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An Investigation of the Order-Disorder Transformation in the Nickel-29.1 Per Cent Molybdenum Alloy by Electrical Resistivity Measurements

Beryle Thomas Lampe

University of Tennessee - Knoxville

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I am submitting herewith a thesis written by Beryle Thomas Lampe entitled "An Investigation of the Order-Disorder Transformation in the Nickel-29.1 Per Cent Molybdenum Alloy by Electrical Resistivity Measurements." I have examined the final electronic copy of this thesis for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science, with a major in Materials Science and Engineering.

E. E. Stansbury, Major Professor

We have read this thesis and recommend its acceptance:

Accepted for the Council:

Carolyn R. Hodges

Vice Provost and Dean of the Graduate School

(Original signatures are on file with official student records.)
December 11, 1963

To the Graduate Council:

I am submitting herewith a thesis written by Beryle Thomas Lampe entitled "An Investigation of the Order-Disorder Transformation in the Nickel-29.1 Per Cent Molybdenum Alloy by Electrical Resistivity Measurements." I recommend that it be accepted for nine quarter hours of credit in partial fulfillment of the requirements for the degree of Master of Science, with a major in Metallurgical Engineering.

Major Professor

We have read this thesis and recommend its acceptance:

[Signatures]

Accepted for the Council:

[Signature]
AN INVESTIGATION OF THE ORDER-DISORDER TRANSFORMATION
IN THE NICKEL-29.1 PER CENT MOLYBDENUM ALLOY BY
ELECTRICAL RESISTIVITY MEASUREMENTS

A Thesis
Presented to
the Graduate Council of
The University of Tennessee

In Partial Fulfillment
of the Requirements for the Degree
Master of Science

by
Beryle Thomas Lampe
December 1963
ACKNOWLEDGEMENTS

The author would like to express his sincere thanks to Dr. E. E. Stansbury for his excellent guidance and direction during this research program. Appreciation of the efforts of Mr. E. H. Honeycutt, Sr., and the entire shop crew of the Department of Chemical and Metallurgical Engineering is also given. Financial assistance by the Oak Ridge Institute of Nuclear Studies and the Atomic Energy Commission, under whose contract the present work was undertaken, is also acknowledged. Finally, special thanks are due to my wife, Betty, for her patience and assistance in the final preparation and typing of the thesis.
This investigation is a continuation of research on the nickel-molybdenum binary alloy system which has been in progress in the Department of Chemical and Metallurgical Engineering of The University of Tennessee for the past several years in association with the Oak Ridge National Laboratory. The purpose of the present investigation was to develop an electrical resistivity method for studying the order-disorder transition in the nickel-molybdenum alloy of stoichiometric composition, $\text{Ni}_4\text{Mo}$.

The alloy containing 29.1 weight per cent molybdenum in nickel was prepared by melting 250-gram ingots in a direct arc furnace under an inert gas. These were homogenized in argon for 100 hours at $1200^\circ\text{C}$ and water quenched to retain the high temperature face-centered-cubic alpha phase. Samples for electrical resistivity measurements were prepared by swaging (or rolling) and machining the homogenized ingots to approximately 0.1 inch diameter rods about 6 inches in length. Pretreatment of the alloy by quenching from above $868^\circ\text{C}$ produced an initial state of retained alpha phase for subsequent resistivity measurements. Heat treatments below this temperature produced the long range ordered $\text{Ni}_4\text{Mo}$ phase.

An apparatus was designed and constructed for the continuous measurement of electrical resistivity at high
temperatures. This apparatus permitted the continuous recording of resistivity-temperature curves during heating and cooling through the transformation temperature of the alloy. It also provided a means to study the kinetics of ordering in the alloy using electrical resistivity as the index of order.

The principal results of this investigation can be summarized as follows:

1. The resistivity-temperature curves for the alloy in the initially ordered state exhibited positive slopes but with a marked negative deviation from linearity which increased rapidly with increasing temperature. The alloy undergoes a discontinuous change in resistivity at the critical temperature (868°C), characteristic of an order-disorder transformation.

2. From 868°C to 1000°C, the alpha phase exhibits a negative temperature coefficient of resistivity which has been attributed to a decreasing degree of short range order with increasing temperature.

3. When the alloy is cooled below the critical temperature a sharp decrease in resistivity occurs at undercoolings of 60°-90°C due to the rapid onset of ordering. The immediate degree of order, however, is not complete and the resistivity-temperature curve on further cooling is cooling-rate dependent. Holding at
temperatures below the transformation temperature resulted in a slow decrease in resistivity as equilibrium was approached.

4. The temperature coefficient of resistivity of the retained alpha phase is negative near room temperature. However, at higher temperatures the resistivity increases rapidly to a maximum near 650°C and then decreases. This behavior has been attributed to the existence of a critical domain size and/or degree of long range order developed on heating.

5. Isothermal transformation of the retained alpha phase to the low temperature beta phase at temperatures below the critical temperature was followed by measuring the change in resistivity which accompanies it. The most rapid transformation was found to occur at temperatures in the range 760°C to 800°C.

6. Isothermal resistivity-time curves were used to construct a time-temperature-transformation diagram for the alloy. The "nose" of the diagram was found to lie within the temperature range 710°C to 775°C. The rate of transformation was extremely slow below 600°C.
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CHAPTER I

INTRODUCTION

This research is a continuation of a study of the nickel-molybdenum system which has been a subject of investigation of the Department of Chemical and Metallurgical Engineering of The University of Tennessee for the past several years. The present investigation was undertaken to obtain information which would permit better understanding of the order-disorder transformation that occurs at the stoichiometric composition, Ni$_{4/3}$Mo. The scope of this research was the establishment of techniques for studying this transformation using electrical resistivity methods and the study of the transformation itself.

A basic concern in the research has been the state of order in the alloy in various equilibrium and nonequilibrium conditions and the terms short range and long range order will be used throughout the following presentation. For this reason, a brief discussion of these concepts is given at this point in the thesis.

In an ideal solid solution the different species of atoms are arranged at random on the atomic positions of the lattice. There are many solid solutions, however, in which a non-random atom distribution exists. Any crystal structure may be considered as a set of sublattices each occupied by a
given type of atom and having the geometry of the space lattice of the crystal. If atoms of one kind in a binary alloy segregate more or less completely on one sublattice, leaving atoms of the other kind to the remaining positions, the resulting structure is referred to as a long range ordered solid solution or superlattice. The formation of superlattices takes place at relatively low temperatures and usually at compositions expressed by a simple formula AB or AB₃ or at compositions near these. At all temperatures above a certain critical temperature, the superlattice is destroyed but when the temperature is again lowered through the critical point, order sets in and increases as the temperature drops, approaching perfection only at low temperatures.

In a fully ordered alloy there are great distances within a crystal throughout which there is a perfect arrangement of A atoms on one set of atom sites and B atoms on the other set. The long range order is defined as to degree by a parameter, S, which varies from zero at complete disorder up to unity at complete order. The degree of long range order for the AB case is defined as the fraction of atoms that are in their "right" positions minus the fraction of atoms that are in their "wrong" positions.

Calculation of the variation of the parameter S with temperature shows that it decreases from unity slowly, upon heating, until the critical temperature is reached where it
then drops off very rapidly, being zero above the critical temperature.

In an actual crystal having even perfect long range order, it is possible to have a parameter value of zero by dividing the crystal into regions called domains each of which is perfectly ordered itself, but out of phase with its neighbor. Therefore, caution must be taken in referring to the degree of long range order. It can be used for a crystal as long as it is applied only within ordered domains and as long as the domain size is large enough to insure that the interfacial area is small so that the number of like atom pairs at the boundaries is negligible, compared to the number of unlike atom pairs.

One factor leading to long range order is that A-B bonds are energetically favorable to A-A or B-B bonds to the extent that one or both of the latter may not exist. This strong A-B bond tendency may persist above the critical temperature for long range order and give rise to a non-random distribution of atom pairs in the solid solution. This leads to a concept of order concerned only with nearest neighbors rather than over large volumes of crystal and is called short range order. Short range order may be defined in terms of the number of "right pairs"; a right pair is a pair of unlike atoms (an AB pair). Short range order exists if the number is greater than for random. At
increasing temperatures the number of AB pairs diminishes until a disordered state is reached corresponding to a random distribution. A short range order parameter, $\sigma$, may be defined as the probability of finding an unlike atom beside a given atom minus the probability of finding a like atom there. It is possible to have $S=0$, but still have a number of AB pairs above the random value.

Bethe's theory (3) predicts that $\sigma$ does not fall entirely to zero at the critical temperature but to a residual value greater than zero, a value which, in turn, gradually decreases as the temperature is further increased. Thus, even at high temperatures there are more than the random number of AB atom pairs but they are unable to link together into a long range ordered arrangement. At $T_c$ (critical temperature) the domains begin to link together or coalesce into long-distance order, and as the temperature is lowered the long-distance order increases toward perfection.

One common method of studying order-disorder transitions in alloys is to measure the change in electrical resistivity accompanying it. When the disordered state is retained at room temperature by quenching from above the critical temperature, the solute atoms produce perturbations in the potential field of the lattice and lattice strains due to atom size differences are superimposed upon the distortions from thermal agitation; all of these contribute to the
electrical resistance. Annealing below $T_c$, the temperature above which long range order does not exist, induces order and removes the component of resistance due to atomic disorder, thereby lowering the resistivity of the alloy. If a highly ordered specimen is slowly heated, it is expected that the total resistivity $P$ ($P = P_0 + P_T$, where $P_T$ is the component that is caused by thermal vibrations of the lattice and is approximately proportional to the absolute temperature and $P_0$ is the component of resistivity due to the state of order) should rise sharply near the critical temperature since the long range order decays rapidly here (8). This effect is seen clearly for the alloy Cu$_3$Au (13).

Electrical resistance measurements also offer a rapid and accurate means of obtaining isothermal transformation data. The electrical resistance method depends in principle upon the change in resistance which accompanies the isothermal transformation. For example, if an alloy initially heated to form the disordered phase is held at any constant temperature lower than the minimum at which it is stable it will in time transform; the progress of this transformation can be followed by the change in resistance which accompanies it. The course of the isothermal transformation is represented by plotting the change in resistance against corresponding elapsed time at constant temperature. Information given by such curves can be used to construct a time-
temperature-transformation diagram. This type of diagram shows the time required for the transformation to begin and to finish at any constant temperature in the range covered by the curves.

For the actual measurement of the resistance there are two accurate methods, the Kelvin double bridge and the method of potential drop. In the double bridge method, the specimen forms one arm of a special Wheatstone network and the resistance is measured by a balance condition. This is probably the most accurate method for measuring a small resistance at room temperature, but at higher temperatures it is not so convenient, as it needs large currents to attain sufficient sensitivity, and if continuous recording is desired these have to be maintained for long periods. In the potential drop method the voltage across the specimen is measured when a known current flows through it. The current is determined by measuring the voltage across a standard resistance in series with the specimen. This investigation is concerned with developing the equipment and techniques for continuously recording resistivity-temperature curves for specimens at high temperatures. These curves provide an excellent means by which to study the order-disorder transition in the alloy Ni\textsubscript{4}Mo.
CHAPTER II

LITERATURE SURVEY

I. THE NICKEL-MOLYBDENUM SYSTEM

A number of investigations of the Ni-Mo system have been carried out during the past twenty years. The equilibrium diagram for the Ni-Mo system in the region of interest in this research is shown in Figure 1, as proposed by Guthrie (6). Under equilibrium conditions alloys containing 29 per cent molybdenum will involve the alpha phase above 868°C and the beta phase below this temperature. The crystal structure of the beta phase is body-centered tetragonal and a comparison of this structure with that of the face-centered-cubic alpha structure shows that it is necessary only for the molybdenum atoms to occupy specific sites on the face-centered-cubic lattice in order to produce essentially the beta-phase structure. Only a slight change in volume is then required for the formation of the equilibrium beta phase. The details of the atom position and the crystallography of the beta phase have been discussed in detail by Guthrie.

Alloys of the beta composition have the potential of exhibiting characteristics of order-disorder transformations since only slight atom movements are needed to convert the alpha phase to beta and the same basic lattice is retained in
Figure 1. Partial Phase Diagram of the Ni-Mo System. After Guthrie (6).
the transformation. The only real difference between this system and the characteristic order-disorder system is that the ordered phase is indicated as existing only for the stoichiometric composition, $\text{Ni}_4\text{Mo}$ (containing 29.1 weight per cent molybdenum). In most alloy systems where ordering occurs, the ordered structure is observed over an extended range of compositions as in the cobalt-platinum system.

Hume-Rothery (7) suggests, however, that the important feature of the order-disorder transformation is that there be essentially no change in the lattice on which the atoms are placed in the two states. In line with this definition, the formation of the intermetallic compound, $\text{Ni}_4\text{Mo}$, is an order-disorder transformation.

Guthrie (6) concluded, as a result of his work, that the beta phase can be considered to be an ordering of the alpha phase. It is proposed that the beta phase nucleates and grows with a crystallographic relationship to the matrix alpha, with coherency existing between ordered plates of beta and the disordered alpha matrix. With further growth of a beta plate, both laterally and in thickness, beta plates will finally impinge.

The alpha to beta transformation in this system results in a rapid and significant increase in hardness which may be brought about by heat treatment cycles somewhat analogous to those for age or precipitation hardening alloys.
Ellinger (5) showed that the rate of initial hardening increased with increasing aging temperature and that the hardness curves for the 27, 31, and 35 per cent molybdenum alloys showed two distinct peaks with a few exceptions. Guthrie (6) presented hardening curves for 28, 29, and 30 per cent molybdenum alloys in which temporary reversals in the hardening are evident.

Newkirk, et al. (9), in their investigation of the cobalt-platinum system, suggest that the hardening that occurs in that system is due to the nucleation and growth of localized ordering which results in a strained matrix. The decrease in the hardening process is attributed to the removal of the strains by processes such as thermal recovery, self-deformation or recrystallization. Such a theory may be applicable to the Ni-Mo system.

The hardness data of Ellinger (5) and Guthrie (6) suggest that appreciable hardening occurs within minutes at temperatures near 800°C. Block (2) used hardness measurements to investigate the time dependence of the rapid initial hardening that accompanies the ordering reaction and to study the kinetic behavior of the transformation. This was accomplished by aging three alloys containing 27, 28, and 29 weight percent molybdenum. These were initially disordered by quenching from 1100°C and then transformed at temperatures ranging from 700°C to 850°C for periods from 0.01 to 1.00 hour. The
time required to increase the hardness to 300 DPH was taken as a measure of the amount of transformation and used for the construction of "C" curves for the three alloys. It was found that the aging curves show a pronounced increase in hardness during the first hour of aging at temperatures between 750° and 825°C, that the rate of hardening was slower and lower hardnesses were attained during aging at 700°C, and that the initial rate of hardening was slower at 850°C. Also, it was found that the most rapid hardening occurred at 800°C, where only about 1.8 minutes were required for the increment in hardness in the 29 weight per cent molybdenum alloy.

In his investigation, Block also found that the temperatures from which the specimens were quenched had little, if any, effect on the subsequent hardness for aging times greater than 0.01 hour. This was borne out in the comparison of the hardness of alloys quenched at 925°C to that of alloys quenched at 1100°C.

The agreement of the hardness data presented by Block (2) and the data of Guthrie (6) and Ellinger (5) was not good. Block's hardness values, although comparable, were consistently higher than those of Guthrie and Ellinger.

II. THE COPPER-GOLD SYSTEM

Dienes (4) studied the kinetics of ordering in AuCu using electrical resistivity as the index of order. His
investigation indicated that the ordering kinetics in AuCu were simple below 360°C and do not appear to proceed by a multistage nucleation and growth process. Rather, it was shown that the data are accurately represented by a chemical rate equation of the third order.

Sykes and Evans (13) have shown that the general character of the transformation in Cu$_3$Au is very similar to that predicted by Bragg and Williams (3). In particular, the transformation takes place continuously from the critical temperature to very low temperatures and the equilibrium condition when produced after long annealing is displaced by a change in temperature, i.e., the equilibrium is a dynamic one. This can be seen from Figure 2(a) which shows that the slower the rate of cooling the lower the final resistivity. At temperatures above 385°C where the alloy is in the disordered state, all three curves coincide. The temperature at which the resistivity begins to decrease rapidly, at the point C, depends to a certain extent on the cooling rate. The point B corresponds to that point at which the rate of atomic diffusion becomes so small that the alloy is effectively "frozen" and further ordering of the structure cannot proceed. The position of B will vary according to the cooling rate. As the cooling rate is increased, B will approach point C. The equilibrium resistivity-temperature curve is shown in Figure 2(b). There is a very large decrease in resistivity
Figure 2. Resistivity-Temperature Curves for Cu$_3$Au. After Sykes and Evans (13).
at the critical temperature, which is in qualitative agreement with the prediction of Bragg and Williams (3) who showed that for Cu$_3$Au the degree of order should increase from zero just above the critical temperature to about 30 per cent just below. This discontinuity in the degree of order is typical of a transformation in which the number of positions of order is one-quarter that of the total number of atomic sites.

Sykes and Evans (13) also noted a hysteretic effect at the critical temperature; in some cases the critical temperature on heating was observed 20°C higher than on cooling. Figure 3 shows the results of an experiment in which a specimen was cooled from 450°C to 250°C at 30°C per hour, and then reheated at 40°C per hour to 450°C. It is noted that the slopes of the heating and cooling curves are identical from 250°C to 330°C.

The alloy "freezes" at 250°C on cooling, and its resistivity decreases with temperature along a straight line. Since the alloy cooled at 30°C per hour is not in equilibrium, it would be expected that the heating curve should fall below the cooling curve as the alloy relaxed toward equilibrium.

III. THE NICKEL-CHROMIUM SYSTEM

Taylor and Hinton (14) concluded tentatively that the anomalous variations in electrical resistivity of Ni$_3$Cr are associated with an order-disorder transformation and that
Figure 3. Resistivity-Temperature Curves for a Heating and Cooling Rate of 30°C/hr. After Sykes and Evans (13).
these are due to the mean free path of the conduction elec-
tions in the lattice being a few interatomic spacings. These
conclusions were strengthened by specific heat and x-ray data.
It was found that the resistivity rises sharply upon cooling
through a narrow "critical" temperature range. Upon anneal-
ing rapidly cooled samples at temperatures below the
"critical" temperature, the resistivity rises until the
equilibrium amount of order is attained. This change in
resistivity, however, is in the wrong direction for long
range order, because it rises by about 7 per cent on cooling
slowly through the critical temperature, whereas for a nor-
mal change, such as occurs in Cu$_3$Au, there is a fall in the
resistivity of more than 50 per cent (13). However, the
anomalous resistivity changes in Ni$_3$Cr were interpreted by
Taylor and Hinton on the basis of an order-disorder transfor-
mation since they concluded that the creation of new sets of
reflecting planes by the ordering process could lead to a
small increase in resistivity if the mean free path of the
conductivity electrons is of the order of a few interatomic
distances. The smooth shape of the resistivity curve was
also explained by assuming the existence of a mixture of
highly ordered and partially ordered regions rather than
homogeneously ordered material.

Nordheim and Grant (11) explained the absence of a dis-
continuity in the equilibrium resistivity curve and the
absence of superstructure lines in the x-ray pattern of Ni$_3$Cr on the basis of short range order rather than long range order. It was suggested that short range order best explains the lattice contraction and heat evolution associated with the increase in resistivity during annealing after nonequilibrium cooling.

IV. THE TITANIUM-OXYGEN SYSTEM

Ames and McQuillan (1), in their investigation of the effect of alloying elements on the anomalous electrical resistivity of metallic titanium, suggested that the deviation from a linear resistivity-temperature relationship for alpha-titanium is a result of a thermally activated process involving the conduction electrons. The extent of the deviation increases with increasing temperature. It was found that the effect of adding the substitutional elements aluminum, tin, zirconium, copper, and niobium to titanium is, in all cases, to increase the magnitude of the high temperature deviation of the resistivity-temperature curve from linearity. Oxygen, an interstitial alloying element, had the opposite effect in that it reduced the deviation from linearity. The resistivity-temperature variation appears to be in agreement with the empirical formula:

$$P_T = a + bT - p \exp(-q/T)$$

(1)
where \( a, b, p, \) and \( q \) are constants for any particular alloy over the temperature range considered.

Wasilewski (15) suggested that the resistivity maxima observed for Ti$_6$O and Ti$_3$O alloys indicate an order-disorder transformation. For some of the higher oxygen alloys (15-27 weight per cent) a negative temperature coefficient was observed at temperatures above 700\(^\circ\text{K}\). He noted that the resistivity maximum and the change in sign of the temperature coefficient were both most marked at the composition Ti$_3$O and present at Ti$_6$O, although reproducible discontinuities have been observed in lower alloys. Although resistivity measurements suggest an order-disorder transformation at the composition Ti$_6$O, it could not be confirmed by x-ray diffraction.
CHAPTER III

EXPERIMENTAL EQUIPMENT AND PROCEDURE

I. ALLOY PREPARATION

The alloys that were used in this investigation were originally prepared by C. E. Sessions, Research Assistant at The University of Tennessee, in the form of several arc-melted ingots weighing approximately 150 grams each.

Electrolytic nickel of 99.87 per cent purity was supplied by the International Nickel Company in the form of blocks approximately 2 inches square and 1/2 inch thick. These were cold rolled to strips 1/16 inch thick and sheared into 1/2-inch squares. These were then pickled in a boiling 20 per cent HCl solution to remove grease and oxide films that had been accumulated during the rolling and subsequent stress-relief annealing procedures.

The molybdenum was supplied by the Climax Molybdenum Company as 1/2 inch diameter rods. A chemical analysis showed these rods to be 99.9 per cent molybdenum with a very low concentration of dissolved gases. Portions of these rods were broken into small irregular pieces weighing about 5 to 10 grams each; these were cleaned by dipping them into a concentrated HCl solution for 5 seconds and then into concentrated HNO₃ for about 15 seconds.
The charge was then weighed to the appropriate composition from the pieces of nickel and molybdenum and placed in a small depression in the water cooled copper hearth of a direct arc furnace. The furnace was closed and evacuated to a pressure of about $10^{-5}$ mm.Hg. After the initial evacuation, the furnace was flushed with argon, re-evacuated, and finally filled with argon to a pressure of 5 psi. Two 50-gram titanium buttons were then melted in a small depression adjacent to that containing the charge in order to absorb residual oxygen left in the furnace. The charge was melted at least twelve times and was turned over after each melting process. This was done in order to insure that all of the molybdenum was dissolved. The dissolution process was materially aided by keeping the mass of the charge small. With this procedure, ingots showing no macroscopic segregation by radiographic analysis were prepared.

The ingots were homogenized in argon for 100 hours at 1200°C and water quenched to retain the alpha phase structure.

The results of a chemical analysis performed by the Lucius Pitkin Company on the two ingots used to prepare the samples used in this investigation are shown below:

<table>
<thead>
<tr>
<th>Ingot</th>
<th>Molybdenum (wt. %)</th>
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<tr>
<td>Ingot #1</td>
<td>29.18</td>
</tr>
<tr>
<td>Ingot #2</td>
<td>29.08</td>
</tr>
</tbody>
</table>
II. PREPARATION OF SAMPLES FOR ELECTRICAL RESISTIVITY MEASUREMENTS

Two homogenized ingots were used to fabricate three samples. These were reduced 10-80 per cent in diameter by cold swaging or cold rolling followed by a subsequent anneal at 900°C for 40 hours. The ingots were reduced from a 0.625-inch diameter to a 0.187-inch diameter in three or four passes.

Nickel-molybdenum alloys, particularly the stoichiometric composition Ni-29.1 per cent Mo, are difficult to cold work. They must be worked while in the high temperature alpha phase which is retained by quenching from temperatures above 868°C. However, during the cold working, the low temperature beta phase starts to precipitate out as evidenced by the appearance of a faint Widmanstatten structure within the alpha grains. Precipitation started to occur after about a 10 per cent reduction in area. This hardens the alloy considerably and makes it susceptible to cracking along the surface.

During the cold working process a considerable amount of surface cracking was encountered. However, no attempt was made to prevent this since all samples were to be machined in a later step.

After each intermediate anneal the samples were cleaned by immersing them in a hot 20 per cent HCl solution. This
removed the grease and oxide film which had formed during the cold working and annealing steps.

Heat treatments during the fabrication process were carried out in a horizontal tube furnace under an argon atmosphere at temperatures between 1100° and 1200° C. A Brown Electronik recorder-controller with a Chromel-Alumel thermocouple maintained the temperature within ±5°C.

Sample heat treatments prior to actual experimental runs were carried out at 1000°C in horizontal Nichrome-wire wound tube furnaces. The tubes were 36 inches long and 2-1/2 inches in diameter; the wire was more closely wound near the ends of the tubes to compensate for heat losses; insulating refractory plugs were placed in both ends to minimize the effects of external air currents. These three factors resulted in a reduction of temperature gradients such that a 10- to 12-inch zone over which the temperature was constant to within ±2°C was realized.

Each furnace was controlled by a Leeds and Northrup Micro-max, Model C, controller equipped with a power duration adjusting type control. This permitted a maximum temperature variation of ±1°C for short time heat treatments and ±3°C for treatments extending for more than 100 hours.

The samples to be heat treated were sealed under a vacuum of 10 to 25 microns of mercury in Vycor capsules. The samples were heat treated for times ranging from 40 to 50
hours at 1000°C and then water quenched.

Prior to heat treatment the samples were fine polished to a high luster using 320, 400, and 600 grit paper.

III. ELECTRICAL CIRCUIT DESIGN

One of the primary purposes of this investigation was to design and build an apparatus which could be used to measure and record the change in resistivity with temperature of alloys up to 1000°C.

As mentioned before, there are two basic methods for measuring resistance, the Kelvin double bridge and the potential drop method. In the double bridge method, the specimen forms one arm of a special Wheatstone network and the resistance is measured by a balance condition. In the potential drop method the voltage across the specimen is measured when a known current is passed through it.

The double-bridge method is probably the most accurate method of measuring a small resistance at room temperature but is undesirable at high temperatures because it needs large currents to attain sufficient sensitivity, and if continuous recording is desired these have to be maintained for long periods. In the potential drop method, the potential drop across the specimen and a standard resistance in series with the specimen are simultaneously recorded so that the resistance is directly determinable even if the current varies.
Both of these methods, however, are difficult to adapt for continuously recording resistance-time and resistance-temperature curves.

In designing an apparatus for continuously recording resistance-time and resistance-temperature curves there is always the problem of current drift. In particular, if the resistance is to be followed by observations of the emf across the sample, the current must be kept constant. To eliminate this problem, a comparative method can be used whereby the potential drop across the sample is compared or balanced against a potential drop across a standard resistance. The standard resistance or resistance network is in series with the test specimen. This eliminates the need for a constant current because as the current changes, the voltage drop across the standard resistance changes proportionally. However, this introduces the problem of comparing the two emf's without shorting out the circuit. This problem is overcome by electrically isolating the potential drop developed across the specimen from the balancing voltage developed across the standard resistance. This is accomplished through the use of an emf-emf converter with the potential drop across the specimen serving as the input signal to this converter. The output signal from the converter is electrically isolated from its input signal.

A schematic diagram of the circuit developed for
Resistance measurements in this investigation is shown in Figure 4. It is essentially a potentiometric circuit wherein the potential developed between two probes which make contact with the test specimen is amplified and then balanced against a potential developed across the lower part of the high resistance portion of the circuit in series with the test specimen. This is known as a "null balance" circuit because in the balanced condition no current flows through the balancing part of the circuit.

As shown in the circuit diagram, Figure 4, a 2.47 ohm resistance circuit (a, b) is connected in series with the specimen across a potential of 3 volts. The voltage source consisted of a 3-volt Edson cell which was chosen for its stable voltage characteristics. The 2.5-ohm resistor was made up of four 10-ohm ceramic precision resistors in parallel. This arrangement allowed for the dissipation of the heat generated by approximately 1 ampere of current flowing through a 2.5-ohm resistor.

The remainder of the circuit involves two variable resistors consisting of a 100-ohm, 10-turn Helipot and a 1000-ohm, 10-turn Helipot plus three precision resistors of 50, 50, and 1000 ohms.

Plastic coated copper wire was used for the conductor in the circuit. All electrical connections were soldered. The circuit was mounted on a piece of Masonite board inside a
Figure 4. Schematic Diagram of Electrical Resistance Circuit.
steel cabinet which was externally grounded.

The potential drop developed across the specimen serves as the input voltage to a Leeds and Northrup Temperature-Emf Transmitter. This instrument, used as an emf-emf transmitter, produces a d-c current output signal which varies linearly with changes in its input emf. An important characteristic of the instrument is the complete isolation of the output from the input signal. The output current (0-4ma.) is fed through a 750-ohm precision dropping resistor to produce the output voltage. The positive lead from the output terminal is connected to the positive input terminal of a Brown Instrument Company "Electronik" servoamplifier and the negative lead is connected to the slidewire of the 100-ohm Helipot. The negative lead from the servoamplifier is connected to the slidewire on the 1000-ohm Helipot.

For any given potential drop across the specimen the servomotor will drive the slidewire of the 1000-ohm Helipot to a "null balance" position, that is, to a position on the slidewire which corresponds to a zero potential drop at the servoamplifier. Any change in the potential drop across the specimen will cause the servo to drive the slidewire to a new balancing position.

The 100-ohm Helipot is used for suppression or elevation of the balancing range of the circuit and remains fixed throughout the duration of any particular run.
The balancing circuit is connected mechanically by the servomechanism to an auxiliary circuit which in turn produces the input voltage to the Mosley Autograph X-Y Recorder. This auxiliary circuit is composed of a 1.35-volt mercury cell with a 10,000-ohm and a 1000-ohm Helipot connected in series. The servomechanism is mechanically connected to the slidewire of the 1000-ohm Helipot. The potential drop across this 1000-ohm Helipot serves as the input voltage to the y-axis of the recorder. When the potential drop across the specimen changes and causes the servo to drive to a new balance point on the balancing circuit, the action of the servo will cause the potential drop across the 1000-ohm Helipot to change accordingly, resulting in a different input voltage to the y-axis. The sensitivity of the y-axis input voltage to changes in the balance point of the balancing circuit can be regulated by changing the setting of the 10,000-ohm Helipot to control the current through the 1000-ohm resistance.

The input voltage for the x-axis is supplied directly from thermocouples.

Double-throw knife switches were inserted at various points in the circuit so that the potential drop across the specimen, the temperature of the specimen, and the thermal emf's could be read at any time during the run without disturbing any of the electrical connections. These measurements were made with a Leeds and Northrup millivolt potentiometer.
In order to keep leakage currents and stray induced voltages to a minimum, the measuring circuit was shielded as much as possible. Shielded cable was used whenever possible and the circuit along with the servoamplifier were built into a steel cabinet which was then grounded. The electrical components of the apparatus used in this investigation are shown in Figure 5.

Since the specimen was heated to high temperatures, several factors must be considered in the choice of lead wires for the current to the specimen and for the measurement of the potential drop across the test section. The current leads are not as critical as the potential leads since the latter may introduce thermal emf's which are significant in comparison to the IR potential drop across the specimen. Thermal emf's will develop at the junctions of the potential leads with the specimen if these junctions are at different temperatures or from inhomogeneities in the lead wires if the inhomogeneities lie in a temperature gradient. Thus, homogeneous lead wires of the same material as the specimen would be desirable. Since this was not possible, the current leads to the specimen were made of 18 gauge Nichrome-V wire and the potential leads were made of 14 gauge pure nickel wire. These leads were spot welded to the specimen using an arc-discharge welder.

The use of pure nickel wire for the potential leads
Figure 5. Electrical Equipment.
resulted in substantially high thermal emf's at high temperatures. Thermal emf's as high as 0.7 millivolts were encountered at temperatures above 600°C. By switching to pure platinum leads, this problem was partially overcome. However, any substantial thermal gradient along the length of the specimen during heating created high thermal emf's regardless of the type of potential leads being used.

IV. MEASUREMENT AND CONTROL SYSTEMS

A horizontal Nichrome-wire wound tube furnace was used to heat the specimens in a vacuum. The furnace consisted essentially of three Nichrome heating elements wound around a 2-inch diameter Inconel tube. The three windings were controlled independently by three Variacs. The heating elements were covered by a ceramic insulated furnace, 20 inches in diameter. The furnace was mounted on movable rollers which allowed it to be rolled aside to permit work to be done on the sample while still mounted in the system. The approximate heat loss from the furnace at 1000°C was 200 watts. The furnace and vacuum system are shown in Figure 6.

The specimen was supported inside the furnace on a prefired lavite support. All of the lead and thermocouple wires from the specimen were insulated by small ceramic tubing. These wires were brought from the specimen through the 3/8-inch Inconel tube of the specimen support back to the
Figure 6. Furnace and Vacuum System.
terminal outlets. They were then soldered to extension leads which were passed through vacuum seals and connected to the external circuitry.

An Inconel and a platinum heat shield were mounted in the furnace about 3 inches apart on each end of the specimen to reduce heat loss from the middle of the furnace by radiation. This led to a more even temperature across the length of the specimen.

Two Chromel-Alumel thermocouples were spot welded to the specimen about 2-1/2 inches apart. One thermocouple was used to supply the input voltage for the x-axis of the Mosley X-Y Recorder. The other was used as the control thermocouple for a Leeds and Northrup "Speedomax" temperature controller-recorder. This controller controlled the power of the main winding (middle) of the furnace. It also recorded the temperature and heating rate.

It was often desirable to heat a specimen very slowly or to hold it at constant temperature while continuously recording the change in resistance. The x-axis of the X-Y recorder was then converted to a time-axis through the use of a synchronized motor-driven potentiometer (10-turn Helipot). A constant voltage was preset across the slidewire of the potentiometer and then, with the proper gear ratio, the synchronized motor was used to drive the potentiometer at the desired speed. The motor drove the potentiometer at a
constant speed, thereby giving a constant millivolt output per unit time interval. This synchronized output voltage was then used as the input to the x-axis.

The pressure of the system was maintained at a value considerably less than 0.5 micron of mercury. The pumping system consisted of a Consolidated Vacuum Corporation oil diffusion pump and a Cenco Hyvac mechanical fore pump. The system could be evacuated to a pressure less than 0.5 micron of mercury in less than 1 hour.

V. MEASUREMENT OF THE VARIATION OF RESISTIVITY WITH TEMPERATURE

The specimens used in this measurement were two cylindrical samples about 5 inches long and 0.100 inch in diameter and one rectangular cross section sample about 6 inches long and with a uniform cross section of about 0.0077 square inch.

The specimens were placed horizontally in the furnace and positioned carefully so that they were in the center of the heating zone. They were heated and cooled at various rates ranging from 30°C per minute to less than 1/20°C per minute. One difficulty that was encountered in heating and cooling of the samples was that of keeping the temperature uniform along the specimen. It was found that any substantial temperature gradient would result in serious thermal emf's, thereby giving erroneous data. Through a trial and
error procedure, the correct voltage settings on the Variacs were found which would result in heating or cooling with essentially no temperature gradient.

The variation of electrical resistance with temperature was measured by the "null balance" method previously described. To calibrate the resistance scale of the recorder, calibrated precision resistors were substituted in the circuit for the specimen before each run. These resistors were constructed using 1-inch lengths of annealed manganin wire placed in parallel between two copper conductors. The substitution of four of these calibrated resistors into the circuit resulted in four known values on the resistance scale.

The temperature scale was calibrated directly in millivolts. All temperature measurements were made with a Chromel-Alumel thermocouple. The "hot" junction of the thermocouple was formed by spot welding it to the specimen while its cold junction was kept in an ice bath at 0°C.

At high temperatures, thermal emf's as high as 0.3 millivolts were encountered. These were measured with a potentiometer by switching off the current and measuring the potential drop across the specimen with zero current. They were recorded and later used to correct the data.

Using the above procedure a continuous plot of resistance versus temperature was achieved. The system was found to be sensitive to resistance changes as small as 0.00005
ohms (less than 1 per cent change).

The resistance data were converted to resistivity data by multiplying by the constant factor \((A/l)\), where \(A\) is the cross section area and \(l\) is the distance between the potential leads on the specimen.

VI. MEASUREMENT OF THE VARIATION OF RESISTIVITY WITH TIME

The electrical resistance method is one of the best ways to study isothermal transformations in alloys. It provides an accurate means of obtaining isothermal transformation data which would otherwise be determined by one of the more laborious methods.

In most of the runs, the samples were annealed at 1000°C for 40 to 50 hours and water quenched. The specimen was then inserted into the furnace and heated rapidly up to the transformation temperature. The time required to reach the annealing temperature ranged from 10 to 25 minutes. Sometimes it was necessary to hold at a lower temperature for several minutes to make power adjustments on the heaters in order to get rid of any temperature gradient across the specimen. In the other runs the specimen was cooled in the apparatus from 950°C to the transformation temperature.

The x-axis on the Mosley recorder was converted to a time-axis for the annealing runs by the method previously
described. The isothermal transformation of the high temperature alpha phase to the low temperature beta phase could be followed continuously at any given temperature by recording the decrease in resistivity with time as the transformation progressed.
CHAPTER IV

EXPERIMENTAL RESULTS

Experimentally determined resistivity-temperature curves for the nickel-molybdenum alloy of the stoichiometric composition, Ni$_{14}$Mo, are shown in Figures 7-12. Polycrystalline samples having an assumed random orientation were used. Samples used for the heating and cooling curves of Figures 7-9 were in the annealed condition, having been annealed at temperatures below the transformation temperature for times exceeding 8 hours. Samples used for the isothermal transformation curves were in the as-quenched condition (alpha phase) having been water quenched from 1000°C after a 40-hour anneal or held 4 hours at 950°C and cooled directly to the transformation temperature.

Figure 7 shows the heating and cooling curves for a heating rate of approximately 16°C/min. and a cooling rate of approximately 6°C/min. The sample was held at 950°C for 5 hours before cooling.

Figure 8 represents the heating curve for a heating rate of 1.5°C/min. The data for this curve came from two different samples, each with the same heat-treatment history, however.

Figure 9 shows the heating and cooling curves in the region of the transformation temperature for heating and
Figure 7. Resistivity-Temperature Curves for Nonequilibrium Heating and Cooling of Ni$_4$Mo.

- Heating rate = 16°C/min.
- Cooling rate = 6°C/min.

(Held at 950°C for 5 hrs. before cooling)
Figure 8. Resistivity-Temperature Curve for Slow Heating.
Figure 9. Resistivity-Temperature Curve for Slow Heating and Cooling Through the Transformation Temperature.

Heating rate = 0.5°C/min.
Cooling rate = 0.5°C/min.
Figure 10. Resistivity-Temperature Curve During Heating for a Sample Initially in the Alpha Phase State.

Heating rate = 16°C/min.
Figure 11. Resistivity-Temperature Curve During Heating for a Sample in a Partially Transformed Condition.

Heating rate = 13°C/min.
Figure 12. Comparison of Resistivity-Temperature Curves During Heating for Samples Initially in the Beta Phase and Alpha Phase, Respectively.
cooling rates of $0.5^\circ\text{C}/\text{min}$. The sample was held at $950^\circ\text{C}$ for 1 hour before cooling. The extrapolated cooling curve shows the probable curve of resistivity against temperature for the alloy in the absence of long range order.

Figure 10 shows the heating curve for a sample which had been heated for 40 hours and quenched from $1000^\circ\text{C}$ to retain the alpha phase. Heating rate for this curve was approximately $16^\circ\text{C}/\text{min}$.

Figure 11 shows the resistivity-temperature curve on heating for a sample that had been previously quenched from $1000^\circ\text{C}$ and then annealed at $620^\circ\text{C}$ for 6 hours and cooled to room temperature. The initial state corresponds to 18 percent transformation to the beta phase. The heating rate was approximately $13^\circ\text{C}/\text{min}$.

Figure 12 shows the heating curves near the transformation temperature for a sample initially in the alpha phase (as-quenched condition) and for a sample in the beta phase (annealed condition). The heating rate for the alpha phase sample was about $16^\circ\text{C}/\text{min}$ and for the beta phase sample, $0.5^\circ\text{C}/\text{min}$.

Figure 13 shows the isothermal annealing curves at temperatures above the transformation temperature for samples with different thermal histories. The samples were heated at about the same rate through the transformation temperature ($868^\circ\text{C}$) but no attempt was made to put the samples in the
Figure 13. Effect of Annealing at Temperatures Above 868°C After Nonequilibrium Heating Through $T_c$. 
same condition at the start of heating.

Figure 14 shows the isothermal annealing curves at temperatures below the transformation temperature for samples that had cooled through $T_c$ after a 1-hour anneal at $950^\circ C$. Cooling rates for the samples were approximately $6^\circ C/min$.

Figures 15, 16, and 17 show the isothermal transformation curves for samples that had either been water quenched from $1000^\circ C$ after a 40-hour anneal or had been furnace-cooled after a 4-hour anneal at $950^\circ C$. The transformation curves in the temperature range $770^\circ -850^\circ C$, represent samples that were furnace-cooled to the transformation temperature and the curves in the temperature range $600^\circ -760^\circ C$ represent water-quenched samples that had been reheated to the annealing temperature. The samples that had been water-quenched to room temperature were rapidly heated to the annealing temperature at about $30^\circ C/min$. The furnace-cooled samples were cooled to the annealing temperature at about $12^\circ C/min$ from $950^\circ C$.

Figure 18 shows the time-temperature-transformation diagram for the alloy $Ni_4Mo$ constructed from data taken from the isothermal transformation curves. This diagram shows the approximate time required for the alpha phase to begin to transform and the time required for approximate completion of the transformation at any constant temperature in the range covered by the curves. The time required for the start of the transformation in the temperature range $710^\circ -775^\circ C$ was too
Figure 14. Effect of Annealing at Temperatures Below 700°C After Nonequilibrium Cooling Through the Transformation Temperature.
Figure 15. Isothermal Transformation Curves for the Temperatures 649°, 738°, 796°, and 827° C.
Figure 16. Isothermal Transformation Curves for the Temperatures 693°C, 716°C, 782°C, and 801°C.
Figure 17. Isothermal Transformation Curves for the Temperatures 663°, 727°, 760°, 774°, and 813°C.
Figure 18. Time-Temperature-Transformation Diagram for Ni-29.1 Weight Per Cent Mo.
fast to be measured accurately by this particular method. Also, the time required for completion of the transformation at temperatures below 650°C and above 830°C was too long to be represented on this plot.

Figure 19 summarizes the effect obtained on thermal cycling the alloy over narrow temperature ranges in the vicinity of the transformation temperature. The arrows indicate the path of the resistivity curve, with double-ended arrows indicating a reversible change in resistivity on heating and cooling.
Figure 19. Effect of Thermal Cycling in the Vicinity of the Transformation Temperature.
CHAPTER V

DISCUSSION OF RESULTS

There were three principal objectives of the research program. The first objective was to design and build an apparatus to continuously measure and record the change in resistivity with temperature of metals and alloys at high temperatures. Second, it was desired to use this method and equipment to study the order-disorder transformation in the nickel-molybdenum alloy of stoichiometric composition, Ni$_4$Mo. Finally, it was desired to use this method to determine the time-temperature-transformation diagram for this alloy.

At the start, it is important to point out that the resistivity-temperature curves presented in this report do not necessarily represent the relationships corresponding to equilibrium conditions. Even with heating and cooling rates as low as 0.5°C/min, the alloy is probably never in equilibrium at any temperature during the heating or cooling. The equilibrium heating and cooling curve would probably fall a little lower than the ones shown in this report at temperatures below the transformation temperature since annealing at these temperatures results in a decrease in resistivity. At temperatures above $T_c$, the equilibrium curve would most likely be slightly higher since annealing at these temperatures results in a slight increase in resistivity as the alloy
approaches equilibrium. Therefore, limited emphasis is placed on the comparison of absolute values of resistivities from one graph to another since these values are a function of heating and cooling rates and dependent upon the previous history of the sample. More significance is placed on comparing the general shapes of the various curves rather than the absolute values of resistivities.

Only a portion of the total data taken during the course of this research will be considered. Inconsistencies and problems arising during the investigation are discussed where pertinent. The discussion is presented in sections. Each section represents a separate phase of the investigation.

I. THE MEASUREMENT OF ELECTRICAL RESISTIVITY

The method and apparatus used in this investigation to measure the change in electrical resistivity with temperature for the alloy Ni$_4$Mo proved to be very satisfactory. As mentioned previously, the method is essentially a potentiometric one wherein the potential developed between two probes which make contact with the test specimen is balanced against a potential developed across part of a resistance circuit in series with the specimen.

The overall performance of the measuring circuit was very reliable. No problems were encountered due to thermal emf's or excessive heating in the resistors. The measuring
range and sensitivity of the circuit proved to be quite adequate; potential drops ranging from 1 to 30 millivolts could be used as the input voltage to the measuring circuit. Resistance changes of less than 1 per cent could be measured on specimens having a resistance of 0.005 ohms.

One serious problem did arise, however, due to the creation of thermal emf's at high temperatures. These emf's were produced partially as a result of the difference in composition of the specimen and lead wires attached to it and partially due to the inhomogeneities in these lead wires. The effect of the dis-similar metal junctions arose whenever the junctions were at different temperatures and, hence, could be decreased by reducing the temperature gradient along the specimen. However, since the lead wires had to pass through a temperature gradient, thermal emf's due to this gradient could be reduced only by using lead wire of a high degree of chemical homogeneity. In this respect, platinum lead wires proved to be more satisfactory than nickel.

Considerable time was spent in overcoming the problem of maintaining a uniform temperature along the sample during heating and cooling. The heating zone in the furnace which had to be maintained at a uniform temperature was about 6 inches in length. A platinum and an Inconel heat shield were placed on each end of the specimen to reduce radiation heat losses. Chromel-Alumel thermocouples were spot welded to the
specimen about 1/2 inch from each potential lead and about 3 inches apart. One couple was used as the control couple to the temperature controller and the other as the measuring couple to the X-Y recorder. This resulted in essentially a "one-point" control, in that the temperature controller controlled the temperature at only one point on the specimen. The central winding of the furnace was controlled by the temperature controller while the two end windings were controlled by hand. The correct settings on the Variac voltage controls to give a heating or cooling rate with no temperature gradient across the specimen had to be found by trial and error. Different settings were required for different heating and cooling rates. This procedure, although adequate, is very undesirable. A remedy to this situation would be to use motor-driven Variacs which could be adjusted to give any desired heating or cooling rate. Also, three-point temperature control would be very desirable, especially during annealing runs. This would involve using a combination of three temperature controllers to control the temperature at three points on the sample. This should eliminate the problem of maintaining a constant temperature along the specimen, thereby reducing the thermal emf's.

The pressure in the system was maintained well below 0.5 micron of mercury as measured by a thermocouple vacuum gauge. No serious oxidation of the sample was observed even
after 30 hours at 950°C. One problem in maintaining the vacuum in the system occurred due to outgassing from the lavite specimen holder during heating. The lavite picks up gases when exposed to the atmosphere during the time the system is open to mount another sample. Upon heating, the lavite outgasses, causing a loss of vacuum until the system can be pumped down again, which requires about 30 minutes. This problem could be eliminated either by prefiring the lavite under a vacuum or replacing it with some other more stable material.

II. THE VARIATION OF RESISTIVITY WITH TEMPERATURE

Figures 7 to 12 show the variation of resistivity with temperature for the alloy under investigation. In Figure 7 it is seen that the heating curve is linear up to about 170°C where there is a marked deviation from linearity. This deviation increases with temperature up to the transformation temperature. As seen in Figure 8, this deviation occurs at a higher temperature (350°C) for a slower rate of heating which indicates that it is heating rate dependent. This same type of deviation is observed in the resistivity-temperature curves for alpha titanium and titanium-oxygen alloys. Ames and McQuillan (1) suggest that this is due to a thermally-activated process involving the conduction electrons. They
also found that the effect of adding various substitutional elements to alpha-titanium was to increase the magnitude of the high temperature deviation. No satisfactory theoretical explanation can be given for the observed deviation in the resistivity-temperature curve for Ni$_4$Mo other than one similar to that suggested for titanium.

The transformation begins at 868°C and takes place over a small temperature interval of about 20°C for the alloy heated at the rate of 16°C/min. For the much slower heating rates the alloy undergoes an almost discontinuous change in resistivity at the transformation temperature 868°C. For the latter case, the resistivity decreases approximately linearly with temperature above the critical temperature up to 1000°C. Thus, in the alpha phase region the alloy has a negative temperature coefficient of resistivity. As the heating rate is increased, the transformation occurs over a small temperature range and peaks before assuming the approximately linear decrease in the alpha phase state. As the heating rate is further increased, the transformation takes place over a wider temperature interval and the peak in the curve is more rounded than that for the slower heating rate.

A negative temperature coefficient of resistivity was observed for Ti-0 alloys above 700°C by Wasilewski (15) and for Ni-Cr alloys above 540°C by Taylor and Hinton (14). Nordheim and Grant (11) suggest that the negative temperature
coefficient of resistivity of the Ni\textsubscript{3}Cr alloy above the critical temperature (544°C) is due to the dispersion of short range order in the alloy. A negative temperature coefficient of resistivity in certain temperature ranges seems to be quite common among alloys of the transition elements.

A peak in the resistivity-temperature curve was not observed for either the Ti-0 or Ni-Cr alloys referred to above. Also, the peak in the heating curve for the Ni\textsubscript{4}Mo alloy is unexplained. Since this peak is not observed for the slowly heated alloy, it must be due in some way to superheating and the resulting transient state which exists during the transformation.

There is a small flattening in the resistivity-temperature curve just below the critical temperature as seen in Figure 9. This flattening is more pronounced the slower the rate of heating or cooling.

Figures 7 and 9 show the hysteresis in the transformation due to nonequilibrium conditions. For a cooling rate of 6°C/min, the transformation temperature is suppressed 61°C. Annealing at temperatures just below the critical temperature for times up to 6 hours produces no noticeable change in resistivity, indicating the transformation has not started even after 6 hours. Since the hysteretic effect decreased with decreasing cooling rate, it is uncertain whether a limiting hysteresis does exist. It is evident that the cooling
rate for equilibrium would be extremely small. Bragg (3) has suggested that the lag at a critical temperature is a result of the change in lattice constant during ordering. The ordered nuclei, when formed, have a lattice constant so different from that of the main crystal that a considerable strain must occur in the disordered lattice when the nuclei form. This strain will tend to prevent the formation of the nuclei.

The loop in the cooling curve shown in Figure 7 is the result of the heat of transformation being large enough to increase the temperature by several degrees during the transformation, thereby, causing the resistivity to increase. The temperature and resistivity will continue to increase until the heat of transformation has been dissipated and the sample begins to cool again. For slow cooling rates such as for the cooling curve in Figure 9, the heat of transformation is dissipated fast enough so that no loop is formed.

It was found that the slower the rate of cooling, the lower the resistivity at any particular temperature below the transformation temperature. This indicates that the transformation is proceeding as the temperature is lowered, although an equilibrium state can be achieved at any particular temperature. Figure 14 shows the continued decrease in resistivity while holding at constant temperature for samples whose cooling was interrupted at 702°C and 593°C, respectively,
after nonequilibrium cooling through $T_c$ at approximately 6°C/min. to the indicated temperature. The resistivity decreases with time as the alloy relaxes toward its equilibrium degree of order at that particular temperature. Although not shown in the figures, the resistivity curve became linear on cooling below 400°C. The temperature at which this occurred varied depending upon the cooling rate; the higher the rate of cooling, the higher the temperature at which this occurs. The onset of this linear decrease in resistivity cannot correspond to the temperature at which ordering ceases since it has been shown by Block (2) from hardness measurements, by Spruiell (12) from x-ray measurements, and in this investigation from isothermal transformation curves, that the ordering rate below 600°C is extremely small. Since the onset of linearity during cooling and the deviation from linearity during heating is rate dependent, it would seem probable that this is a thermally activated process involving the conduction electrons similar to that observed in some titanium alloys.

Figure 9 includes the extrapolated cooling curve which should be the probable curve of resistivity as a function of temperature for the alloy during rapid cooling from 1000°C in the absence of long range ordering. If the negative temperature coefficient of resistivity above 868°C is due to short range order, then this extrapolated curve represents
the effect of increasing short range order on the resistivity. As should be expected, the extrapolated value for the resistivity at room temperature is much higher than the observed room temperature resistivity of the quenched samples. The resistivities of quenched samples at 25°C were about $1.3 \times 10^{-6}$ ohm-cm, whereas the extrapolated value was $1.58 \times 10^{-6}$ ohm-cm. The former value should be smaller since it represents a "quenched-in-state" of lower short range order than for the state corresponding to the extrapolated value.

Figure 10 shows the heating curve for a sample initially in the alpha phase state obtained by quenching from 1000°C after a 40-hour anneal. The resistivity decreases slightly upon heating to about 325°C and then the resistivity-temperature curve undergoes a sharp change upward. The resistivity reaches a maximum at about 650°C with a value of $1.42 \times 10^{-6}$ ohm-cm. The curve then decreases sharply until the transformation temperature is reached. At the transformation temperature the sample undergoes the order-disorder transformation producing the usual rise in the resistivity-temperature curve. The large difference in behavior during heating of the quenched sample and the previously slowly cooled sample is shown in Figure 12.

Figure 11 shows the heating curve for a quenched sample that had been partially transformed by annealing for 6 hours at 620°C, cooled to room temperature, and then reheated.
The sample had been about 18 per cent transformed to the beta phase by the pre-treatment. The resistivity-temperature curve increases linearly to 200°C and then deviates from linearity as it continues to rise to a maximum at 680°C, from which the resistivity decreases rapidly until the transformation temperature is reached. At the transformation temperature the resistivity undergoes the usual sharp increase to a maximum but from the maximum the resistivity drops sharply to a value equal to that at the start of the transformation. From this secondary minimum at 880°C, the curve again rises sharply and then decreases linearly with temperature from 890°C. No explanation can be given for the peculiar shape of the anomaly in the resistivity-temperature curve shown in Figure 11 although it was observed during several heating cycles.

The large increase in resistivity to a maximum around 650°C for both the quenched sample and the partially transformed sample shown in Figures 10 and 11 is probably due to a combination of several factors. As the quenched sample is heated, the resistivity-temperature curve starts to rise sharply at about 400°C. This increase in resistivity could not be due to the thermal vibrations of the lattice alone since the resistivity increases too rapidly. It is also difficult to explain it in terms of changes in atomic configurations if the hardness data of Block (2) and x-ray data of
Spruiell (12) are taken as indicating that no change in the state of order occurs below 600°C in reasonable times. The explanation for the increase in resistivity, therefore, remains obscure.

Spruiell (12) has concluded that the short range order of the quenched state is one of small randomly oriented domains of the long range ordered structure. Changes in the intensity of x-ray diffuse scattering within 1/2 hour at 600°C indicates beginning of domain growth. As the long range ordered domains grow, the resistivity should decrease since the final long range ordered state is one of lower resistivity. This growth continues on heating and is accompanied by a decrease in resistivity until an equilibrium state is reached.

Another large contributing factor to the resistivity could be the strain introduced in the lattice due to the nucleation and growth of long range order. The removal of this strain by thermal recovery processes should also cause the resistivity to decrease.

Since the partially transformed alloy (Figure 11) has a lower resistivity at room temperature than does the as-quenched alloy and an entirely different resistivity curve on heating, it is quite evident that permanent changes have occurred while heating to 620°C and annealing at this temperature for 6 hours. As this alloy is heated from room...
temperature, its resistivity increases parallel to that for the fully ordered state (Figure 8) and hence is due mostly to thermal vibrations of the lattice until the effect of further ordering causes the resistivity to decrease. The peak in the resistivity-temperature curve occurs at a temperature of about 680°C for the partially ordered alloy as compared to about 650°C for the as-quenched alloy.

III. THE VARIATION OF RESISTIVITY WITH TIME

Figure 13 shows the isothermal annealing curves for samples annealed at temperatures above the transformation temperature after nonequilibrium heating through $T_c$. It can be seen from the resistivity-time curves that the resistivity increases as the alloy relaxes toward equilibrium. This is the result of an incomplete transformation or incomplete disordering as the alloy is heated through the transformation temperature.

Figures 15, 16, and 17 show the isothermal annealing curves for temperatures below the critical temperature (868°C). Before discussing the curves of resistivity as a function of time at various subcritical temperatures, several general remarks concerning the objectives and interpretations of the curves should be made. In the first place, Spruiell (12) and Guthrie (6) have conclusively shown that the overall transformation of the alpha phase to the beta phase results in a
long range ordered structure. It is also established that the long range order develops from an alpha phase which contains short range order and that there is a relationship between the short and long range ordered structures. As a consequence, the nuclei for the transformation pre-exist on cooling below \( T_c \) and are immediately available for growth. There is, therefore, no need for nucleation to occur in the conventional sense and a rapid rate of transformation at some degree of undercooling might be expected.

The above factors cause emphasis to be placed on the necessity to cool the sample as rapidly as possible to the transformation temperature. Practical attainment of the necessary conditions for strictly isothermal transformation measurement was limited by the maximum heating and cooling rates of the sample in the apparatus relative to the transformation rates. The maximum rates of heating and cooling were limited to approximately \( 30^\circ C/min \) and \( 12^\circ C/min \), respectively, by the construction of the equipment. These rates are too slow to reasonably follow the progress of the transformation at all temperatures since Block (2) has shown that the hardness has already increased to 300 DPH after 1.2 minutes at \( 800^\circ C \). This is consistent with the observations that the resistivity-temperature curve for the fastest cooling rate as shown in Figure 7 undergoes a sharp decrease at \( 782^\circ C \) due to the onset of the transformation. Hence, it was not
possible to make reasonable isothermal transformation measurements below this temperature using the procedure of simply furnace-cooling the sample to the transformation temperature. As a consequence, the "isothermal" transformations were conducted by cooling the specimen directly in the apparatus to the higher subcritical temperatures; the measurements at the lower temperatures were made on samples quenched in water from 1000°C and rapidly heated in the resistivity apparatus to the transformation temperature. In presenting the curves for the isothermal transformations, Figures 15 through 17, it was pointed out that direct cooling to temperature was used for transformations from 850°C down to 770°C. In the temperature range 600°C to 760°C, previously quenched samples were heated to temperature.

It was found that annealing at temperatures as much as 15°C below the transformation temperature for as long as 6 hours produced no detectable change in resistivity. The same was true for annealing at temperatures below 600°C.

Isothermal transformation curves such as those shown in Figures 15 through 17 were used to construct the time-temperature-transformation diagram shown in Figure 18. This diagram shows the time required for the alpha phase to begin to transform to the beta phase and the time required for approximate completion of the transformation at a constant temperature. The transformation was considered to be completed
when no change in resistivity was observed after an interval of 1 hour.

The "nose" of the TTT curve was found to lie within the temperature range 710°C to 775°C. The time required for the start of transformation in this region was too fast to be accurately measured by the method used in this investigation. Using hardness measurements, Block (2) found the nose of the curve to be at about 800°C.

It is recognized that the TTT diagram presented represents the general pattern of transformation, particularly in regions where the transformation occurs rapidly. It is not to be regarded as being a highly precise quantitative representation of the transformation. When transformation begins within a few seconds and proceeds very rapidly as, for example, in the "nose" region of the diagram, the time required for the specimen to reach the actual annealing temperature is a considerable portion of the total time required for the transformation. Also, the heat generated by the transformation may cause the specimen to be heated to a slightly higher temperature, thereby accelerating or decelerating the transformation. Despite these limitations, a beginning and ending curve, even in the "nose" region, can be located with sufficient accuracy to show the transformation characteristics of the alloy.

Although the time-temperature-transformation diagram
applies strictly only to transformations occurring at a constant temperature, the information which it contains can be applied, to some extent, to the more practical problem of transformation of the alpha phase to the beta phase on continuous cooling. As a consequence, it should be useful to attempt to rationalize the resistivity behavior on cooling shown in Figures 7 and 9 by this analysis. If the cooling curves are superimposed upon the TTT diagram, it can be seen that for slow rates of cooling the transformation will tend to begin at a comparatively high temperature and the alpha phase will transform almost completely to the beta phase in this temperature range. As the cooling rate is increased, the transformation will tend to begin more quickly and at a lower temperature. However, this may result in a transformation that is not as complete as that for the slower cooling rate because of the shape of the TTT curve at lower temperatures. Hence, the degree of long range order in a slowly cooled sample should be greater than that in a sample that has been cooled at a faster rate. Since the resistivity is a function of the long range order existing at any temperature, the resistivity-temperature curves will be cooling-rate dependent. In particular, due to the shape of the TTT diagram the transformation will be rapid and the corresponding decrease in resistivity large as the cooling curve first enters the upper part of the diagram. This rapid drop in
resistivity is evident in Figures 7 and 9. However, as the cooling curve passes into the lower temperature region of the diagram, the transformation rate will be slower and, hence, the rate of decrease of resistivity will be less. This latter fact causes the resistivity curve at lower temperatures to be particularly cooling-rate dependent.

If the rate of cooling is increased to such an extent that the alloy is cooled below the "nose" of the TTT diagram in a shorter interval of time than that required for the transformation to begin, then the alpha phase will not transform but will be retained at room temperature.

Samples cooled at a rate sufficiently rapid to avoid the "nose" of the TTT diagram will consist of the disordered retained alpha phase at room temperature. There will also be a range of cooling curves between these two limits which represent an incomplete transformation of the alpha phase to the beta phase resulting in different resistivity-temperature curves on subsequent reheating. It is also evident from the resistivity-temperature curves that the cooling rate will have to be extremely slow in order for the transformation to occur near the critical temperature of 868°C.

IV. THE EFFECT OF THERMAL CYCLING

The effect of thermal cycling over a narrow temperature range in the vicinity of the transformation temperature
is seen in Figure 19. The arrows indicate the path of the resistivity curve, with double-ended arrows indicating a reversible change in resistivity on heating and cooling. As the alloy is heated and cooled between A and C, the electrical resistivity-temperature curve retraces itself. As it is heated through C, there is a marked anomaly in the curve, indicating transformation. The resistivity changes reversibly between D and E. On cooling, the resistivity changes reversibly between E and F. Cooling through F produces a rapid decrease in resistivity which is reversible down to approximately point G. Upon reheating at any point below G, the curve will not retrace itself.

At point H, the heat liberated due to the exothermic transformation causes the sample to heat up to a higher temperature, thereby increasing the resistivity to point I. At point I most of the heat of reaction has been liberated and the specimen starts to cool again with a resulting decrease in resistivity. On further cooling from point I, the cooling curve approaches the heating curve until it intersects it at point A.

On reheating at any point between G and I, the heating curve will retrace the path of the cooling curve to point I and then decrease with temperature until it intersects the normal heating curve at point C. It will then retrace the normal path through the transformation. On
reheating at points between I and A, the curve will increase or decrease with temperature and intersect the normal heating curve at point C, retracing the curve through the transformation.

The transformation will begin at the same temperature during heating regardless of the heating rate, but the transformation temperature during cooling is rate dependent.

The heating and cooling rate for the curves shown in Figure 19 is approximately 10°C/min.
An apparatus was constructed for studying the variation of the electrical resistivity with temperature of metals and alloys. It was demonstrated that the equipment could follow and record resistance as a function of time or temperature with a sensitivity of better than 1 percent in the resistance range of 0.005 ohms. The apparatus and techniques were developed to study the order-disorder transition in the nickel-molybdenum alloy of stoichiometric composition, Ni$_4$Mo. The results of this investigation permit the following conclusions:

1. The resistivity-temperature curve for this alloy in the initially ordered state exhibits a marked negative deviation from linearity which increases rapidly with increasing temperature. At the critical temperature (868°C) the alloy undergoes a discontinuous change in resistivity.

2. At 868°C the alloy transforms to the alpha phase and exhibits a negative coefficient of resistivity to 1000°C. This can be attributed to decreasing short range order on heating above the transformation temperature.

3. The rate of isothermal transformation of the
retained alpha phase to the beta phase is temperature dependent and gives rise to a "C" type time-temperature-transformation curve. The "nose" of the curve lies within the temperature range 720° to 775°C.

4. The resistivity-temperature curve is cooling-rate dependent. When the alloy is cooled below the critical temperature (868°C), a sharp decrease in resistivity occurs at the onset of ordering. The transformation on cooling may be predicted approximately from the time-temperature-transformation diagram. The degree of long range order, and likewise the resistivity of the alloy at temperatures below the temperature of initial rapid transformation, is dependent upon the cooling rate. Holding at temperatures below the transformation temperature results in a slow decrease in resistivity as equilibrium is approached.

5. The resistivity-temperature curve for the retained alpha phase exhibits a negative slope up to 350°C. This negative temperature coefficient does not seem to be associated with changing short range order since the time-temperature-transformation diagram implies negligible atomic mobility in this temperature range. On heating above this temperature the resistivity increases rapidly to a maximum near 650°C. No
explanation can be given for the peak in the curve other than being a resultant effect of domain size, degree of order, and strain.
LIST OF REFERENCES
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APPENDIX A

CIRCUIT ANALYSIS

The electrical circuit shown in Figure 20 for the measurement of resistance was designed on the basis of the following requirements:

1. The magnitude of the voltage source had to remain essentially constant; therefore, the current drain on the battery had to be relatively small.

2. The current through the specimen had to be approximately 1 ampere in order to get a measurable millivolt drop across the specimen.

3. The maximum voltage drop across the balancing resistor (1000-ohm Helipot) had to be greater than 1 volt in order to have the range necessary to balance against the maximum amplified voltage drop across the specimen which was estimated to be on the order of 1 volt.

4. Heating due to the IR drop across the various resistors had to be kept at a minimum. Heat dissipation in all precision resistors and Helipots had to be kept below 1 watt to insure the accuracy of the resistors.

5. The temperature of the "dropping" resistor A (Figure 20) had to be kept constant and a method for
Figure 20. Schematic Diagram of Measuring Circuit.
dissipating the heat generated in this resistor had to be devised.

In making the circuit analysis, it was assumed that the resistance of the specimen was negligible in comparison with the other resistances in the circuit and, therefore, could be neglected. Since the emf-emf converter, the servoamplifier, and the auxiliary circuit are ineffective at "null balance" condition, they need not be considered in the analysis of the resistance network.

Many combinations of resistances and voltages were found adequate, but the combination shown in Figure 20 was considered the best one to use in this particular case.

Calculated voltage drops and power losses for the various components of the circuit are shown in Table I.

The 3.6 watts generated in the 2.5-ohm dropping resistor was enough to cause considerable heating; therefore, it was necessary to replace the 2.5-ohm precision resistor with four 10-ohm ceramic insulated precision resistors connected in parallel to give the same magnitude of resistance. The ceramic insulated resistors were tubular and had a large surface area which allowed for the rapid dissipation of the heat.
### TABLE I

CIRCUIT DATA

<table>
<thead>
<tr>
<th>Resistor</th>
<th>Voltage Drop (volts)</th>
<th>Power Loss (watts)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>3.0</td>
<td>3.600</td>
</tr>
<tr>
<td>B</td>
<td>1.6</td>
<td>0.050</td>
</tr>
<tr>
<td>C</td>
<td>1.3</td>
<td>0.020</td>
</tr>
<tr>
<td>D</td>
<td>1.7</td>
<td>0.003</td>
</tr>
<tr>
<td>E</td>
<td>1.3</td>
<td>0.030</td>
</tr>
<tr>
<td>F</td>
<td>1.7</td>
<td>0.003</td>
</tr>
</tbody>
</table>
VITA

The author was born in Mexico, Missouri, on January 23, 1939. He received his primary and secondary education at the Wellsville Grade and High Schools; he then attended Hannibal LaGrange College and Missouri School of Mines and Metallurgy. In June of 1961 he received a Bachelor of Science Degree in Metallurgical Engineering.

The author entered the Graduate School at The University of Tennessee in the fall of 1962 after working for the Atomic Energy Commission in Oak Ridge for approximately one and one-half years. Graduate studies in Metallurgical Engineering were aided by a fellowship from the Oak Ridge Institute of Nuclear Studies and by a research assistantship on the UNC contract under which this thesis was written.

Plans for the immediate future involve working for the Western Electric Company in Kansas City, Missouri, as a Planning Engineer in their Chemical and Metallurgical Engineering Department.