ordering. A further observation is that once a calibrated type K thermocouple is installed in a furnace, its position should not be changed unless it is recalibrated or reheated or both.

5. CONCLUSIONS

The conclusions from this study of the effects of short-ranged ordering of Chromel on the accuracy of temperature measurements with type K thermocouples are as follows:

1. Prior thermal treatment of a type K thermocouple affects the temperature measurement accuracy of this thermocouple.
2. Short-ranged ordering between 200 and 600°C (392 and 1112°F) and disordering above 600°C of the Chromel thermoelement cause temperature measurement errors of up to 1.7%.

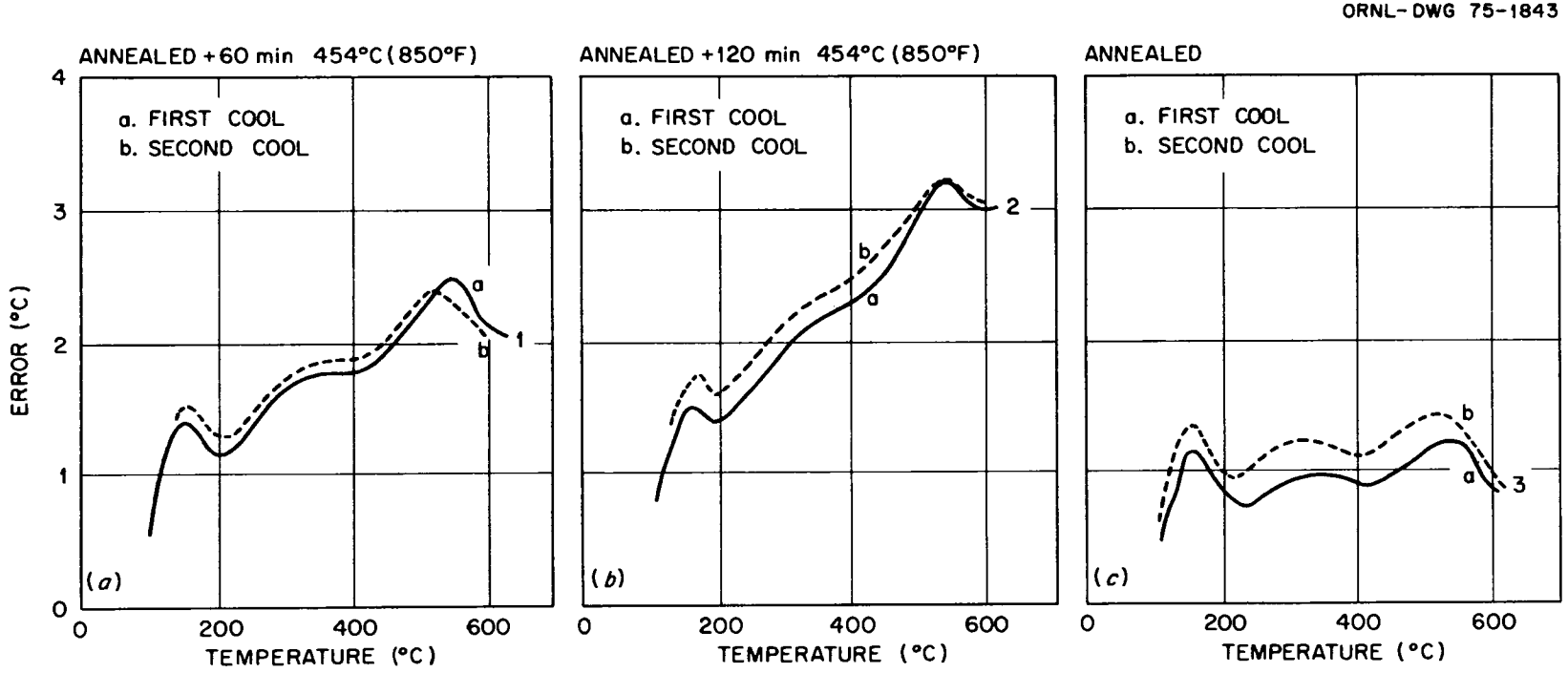

Fig. 26. Calibration data for three thermocouples on first and second cooling: (a) annealed plus 1 hr at 454°C (850°F); (b) annealed plus 2 hr at 454°C (850°F); and (c) annealed 2 hr.

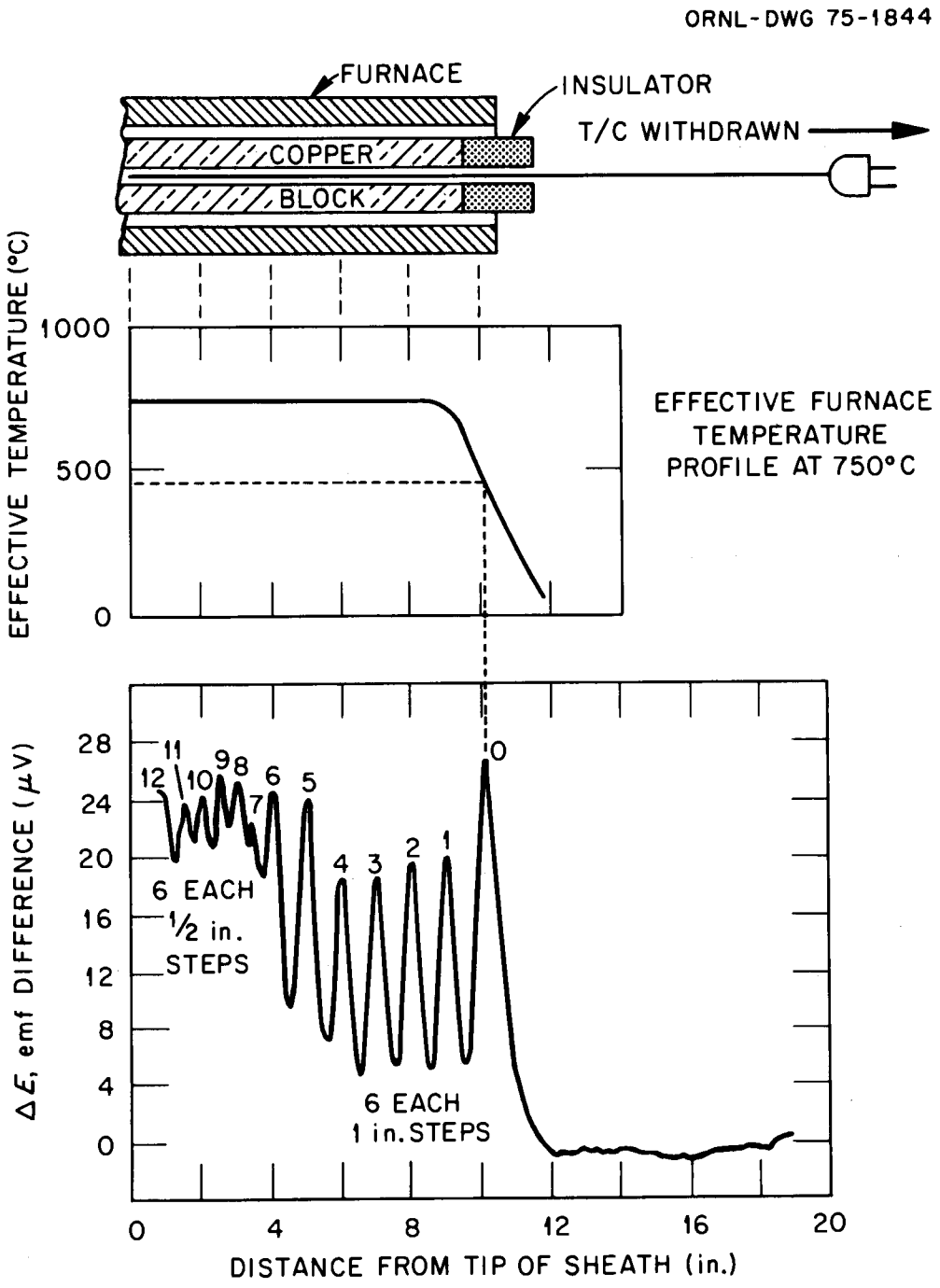

Fig. 27. EMF difference, ΔE, vs distance from tip of thermocouple used in furnace temperature profile measurement.

3. Order-disorder transformations are reversible; errors incurred during use of a type K thermocouple are eliminated when it is returned to its original condition by reannealing.
4. Thermal emf's are generated only in temperature gradients [Eq. (1)]; errors due to ordering occur even if a thermocouple hot junction is above 600°C (1112°F) because some segment of the thermocouple is in a temperature gradient in the critical temperature range where ordering occurs.
5. Temperature measurement errors are reduced to the calibration repeatability (±0.1°C) by partially ordering and calibrating type K thermocouples prior to use. The amount of initial order to introduce in the Chromel thermoelement depends on its intended application.
6. The optimum order that minimizes temperature measurement error is formed by heating the thermocouple for 80 min at 454°C (850°F) for an application having heating and cooling rates of about 1°C/min.
7. For applications in which lower heating and cooling rates will be experienced, heating the thermocouple at a lower temperature for a longer time is suggested. Conversely, if the heating rates will be higher, heating the thermocouples at a higher temperature for a shorter time is recommended.
8. Figure 20 will serve as a guide to predict the amount of order that a given heat treatment will produce.
9. Change in calibrations of type K thermocouples due to formation of short-ranged order in the Chromel thermoelements calculated using Eqs. (2) and (3) and ΔE of the ITF were the same as the actual changes in calibrations measured for the thermocouples.
10. Partially ordered thermocouples will reduce temperature measurement errors if, any only if,:

    a. The calibration procedure has approximately the same heating and cooling rates, thermocycles, and temperature profiles as the application.
    b. Once installed, the partially ordered thermocouple is not moved in the temperature gradient.

c. The thermocouple is not subjected to excessively higher or lower heating rates than those for which the partially ordered state is optimum.

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39. The tube furnace was 16 in. long and 2-1/2 in. ID. The copper block was about 2-7/16 in. in diameter and had 12 holes, 1/4 in. ID, in which the thermocouples to be calibrated were placed.

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