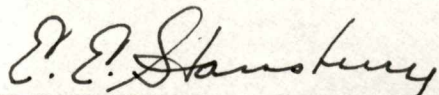


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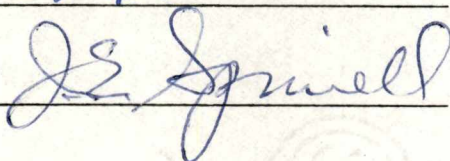
I am submitting herewith a thesis written by K. Vasudevan entitled "The Effect of 0-4 Weight Percent Chromium on Transformations of Alpha Phase Ni-Mo-Cr Alloys With Nickel:Molybdenum Atom Ratio Equal to 4:1." I have examined the final copy of this thesis for form and content and recommend that it be accepted in partial fulfillment for the degree of Master of Science, with a major in Metallurgical Engineering.



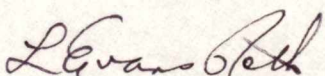
E. E. Stansbury, Major Professor

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Vice Chancellor
Graduate Studies and Research

THE EFFECT OF 0-4 WEIGHT PERCENT CHROMIUM ON TRANSFORMATIONS
OF ALPHA PHASE Ni-Mo-Cr ALLOYS WITH NICKEL:MOLYBDENUM
ATOM RATIO EQUAL TO 4:1

A Thesis
Presented for the
Master of Science
Degree
The University of Tennessee, Knoxville

K. Vasudevan

August 1982

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DEDICATION

This thesis is dedicated to my parents, Mr. and Mrs.
K.S.Krishnaswami.

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ABSTRACT

The effect of 0-4 wt.% Cr on transformations of the alpha phase in Ni-Mo-Cr alloys with nickel:molybdenum atom ratio equal to 4:1 is reported using resistivity and hardness measurements, optical and scanning electron microscopy, and x-ray diffraction methods. The resistivity was measured during continuous heating, cooling, or isothermally for periods of more than a day on alloys in various initial states including cold worked. The isothermal transformation behavior of the short range ordered alpha phase was also studied at 600, 700, 800 and 850°C for times upto 4500 hours.

The SRO "K-State" effect exists in all $\text{Ni}_4\text{Mo} + (0-4) \text{ wt.}\% \text{ Cr}$ alloys in the retained alpha phase as shown by a negative temperature coefficient of resistivity and a decrease in resistivity with cold work. The resistivity decreases with an increase in cold work to 68% RA and then increases. This indicates that decrease in SRO compensates for the increase in resistivity caused by increased defect concentration to 68% RA. Above 68% RA the converse is true. The SRO resistivity decreases linearly with an increase in chromium content. The lattice parameter of the alpha phase Ni_4Mo increases with an increase in chromium content. The critical temperature of the order-disorder transformation decreases with an increase in chromium content, which is 868 ± 2 , 865, 850, 845 and 825°C for the Ni_4Mo , 0.41, 0.54, 0.74 and 2.08 wt.% Cr alloys respectively. About 3 wt.% Cr is sufficient to suppress long range ordering of Ni_4Mo in alloys cooled at rates faster than 1°C/min from above the critical temperature.

Based on isothermal resistivity measurements at 700°C, time of initiation of ordering of Ni_4Mo is not influenced by prior cold work. However, at later stages of aging the ordering rate is higher the greater the degree of prior cold work. Cold work more than 68% RA substantially increases the ordering rate at all times beyond 20 minutes. Ordering in cold worked Ni_4Mo at 700°C, can be said to occur by a process of heterogeneous nucleation which appears optically as a homogeneous reaction.

Based on resistivity measurements and microstructure, ordering in Ni_4Mo is complete in 24 hours at 850°C, 10 hours at 800°C, 96 hours at 700°C and 2000 hours at 600°C. The kinetics of ordering of Ni_4Mo are only slightly affected by additions of chromium to 0.74 wt.%. At 2.08 wt.% Cr and above, the rate decreased substantially at all temperatures but 700°C.

Distinct $\{111\}$ f.c.c. striations are observed in the beta phase microstructure on isothermal aging. Since the striations usually form before the maximum hardness, it is suggested that they are mechanical twins introduced by stresses from the small lattice parameter changes associated with the ordering. Also, tapered $\{110\}$ f.c.c. striations are observed in the beta phase, often coexisting with the $\{111\}$ f.c.c. striations. In the higher chromium-containing alloys, short Widmanstätten plates, tentatively identified as beta phase, form parallel to $\{111\}$ f.c.c. planes.

The long range ordered beta domains possess six distinct orientations in correspondence to a $\{110\}$ f.c.c. habit plane. Time at temperature results in growth of domains to large amoeba-shaped,

irregularly bounded regions. Domain growth is inhibited by the addition of chromium and often domains appear as doe-eye or flame-shaped formations.

Based on hardness, resistivity and optical microstructure on alloys aged for times to 4500 hours, the solubility of chromium in the beta phase is about 4 wt.% at 600°C and about 0.4 wt.% at 700, 800 and 850°C. Widmanstatten gamma phase is observed in chromium containing alloys. In the higher chromium alloys, the gamma phase is present in two morphologies, namely, thin Widmanstatten gamma striations/plates parallel to {111} f.c.c. planes and massive Widmanstatten plates. The formation of the Widmanstatten gamma plates is associated with a high hardness. In alloys located in the three phase $\alpha + \gamma + \delta$ region (higher temperatures), a discontinuous precipitation of δ and γ phases is observed.

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CHAPTER I

INTRODUCTION

Nickel base alloys are of great commercial importance because of their high temperature mechanical properties combined with excellent corrosion resistance in aqueous media and at high temperatures. A considerable amount of work has been done over the years in the Department of Chemical, Metallurgical and Polymer Engineering at the University of Tennessee, Knoxville on Nickel-Molybdenum alloys, particularly ones containing 10 and 20 at.% Mo. The former exists as a short range ordered alloy while the latter undergoes long range ordering below 868°C. These alloys have been shown to exhibit a wide range of physical and mechanical properties which correlate well with internal structure. Besides the binary Nickel-Molybdenum, ternary alloys containing iron, silicon, aluminum etc. have also been studied.

Several commercial alloys are closely related to the Ni-20 at% Mo alloy. The initial alloy was Hastelloy B, produced by the Stellite Division, Cabot Corporation (1). This was essentially a Nickel-Molybdenum alloy with a composition of Mo-28 wt.%, Fe-5 wt.%, Co-2.5 wt.%, Cr-1 wt.% max., C-0.05 wt.% max., Si-1.0 wt.% max. and balance Ni. Hastelloy B is particularly well suited for equipment handling hydrochloric acid at all concentrations and temperatures including the boiling point. It is also resistant to hydrogen chloride gas, and sulphuric, acetic and phosphoric acids. However, it has one serious limitation, viz. weld decay (Hodge and Kirchner,2). Following the weld fabrication of process equipment, a solution treatment followed by

rapid cooling is required to restore the weld areas to their optimum corrosion resistance. The need for this heat treatment severely limits the size of weld fabrications that can be utilized.

The presence of iron and carbon in the alloy promote the precipitation of carbides along the grain boundaries. According to Svistunova (3), the influence of iron is to increase the kinetics of precipitation. Without the solution heat treatment, however, Hastelloy B exhibited Knife-Line Attack (KLA) immediately adjacent to the weld and/or heat affected zone (HAZ) attack at some distance from the weld. Flint (4,5) in investigating these phenomena in Nickel-Molybdenum alloys, attributed the susceptibility of the KLA region to the formation of Mo_6C and the HAZ region to the formation of M_2C .

The presence of iron (which supplies carbon) is chiefly responsible for carbide precipitation (2). Flint (4,5) concluded that good corrosion resistance could be obtained in the absence of iron, by increasing molybdenum to more than 30 %, but these alloys are difficult to work. Experiments conducted at the Cabot Corporation have shown that decrease of iron can decrease the ductility (2). This decrease in ductility has also been studied by Clausing (6) and by Roan and Brooks (7) both confirming the importance of the formation of the beta phase (which is the ordered Ni_4Mo phase of alpha). Snyder and Brooks (8), investigated extensively the effect on ductility of the formation of long range order. Norem and Stansbury (9) have studied the Ni-Mo-Fe ternary system including alloys near and at the Ni_4Mo composition, but other than hardness they did not conduct mechanical property measurements showing the decrease in ductility due to

ordering. They did however, observe that about 4 wt.% Fe was sufficient to suppress the ordering transformation.

Extensive work on the effect of iron on transformations in Nickel-Molybdenum alloys has been done by Lei and Stansbury (10). They studied the presence of the short range ordered K-state effect (10). Also in agreement with Norem and Stansbury (9), they found that about 4.4 wt.% Fe was sufficient to suppress long range ordering on slow cooling from above the ordering temperature. Decrease in hardness and in the ordering temperature with increasing iron was observed. The Widmanstätten precipitation of the gamma phase in higher iron containing alloys was also reported.

The corrosion problems associated with welded Hastelloy B, led to research by the Cabot Corporation for modifications in the composition of the alloy to improve its performance in the as-welded condition (2). Reducing carbon to prevent carbide precipitation is the the best method, but until recently this was considered impractical for volume production. Varying amounts of niobium, tantalum, vanadium and zirconium were introduced. Although addition of these elements did retard carbide precipitation, even large quantities (V upto 2%) were not sufficient to produce an alloy that could be satisfactorily used in the as-welded condition. As a consequence, work was directed towards developing Hastelloy B2, a low carbon, low iron, low silicon version of Hastelloy B that could be used in the as-welded condition. The composition of this alloy is Mo-26-30 wt.%, Fe-2.9 wt.% max, Cr-1.0 wt.% max, Co-1.0 Wt.% max, C-0.015 wt.% max, Si-0.1 wt.% max and balance Ni.

Alloy B2 has a microstructure similar to that of Alloy B with the exception of large primary carbides. Moreover, the corrosion resistance and mechanical properties are also similar. However, the most conspicuous difference is that Alloy B2 resists grain boundary precipitation of carbides in the heat affected zone, thus making it suitable for most chemical process applications in the as-welded condition. Besides, this alloy has excellent resistance to pitting and stress corrosion cracking.

Alloy B and B2 are essentially similar in composition, except that B2 contains lower iron, carbon and silicon. It is difficult to predict the exact variables responsible for prevention of carbide precipitation at the grain boundaries. Lowering the iron and especially carbon is chiefly responsible. However, decreasing the iron results in loss of ductility by enabling long range ordering to occur under sufficiently slow cooling conditions. The effects of iron and carbon on the phase changes are known (4,5), but those of chromium and silicon, especially chromium are unknown. Moreover, it is unclear as to whether a single element is responsible for prevention of carbide precipitation or a combination of factors are responsible. To date there is no reported work on the effect of chromium in low amounts on transformations in the Nickel-Molybdenum system. In alloy B the iron is 5 wt.% and chromium 1 wt.%. It is possible that this high an iron content has camouflaged any effects of chromium.

There is evidence to show that chromium influences the physical metallurgy of Nickel-Molybdenum alloys (Lei and Stansbury, 10). Resistivity measurements of Hastelloy B2, 1 wt.% max. Cr and Alloy B

the same iron with no chromium show remarkable differences. Thus chromium is definitely affecting the phase transformations in the Nickel-Molybdenum system.

The purpose of this research is to investigate the effect of 0-4 wt.% Cr on transformation characteristics of Nickel-Molybdenum alloys with Nickel:Molybdenum atomic ratio equal to 4:1. The basic research centers around the study of electrical resistivity, hardness measurements, optical and scanning electron microscopy and x-ray diffraction.

CHAPTER II

REVIEW OF LITERATURE

Elementary Concept of Order-Disorder

A large number of solid solutions become ordered at low temperatures. The process of ordering involves a change from a nearly statistically random distribution of atoms among the atom sites to a more regular arrangement, whereby designated sites are occupied predominantly by one kind of atom. In a disordered alloy of composition AB, for instance, any given atom site is occupied indifferently by either A or B atoms, but on ordering, A and B atoms segregate more or less completely to designated sites, so that the resulting arrangement can be described as a lattice of A atoms interpenetrating a lattice of B atoms. This arrangement may occur with little or no deformation and is often referred to as a superlattice (11).

The possibility of ordering was first suggested by Tammann (12) in 1919 and its first evidence was observed by Bain (13) in 1923 and Johansson and Linde (14) in 1925. They observed that an ordered alloy showed extra superlattice lines in x-ray powder diffraction patterns.

The formation of superlattices, frequently described as long range order (LRO), takes place at relatively low temperatures and usually at compositions expressed by a simple formula such as AB or AB_3 or at compositions near these. At all temperatures above a certain critical temperature the usual randomness occurs; when the temperature is lowered through the critical point, order sets in and increases as

the temperature decreases, approaching perfection only at low temperatures. The degree of long range order has been defined by Bragg and Williams (15) as

$$S = (p-r)/(1-r)$$

where, p = the probability that an ordered position is occupied by a wrong atom and r = the probability if completely disordered.

Short range order (SRO), in contrast can occur over certain ranges of composition and at temperatures above the LRO critical point; the structure is neither perfectly random nor perfectly ordered. This concept was introduced by Bethe (16) to obtain quantitative agreement with experiment. It is a local deviation from randomness in successive coordination shells about an atom and atoms of a given kind may or may not be related to long range sublattices. The SRO parameter α_i , has been defined by Cowley (17) as

$$\alpha_i = 1 - (n_i/X_A C_i)$$

where, C_i = the number of atoms in the i -th shell about a given B atom, n_i = the average number of A atoms in the i -th shell and X_A = the atomic fraction of A atoms.

Solid solutions may show SRO without undergoing LRO under any condition. On the other hand, alloys which can LRO, usually show SRO, observable when the LRO is suppressed or when the temperature is above the LRO critical temperature. The short range order, in contrast to the long range order, does not have a critical transition temperature, as shown, for example by Spruiell (18) and Chang (19); SRO exists in the Ni_4Mo composition alloy quenched from 1000°C and probably exists up to the melting point.

An important point is whether ordering is a First Order or Second Order transformation. Phase transformations may be classified in the thermodynamic sense according to the degree of the lowest derivative of the free energy that shows a discontinuity (11).

A transformation is said to be of the first order if the free energies are equal at the transformation temperature but the entropies and volumes of the two phases differ, and of the second if the free energies, the entropies, and the volumes are equal but the heat capacities or compressibilities differ. Besides the second order transformation also requires identical composition of the two phases. Thus a first order transformation appears on a phase diagram as two lines bounding the region where two phases of different compositions coexist in equilibrium, but a second order transformation appears as a single line (11).

The question of whether superlattice changes are first or second order thermodynamic transformations has attracted much discussion. In the early stages of order-disorder theory, there was a tendency to regard almost all superlattices as second order transitions (based on the Bragg-Williams theory, 15), but it has become increasingly evident that many of these changes are first order. Insofar as it is possible to generalize from the limited number of types of transition, it seems that changes from $L2_0$ or DO_3 structures to disordered b.c.c. structures may be second order, and all others are first order. One point in the Bragg-Williams theory which emerges as a consistency with a first order transformation, is the discontinuous drop in the degree of order at T_c , for an A_3B alloy. But for AB alloy there is a gradual decrease (20).

Gibbs (21) pointed out that two types of transformations can occur in physical systems : I) those which are large in degree and small in extent and II) those which are small in degree and large in extent. Christian (20) named the first type as "heterogeneous transformations" and the second type as "homogeneous transformations".

In Type I transformations, the formation of a superlattice is assumed to be a nucleation and growth process, beginning at discrete centers, and continuing outwards until the disordered regions are consumed (20). Thus this transformation is characterized by microscopically distinct regions of fully transformed precipitates in the untransformed parent matrix (22). Since the precipitates are independently nucleated, they will not necessarily be in phase and a substructure of antiphase domains may result (20).

In Type II transformations, the reaction is treated as a continuous process of atomic interchange, proceeding simultaneously in all parts of the assembly, and being analogous to a homogeneous chemical reaction (20). No distinct interface exists between the parent and product phases.

The two mechanisms are related to corresponding descriptions of the nature of changes in thermodynamic parameters, a nucleation and growth reaction being more probable if there is a classical first order change, and a homogeneous reaction being more feasible if there is no discontinuity in volume in passing from the disordered to the ordered phase i.e. a second order change. Although the concept of a homogeneous reaction has some plausibility when applied to an order-disorder change, most experimental evidence suggests that

superlattices have to be nucleated in the disordered lattice, atleast at high temperatures. However, the change in long range order produced by a change of temperature within the region of stability of the superlattice is probably correctly regarded as a homogeneous reaction (20).

Experimental Techniques for Order-Disorder Studies

This section provides a brief review of the relative merits and shortcomings of different experimental techniques.

The scattering pattern of an incident wave or particle beam will reveal the arrangement of atoms on the lattice sites. A random arrangement of atoms will have a different atomic scattering factor and consequently different structure factors than an ordered arrangement. As a result the x-ray diffraction method can reveal such an arrangement as the intensity and scattering angles for this arrangement will be different. Thus an ordered alloy will show besides fundamental lines, extra superlattice lines on the x-ray diffraction pattern. Guthrie and Stansbury (24) studied the beta phase in Ni_4Mo by using x-ray powder technique and confirmed its structure as body centered tetragonal in agreement with Harker's (25) earlier report.

The x-ray powder technique is limited in its ability to study short range order. A special x-ray technique (17,18), using a single crystal sample is required for this. Unfortunately single crystal samples are very difficult to prepare and the experimental process is tedious. However, α_1 , the SRO parameter can be determined by this method. This was accomplished by Spruiell (93) in detail for 10 and 20 at.% Mo in nickel alloys. By using x-ray diffraction methods, from the

width of x-ray reflections, domain sizes together with lattice strains can be calculated and from the integrated intensities of various diffraction lines, the degree of long range order can be determined (26).

Many ordering systems have been studied using various microscopical techniques. For example, Newkirk et al. (27), compared optical microstructures of the CoPt alloy with a precipitation reaction. A better simile was suggested by Rudman (28) who compared the microstructure with a recrystallization process, on a qualitative basis. In recent years optical microscopy has been superseded by transmission electron microscopy and many predicted defects viewed directly. Electron and neutron diffraction methods can be used effectively to get information on both SRO and LRO. These techniques are especially useful when the atomic scattering factors of two kinds of atoms are so close that their positions cannot be distinguished by x-ray diffraction. However, these methods fall short when a relation between degree of ordering, temperature and time are desired on a continuous basis. Field ion microscopy has also been used in recent years for studying finer details of the ordering process (55).

The relation between ordering, temperature and time can also be studied by calorimetry i.e. by measuring the specific heat. At temperatures below the critical temperature, changes in the degree of order S on heating to make a specific heat measurement, atoms jumping from right to wrong positions will require an increase in energy reflected by an increase in specific heat. Quantitative calorimetry yields specific heat which can be related to the degree of order but this does not help in understanding the atomic arrangement.

The changes in ordering as a function of temperature and time can also be studied by measuring the variation in electrical resistivity during heating, cooling or isothermal holding. The electrical resistivity of metals can be attributed to the degree of scattering of electrons. In a metal above 0°K, scattering occurs because the lattice of atoms is in a state of continual vibration. Since the amplitude of vibration and consequently electron scattering increases with increasing temperature, electrical resistivity increases with temperature. In disordered alloys the random atomic arrangement will result in a higher resistivity than that of ordered alloys. This appears always to be true for LRO; however, there may be states of SRO for which the resistivity is higher than that of a random solid solution.

The measurement of electrical resistivity lends itself quite gracefully for studying order-disorder transformations. Large differences in resistivity are usually observed between LRO and SRO or random states and measurable differences may exist within states of SRO and perhaps within LRO. Moreover, the precision of the measurement is usually very high and the amount of metal required for specimens is small. Techniques are available to record the resistivity as a function of temperature and time for different heating and cooling rates and to accomplish such measurements on a number of alloys within a short time. Also it is possible to indirectly relate the resistivity to the degree of long range order.

Mechanical properties such as hardness, tensile strength and ductility change with ordering. These properties are useful for

studying the kinetics of ordering and are also important from an industrial standpoint. However, these tests with the exception of hardness, are destructive in nature and hence a large quantity of material is required. The usual practice is to perform such tests on samples whose transformation behaviors have been pre-determined by other measurements such as electrical resistivity.

The Nickel-Molybdenum System

Nickel-Molybdenum alloys have been studied extensively in the past, with four complete phase diagrams being published. An early extensive report was published by Grube and Schlect (29), who reported the previous work of Baar (30), Dreibholz (31), and Koster and Schmidt (32) along with their own work. Subsequent reports were based on a early research by Ellinger (33), a diagram by Hansen (34) based on analysis of existing data and a more recent diagram by Casselton and Hume-Rothery (35). In the binary system there are three ordered phases, commonly designated by β , γ , and δ or respectively ordered Ni_4Mo , Ni_3Mo and NiMo . Guthrie and Stansbury (24) investigated the nickel-rich portion of this system using x-ray diffraction and optical metallography and proposed the partial phase diagram shown in Figure II-1. A description of the phases occurring in this system is presented in the following.

Short range ordered α phase. The alpha phase is a nickel-rich terminal solid solution with a face centered cubic structure having a lattice expansion of 0.033 nm per wt.% Mo (24). The lattice parameter of the Ni_4Mo alloy is 3.608 Å. This alpha phase manifests a temperature-dependent SRO, similar to many nickel base solid solution

Ni—Mo PHASE DIAGRAM

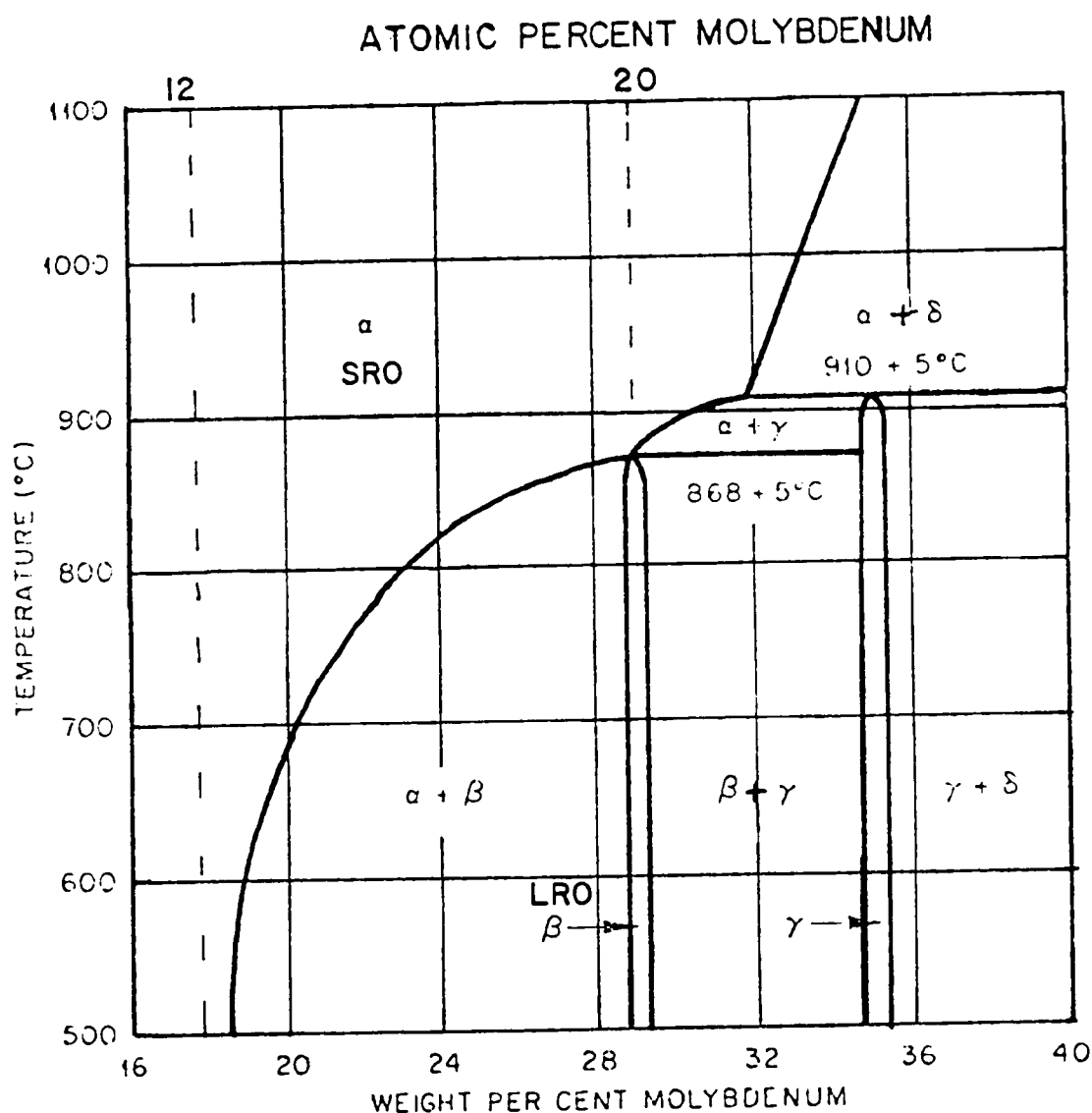


Figure II-1. A portion of the nickel-molybdenum constitution diagram.

Source: P. V. Guthrie and E. E. Stansbury, "X-Ray and Metallographic Study of the Nickel-Rich Alloys of the Nickel-Molybdenum System" II, ORNL-3078, Oak Ridge National Laboratory, (1961).

systems such as Nickel-Chromium, Nickel-Vanadium and Nickel-Tungsten. This phase also exhibits a resistivity anomaly known as the "K-State".

The K-State was first proposed by Thomas (36), who studied alloys of Nickel-Chromium, Nickel-Copper, Nickel-Aluminum etc. Upon annealing previously cold worked specimens he found an anomalous increase in resistivity over a certain temperature range. Also specimens which had been well annealed to develop the K-State, showed a decrease in resistivity on subsequent cold working. These effects are opposite to those found in normal alloys.

While in most systems the K-State is characterized by an increase in resistivity, there are systems in which the resistivity decreases on annealing (Damask,37,38). Besides resistivity, other properties such as elastic modulus, tensile strength (39), hardness (40), thermal expansion (41), and specific heat (42), have been shown to behave anomalously with the formation of a K-State.

The K-State has been investigated by resistivity measurements by Baer (43), Lampe (44) and Chang (19). They observed changes in resistivity near 500°C. These changes were very much heating rate dependent; higher the heating rate lower was the resistivity (19). Stansbury, Brooks and Arledge(42) in calorimetric experiments on a Ni-15 at.% Mo alloy, found anomalous behavior in specific heat at 500°C. Lefevre et al. (45) investigated Nickel-Molybdenum alloys containing 10.5 and 14 at.% Mo and on the basis of x-ray and resistivity measurements concluded that the K-State was dependent on the degree of SRO in water quenched alloys. Lei (10) found that resistivity in Ni_4Mo alloys, decreases with an increase in cold work.

Also alloys containing iron had lower values of resistivity than the binary Ni_4Mo .

The explanation of the K-State phenomenon vary and depend on the particular alloy. Several theories have been advanced to explain the decreased resistivity with cold work on the basis of changes in the electronic configuration of the alloy as a result of lattice distortions (46,47). It is generally agreed (10,19,45), that in Nickel-Molybdenum alloys the decrease in resistivity with cold work is due to a decrease in SRO in cold worked alloys. Also the further decrease in resistivity in non-LRO alloys of 4Ni: Mo ratio but containing iron was explained by Lei (10) to be due to decreased SRO existing in alloys containing iron.

Although it is widely agreed that SRO is responsible for the K-State, it is not clear how this might increase resistivity. Since most of the K-State alloys contain at least one transition element, significance has been frequently attached to the presence of an unfilled d-shell (36,48). Others have explained the increase in resistivity by picturing the SRO as microdomains (49) or at least non-random atom configurations providing more effective electron scattering than for the random solid solution. These explanations however, are complicated by the fact that SRO increases resistivity (K-State) in some systems and decreases resistivity in others (37,38).

Considerable work has been done in the past few years to understand the nature of SRO in Nickel-Molybdenum alloys using x-ray diffraction (18,51), electron microscopy (52-60), and field-ion microscopy (55,61). Spruiell and Stansbury (18) were the first to

study local atomic arrangements in the SRO state by measuring the diffuse intensity in the $h_1, h_2, 0$ plane of reciprocal space for single crystals of nickel-rich alloys containing 10.7 and 20 at.% Mo after varied thermal history. They interpreted the SRO state as being built up of small regions (microdomains) having the long range ordered structure. Ruedl (52) confirmed this microdomain concept by means of dark field electron microscopy. Okamoto et al. (55) observed this $(1 \frac{1}{2} 0)$ type of SRO in both quenched Ni_4Mo and Ni_3Mo .

On the other hand, Clapp and Moss (62), based on a statistical thermodynamic model explained the $(1 \frac{1}{2} 0)$ SRO diffuse maxima without any form of LRO or microdomains. Chevalier and Stobbs corroborated this model on the basis of TEM observations (58,60).

Thus it is clear that the nature of SRO in Nickel-Molybdenum alloys is shrouded in controversy and additional research is required to resolve these differences.

β phase-- Ni_4Mo . The crystal structure of the beta phase was first determined by Harker (25) to be body centered tetragonal with cell dimensions, $a = 5.731 \text{ \AA}$, $c = 3.571 \text{ \AA}$ and $c/a = 0.623$. Subsequent researchers have confirmed this (24). Guthrie and Stansbury (24) showed that the beta phase could be derived from the alpha phase by the equivalence of ordering of molybdenum atoms and allowing a slight shift in interplanar spacing. This structural model is shown in Figure II-2.

On a (001) plane of nickel atoms, molybdenum atoms on successive [110] rows of atoms are arranged such that they are at the greatest distance from molybdenum atoms on a previous [110] row. When a second

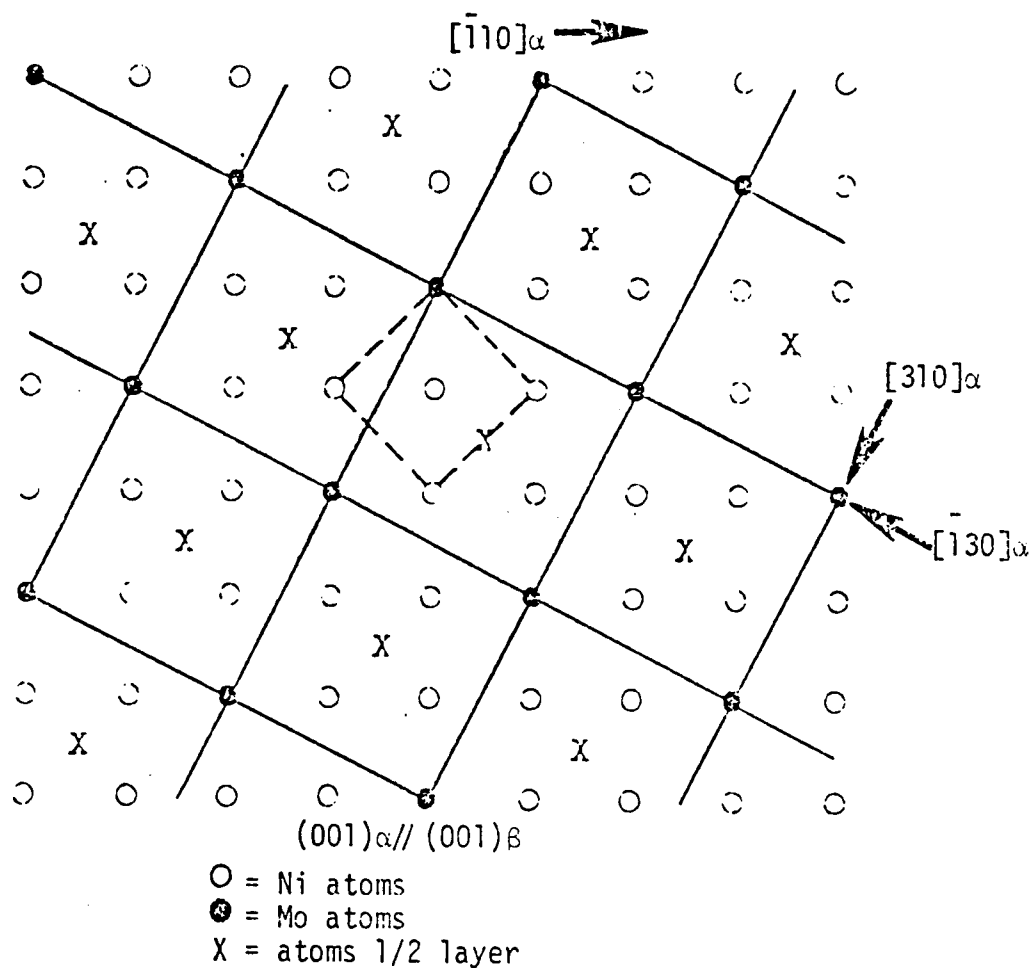


Figure II-2. Schematic representation of β -superlattice and its orientation with f.c.c. α -lattice. Dotted lines outline f.c.c. unit cell.

Source: T. S. Lei, "The Effect of 0-8 Wt.% Iron on Transformations of Alpha Phase Ni-Mo-Fe Alloys with Ni: Mo Ratio Equal to 4:1", Ph.D. Dissertation, The University of Tennessee, (1979).

(001) of atoms is arranged on top of this, the molybdenum atoms occupy positions marked with an X in Figure II-2. The third layer is arranged exactly as the first one and so on. This ordered structure contains eight nickel and two molybdenum atoms. Guthrie and Stansbury (24) in analysing their x-ray diffraction data felt that the 20 at.% Mo alloy on aging below T_c , first transformed to a face centered tetragonal structure with $c/a = 0.986$ and subsequently to the body centered tetragonal structure.

There are thirty possible ways for beta to nucleate from a single alpha lattice (24,25). The c axis of the tetragonal cell can be any one of the three original cube axes of the f.c.c. cell and the tetragonal a axis can be inclined positively or negatively to the original cell (Figure II-3). Finally, each one of the first five atoms in the [110] row could serve equally well as the origin and hence there are $3 \times 2 \times 5 = 30$ ways of nucleating beta. Of these, however, only six produce different orientations of beta, each having five starting positions. Each of these beta variants can result in a uniquely oriented LRO domain.

γ phase-- Ni_3Mo . Saito and Beck (63) reported that the gamma phase is an orthorhombic unit cell containing six nickel and two molybdenum atoms. The unit cell dimensions are: $a = 5.064 \text{ \AA}$, $b = 4.448 \text{ \AA}$ and $c = 4.224 \text{ \AA}$. The crystal structure of Ni_3Mo is shown in Figure II-4. The relation between the superlattice unit cell and the basic f.c.c. unit cell is also shown. If the orthorhombic distortion (slight relative to the corresponding orthohexagonal cell) is disregarded, the structure may be described in terms of a close packed hexagonal cell, stacked in the sequence abab.... (63,64).

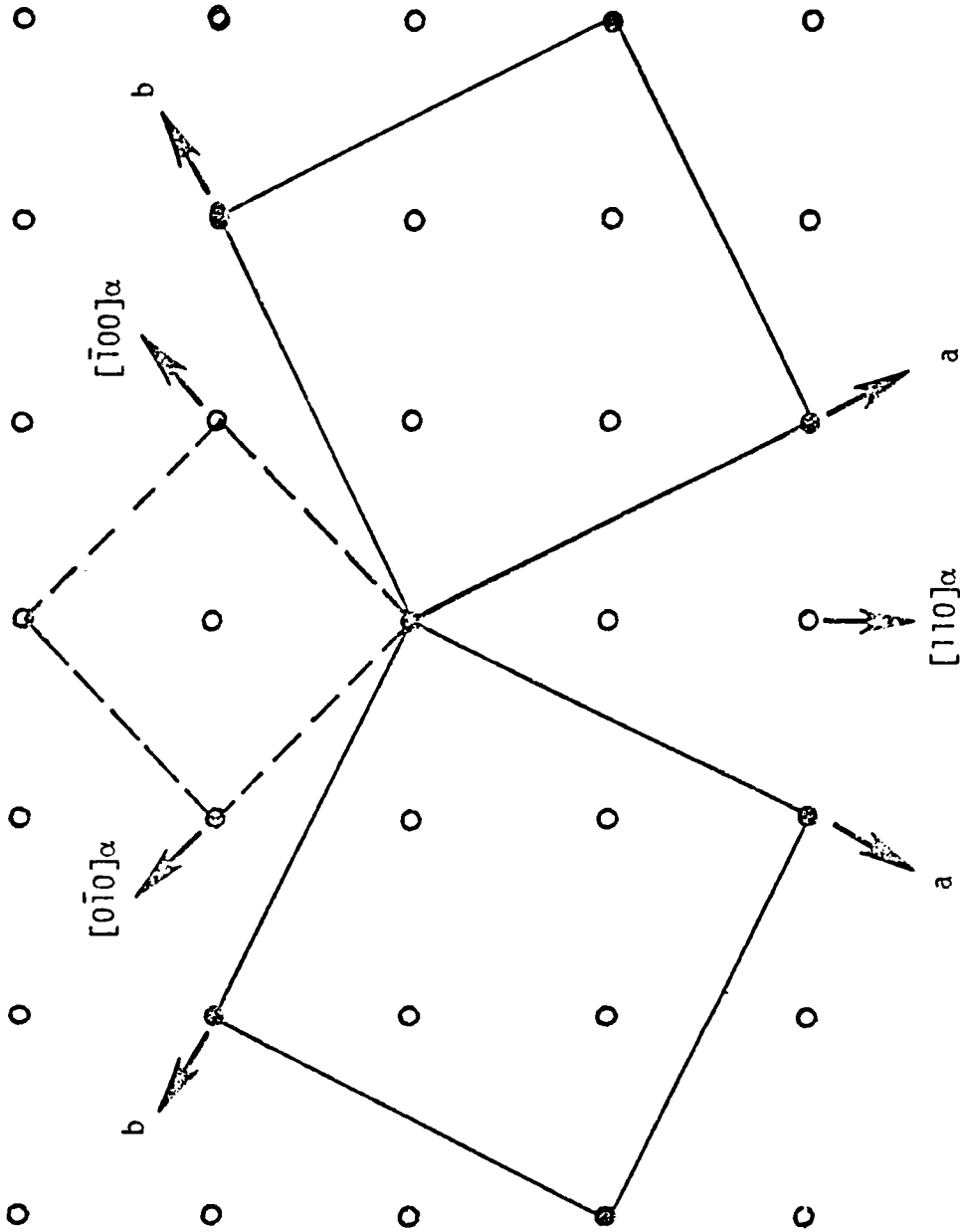


Figure II-3. Two anti-parallel twins of ordered Ni_4Mo related to f.c.c. matrix. $[001]_\beta // [001]_\alpha$.

Source: T. S. Lei, "The Effect of 0-8 Wt.% Iron on Transformations of Alpha Phase Ni-Mo-Fe Alloys With Ni:Mo Equal to 4:1", Ph.D. Dissertation, The University of Tennessee, (1979).

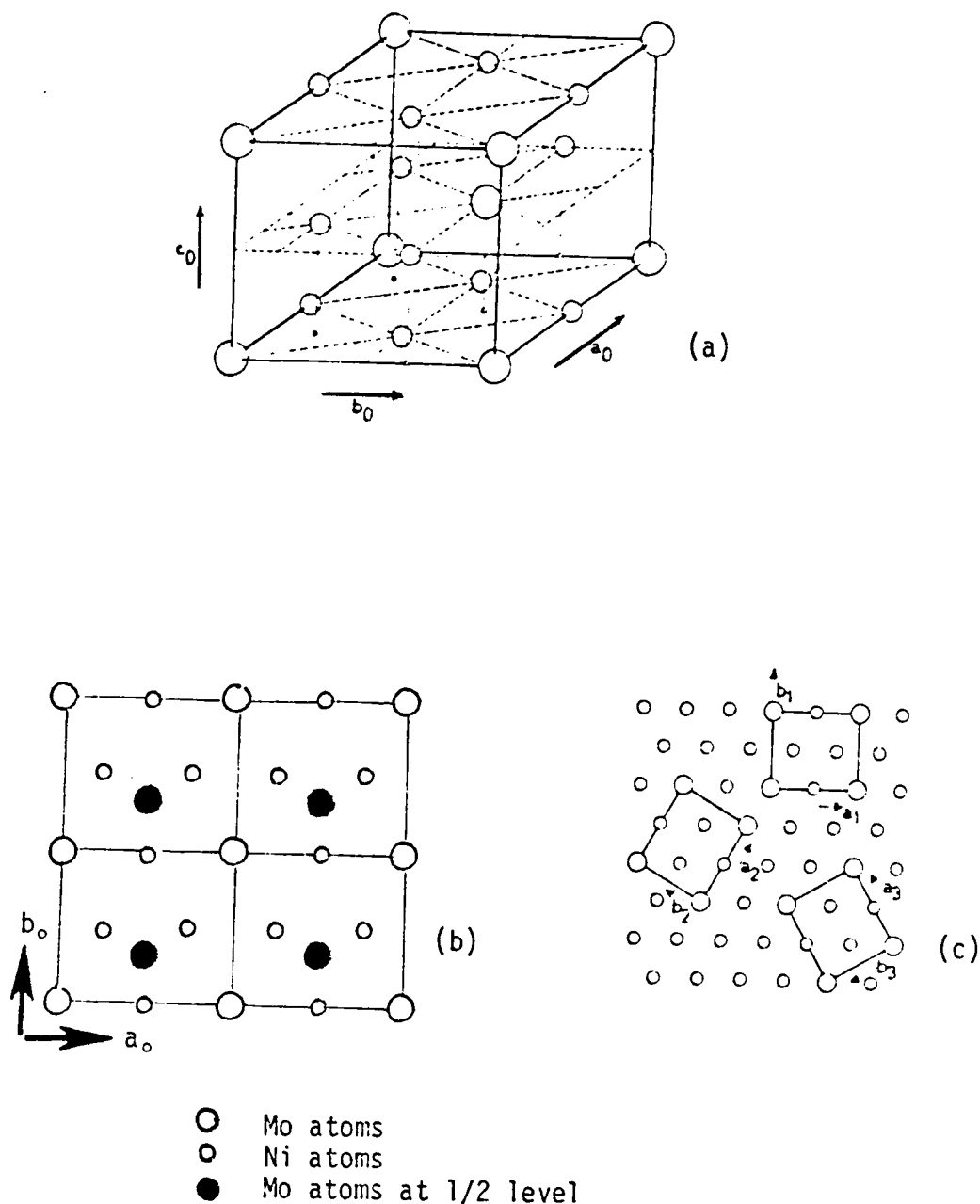


Figure II-4. Crystal structure of LRO Ni_3Mo .

a) Unit cell structure of Ni_3Mo . b) Close-packed ordered layer.
c) Twin relationship between different domains.

Source: T. S. Lei, "The Effect of 0-8 Wt.% Iron on Transformations of Alpha Phase Ni-Mo-Fe Alloys With Ni:Mo Equal to 4:1", Ph.D. Dissertation, The University of Tennessee, (1979).

The structure can be further built in the hexagonal matrix in three different orientations which differ roughly by 120° . The ordered structure can therefore adopt 21 (3×7) different positions within the hexagonal matrix. However, there are twelve possible orientations for the gamma superlattice with respect to the f.c.c. alpha phase, since the c face of the gamma can assume three orientations and the basal plane of the hexagonal structure can be any one of the four {111} planes of the f.c.c. lattice. Ruedl and Amelinckx (64) showed through TEM studies that the [111] direction of the f.c.c. coincides with the [001] direction of the orthorhombic ordered cell, and the close packed directions in these planes are nearly parallel, suggesting that the transition to Ni_3Mo is a shear transformation along close packed planes.

The transformation of alpha phase to gamma phase is quite complicated. It has been shown that quenched Ni_3Mo also displays a SRO similar to that in Ni_4Mo (55). In the transformation of alpha to gamma phase, Saburi et al. (53) first reported the formation of metastable Ni_2Mo in the initial stages of ordering.

The metastable Ni_2Mo phase has been described as an isotype of ordered Pt_2Mo with a body centered orthorhombic structure. The exact lattice parameters have not been determined, but can be derived from the basic f.c.c. unit cell because it can be considered as a direct superlattice (65-67). These are : $a = \sqrt{2} a_{\text{fcc}}/2$, $b = 3/2 a_{\text{fcc}}/2$ and $c = a_{\text{fcc}}$.

The transformation of alpha to gamma phase was said by Saburi et al. (53) to occur in four stages: a) decomposition of alpha to beta

and Ni_2Mo , b) growth of beta domains and coagulation of Ni_2Mo along beta boundaries, c) nucleation of gamma at grain boundaries and d) subsequent growth of gamma to consume previous beta + Ni_2Mo . Subsequent work has verified this (65). Van Tendeloo et al. recently reported (68), the presence of a new metastable intermediate phase having a DO_{22} structure during the early stages of ordering of Ni_3Mo . The phase was observed only under certain conditions and was generated immediately from the SRO state. Subsequently Ni_4Mo and Ni_2Mo are formed and then ordered Ni_3Mo .

δ phase-- NiMo . The structure of delta phase was determined by Shoemaker and Shoemaker (69) as being orthorhombic with a tetragonal symmetry. Its lattice dimensions are $a = b = 9.108 \text{ \AA}$, $c = 8.852 \text{ \AA}$. Very little work has been done on this phase. Guthrie and Stansbury (24) showed that near the alpha-delta phase boundary, the delta develops as a precipitation outlining the original alpha grains. Van Tendeloo et al. (70) have studied this alloy using electron diffraction and electron microscopy and observed a remarkable structure consisting of antiphase boundaries, inversion boundaries and permutation twins.

The Ni-Mo-Fe System

Norem and Stansbury (9) investigated the phase relationships of the ternary Ni-Mo-Fe system. Their proposed isothermal section for 700°C is shown in Figure II-5 along with letters identifying alloys used in the investigation. Composition heat treatment temperatures and maximum times of heat treatment of alloys near Ni_4Mo (beta phase) composition are given in Table II-1.

TABLE II-1

Composition, Temperature and Maximum Times of Heat Treatment of Alloys near the Ni_4Mo Composition in the Research of Norem and Stansbury.

Alloy	Composition, wt.%			Maximum Heat Treatment Time, hrs				
	Ni	Mo	Fe	700°C	800°C	860°C	890°C	950°C
A	70.11	29.89	0	3400	275	3400	1000	1000
B	62.98	33.00	4.02	3400	275	3400	1000	1000
F	71.39	28.61	0	3400	275	3400	1000	1000
G	69.57	26.44	3.99	3400	275	3400	1000	1000
P	78.99	21.01	0	3400	275	3400	1000	1000
Q	73.94	19.03	7.03	3400	275	3400	1000	1000

Source: W. E. Norem and E. E. Stansbury, "An Investigation of Nickel-Rich Alloys Containing Molybdenum and Iron, Report to Union Carbide, Oak Ridge National Laboratory, Oak Ridge, Tennessee, (1963).

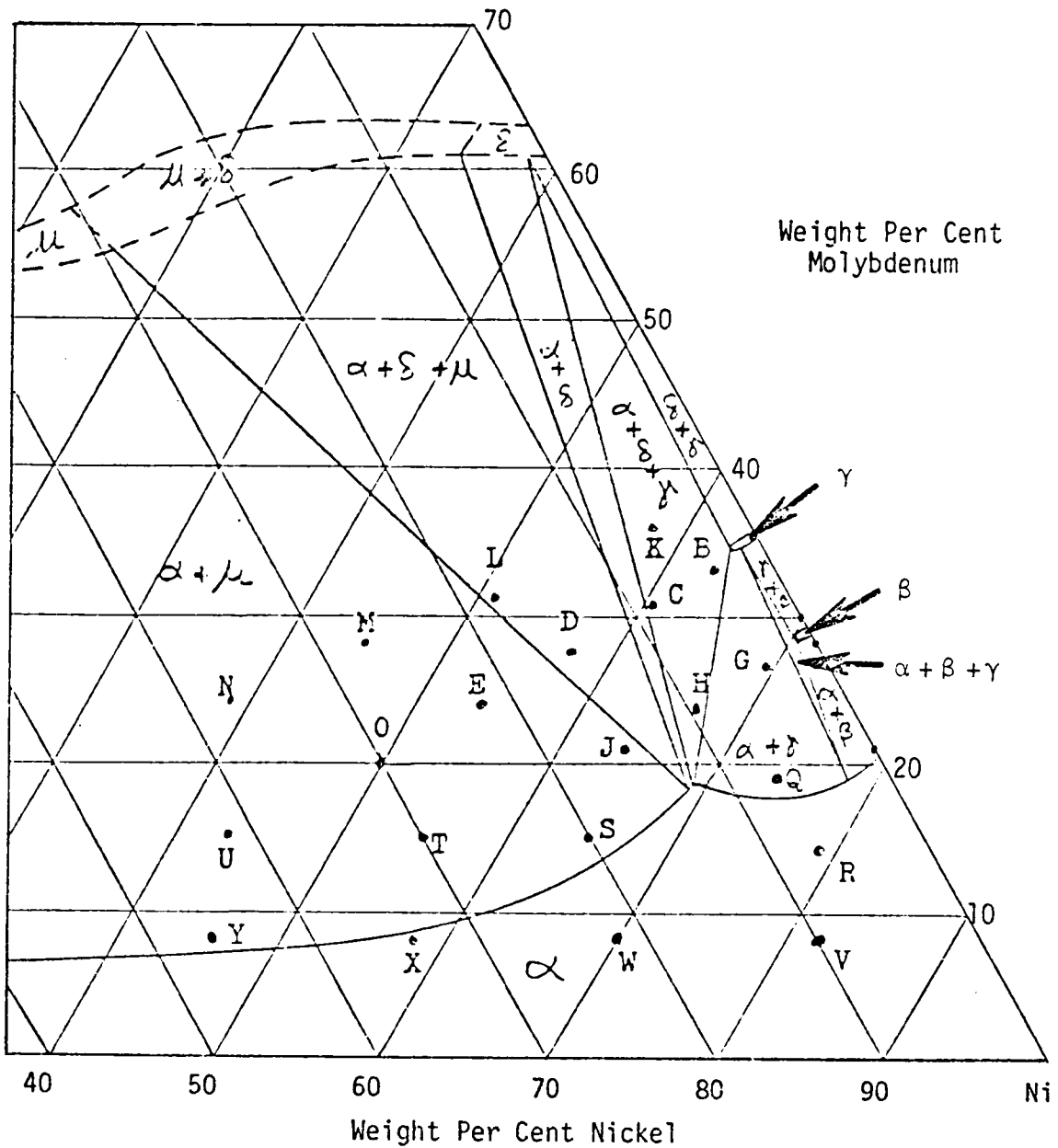


Figure II-5. Proposed diagram for the Ni-Mo-Fe system at 700°C.

Source: W. E. Norem and E. E. Stansbury, "An Investigation of Nickel-Rich Alloys Containing Molybdenum and Iron", Report to Union Carbide, Oak Ridge National Laboratory, Oak Ridge, Tennessee, (1963).

A schematic phase diagram resulting from this work (9) constructed by Lei (10), is shown in Figure II-6. It should be remembered that these ternary sections are not necessarily identical to the equilibrium phase diagram for this system. There are significant differences between alloys of the same composition treated for 1000 hours and 3400 hours and hence there is no reason to assume that the 3400 hour sample represents the equilibrium state. However, there are occasions when an alloy after being held for a sufficiently long time at a particular temperature may show indications of having attained equilibrium. In such cases verification of equilibrium can be done by using scanning and transmission electron microscopy to determine the local identity and composition of phases.

It was found in this investigation (9) that addition of small amounts of iron rapidly suppresses the formation of the beta phase. In fact Alloy G, containing 4 wt.% Fe showed no beta phase at any temperature. Earlier work done by Stansbury (71) at the University of Tennessee indicated that the solubility of iron in Ni_4Mo is about 3 wt.% at 700°C, 2.5 wt.% at 800°C and less than 2.5 wt.% at 850°C. Lei (10) in slight contrast to this, reported the solubility of iron in the beta phase as 4.5 wt.%, 3.2 wt.%, 1.3 wt.% and 0.3 wt.% at 600, 700, 800 and 850°C respectively.

A two phase alpha and gamma field was found to exist between 868 and 910°C. This field varies only slightly with temperature. At temperatures below 868°C, the critical LRO temperature for beta phase, a three phase $\alpha + \beta + \gamma$ field exists. In alloys containing higher amounts of iron a three phase $\alpha + \gamma + \delta$ was found to exist.

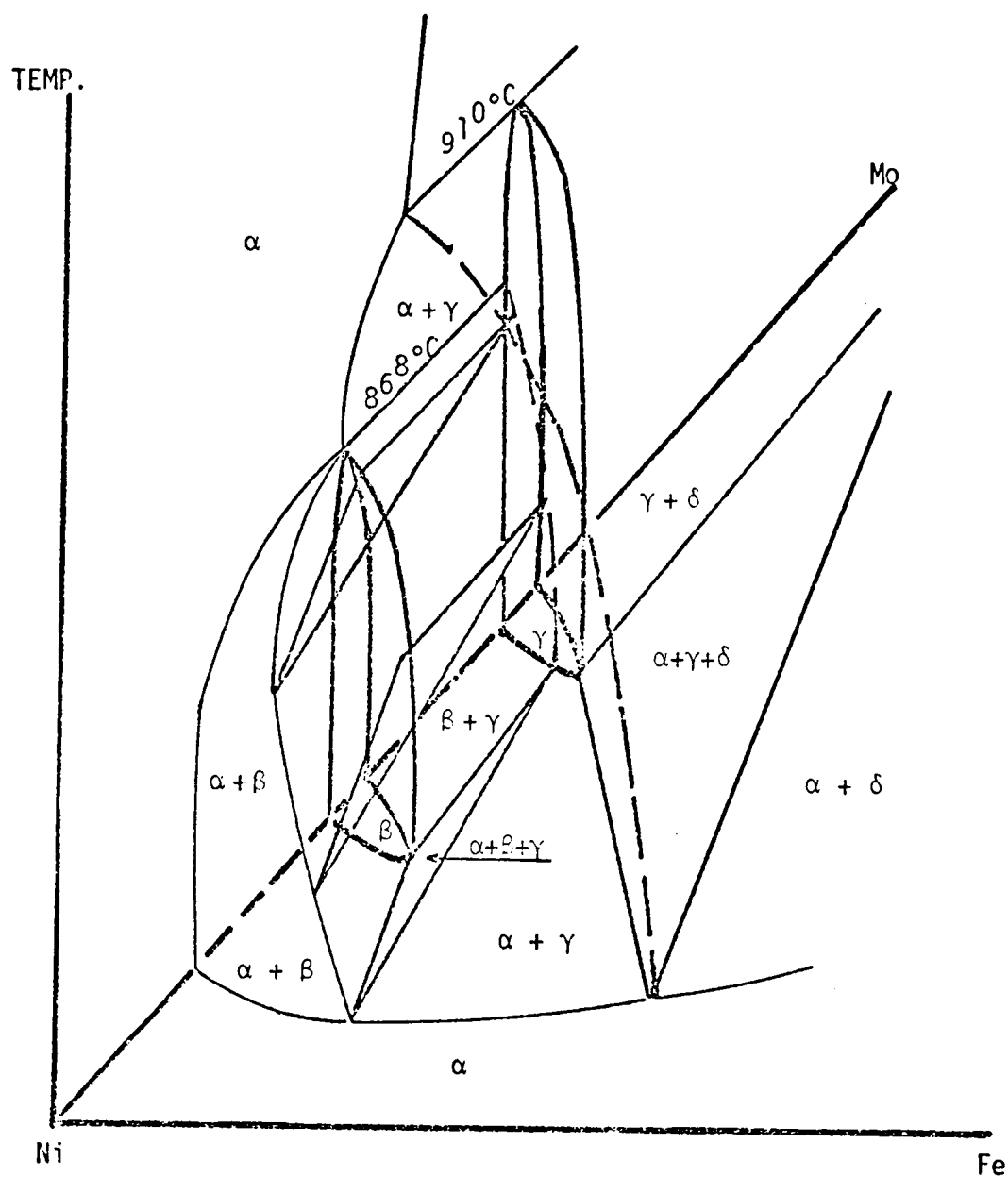


Figure II-6. Schematic drawing of Ni-Mo-Fe phase diagram around the section of the β -phase.

Source: T. S. Lei, "The Effect of 0-8 Wt.% Iron on Transformations of Alpha Phase Ni-Mo-Fe Alloys With Ni:Mo Ratio Equal to 4:1", Ph.D. Dissertation, The University of Tennessee, (1979).

Kinetics of Ordering.

The parameters S and α_j describe the long range order and short range order at equilibrium for each temperature. The values of these parameters are not established instantaneously, but are time dependent in response to the diffusive rearrangement of atoms on lattice sites. This time for attaining equilibrium is system dependent and relates to the usual kinetic factors of the the actual temperature and difference between the actual and the critical temperatures. For example, beta brass is completely is completely ordered after cooling from above the critical temperature, while Cu_3Au must be held for hours below the critical temperature in order to attain equilibrium.

The status of kinetics of ordering has been recently reviewed by Yamuchi and DeFontaine (72). They have pointed out that difficulties exist in evolving a kinetic model because of the inherent nature of ordering. In their words, "the subject presents great conceptual and mathematical difficulties so that a theoretical treatment that is both general and tractable is out of the question". Especially there is difficulty in describing the state of order of a system.

As early as 1936, Sykes and Evans (73) studied the kinetics of ordering in Cu_3Au and concluded that the process of ordering was complex and took place by nucleation and growth. In the simplest treatment of kinetics three parameters are required to describe the state of the alloy, 1) the fraction of alloy that is ordered, 2) the domain size of the ordered material and 3) the degree of long range order within the domains (77). To formulate a quantitative theory in terms of a kinetic approach has proved very difficult for a nucleation

and growth model because experimentally only one property, namely, a function of all the above is usually measured. Most of the earlier theories (74-76), notably that of Dienes (75), treated ordering as a homogeneous chemical reaction and derived equations for the homogeneous increase in order.

From the results of measured quantities, in almost every ordering system, little doubt remains that the processes involved, regardless of the operative mechanisms, are diffusion controlled. The diffusion coefficients are lower in ordered than in disordered alloys. But since ordering has to be preserved in a superstructure, the normal mechanism of nearest neighbour exchange with vacancies is inapplicable because it is energetically unfavorable (26). Nevertheless Sato and Kikuchi (78) recently adopted a path probability technique and considered the kinetics of the order relaxation process to occur via a vacancy mechanism in a manner parallel to atomic diffusion.

In recent years theoretical attempts have been made to draw an analogy between certain ordered structures and spinodal decomposition (79,80). Ling and Starke (80) used a novel approach by assuming a periodic composition fluctuation in the disordered state prior to subsequent ordering. On applying Cahn's (79), earlier established spinodal decomposition relationships to this, they obtained excellent fit of their theory with experimental results for Ni_4Mo , Mg_3Cd , CuAu and Cu_3Au .

X-Ray diffraction measurements have been largely used to determine the variation of the degree of order with time. But this is possible only at room temperatures. Resistivity measurements are

useful for studying the kinetics on a continuous basis at elevated temperatures and attempts have been made to relate the resistivity to the degree of order. Muto (81) investigated this theoretically and proposed an equation of the form:

$$\rho = \rho' + \rho''S + \rho'''S$$

Using the relations $\rho = \rho_{dis}$ at $S=0$ and $\rho = \rho_{ord}$ at $S=1$ and further assuming $(d\rho/dS)_{S=0} = 0$, he arrived at

$$(\rho - \rho_{ord})/(\rho_{dis} - \rho_{ord}) = 1 - S^2$$

Dienes (82) performed a purely phenomenological analysis of isothermal resistivity in Cu_3Au and obtained an activation energy of 29 Kcal. Further kinetic analysis was done by transforming raw resistivity data into isothermal order parameter-time curves using the above relation, and obtained an activation energy of 28.5 Kcal thus showing excellent fit.

Continuous heating and cooling kinetics in Ni_4Mo and Ni-Mo-Fe alloys. Lei (10) studied extensively the ordering kinetics in Ni_4Mo and $Ni_4Mo + 0-8$ wt.% Fe alloys using electrical resistivity measurements. His results of resistivity measurements on continuous heating and cooling of Ni_4Mo and an alloy containing 4.41 wt.% Fe alloy are shown in Figures II-7 and II-8 respectively. The symbols H, C and I in the figures indicate heating, cooling and isothermal runs. The numbers 1, 2 etc. indicate sequence of runs.

Starting from a 75% reduction in area cold swaged state (curve 1H), it can be seen from Figure II-7 that the resistivity increases gradually with an increase in temperature. The curve is linear to about 300°C after which there is an additional increase in resistivity

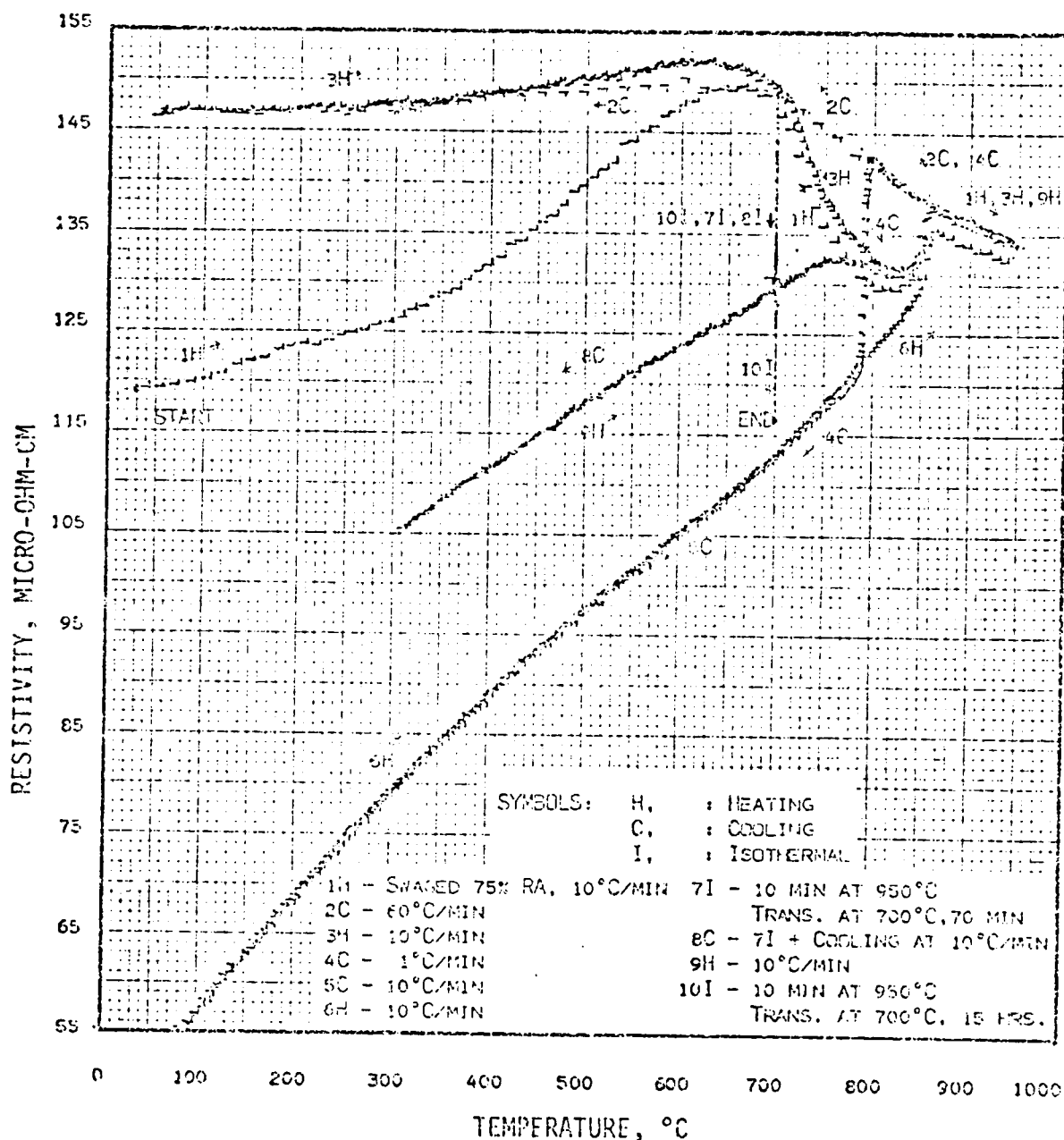


Figure II-7. Resistivity-temperature curves for Ni_4Mo composition alloy following indicated sequence of heating, cooling and isothermal transformation. Initial condition - water quenched from 950°C and swaged 75% RA.

Source: T. S. Lei, "The Effect of 0-8 Wt.% Iron on Transformations of Alpha Phase Ni-Mo-Fe Alloys With Ni:Mo Ratio Equal to 4:1", Ph.D. Dissertation, The University of Tennessee, (1979).

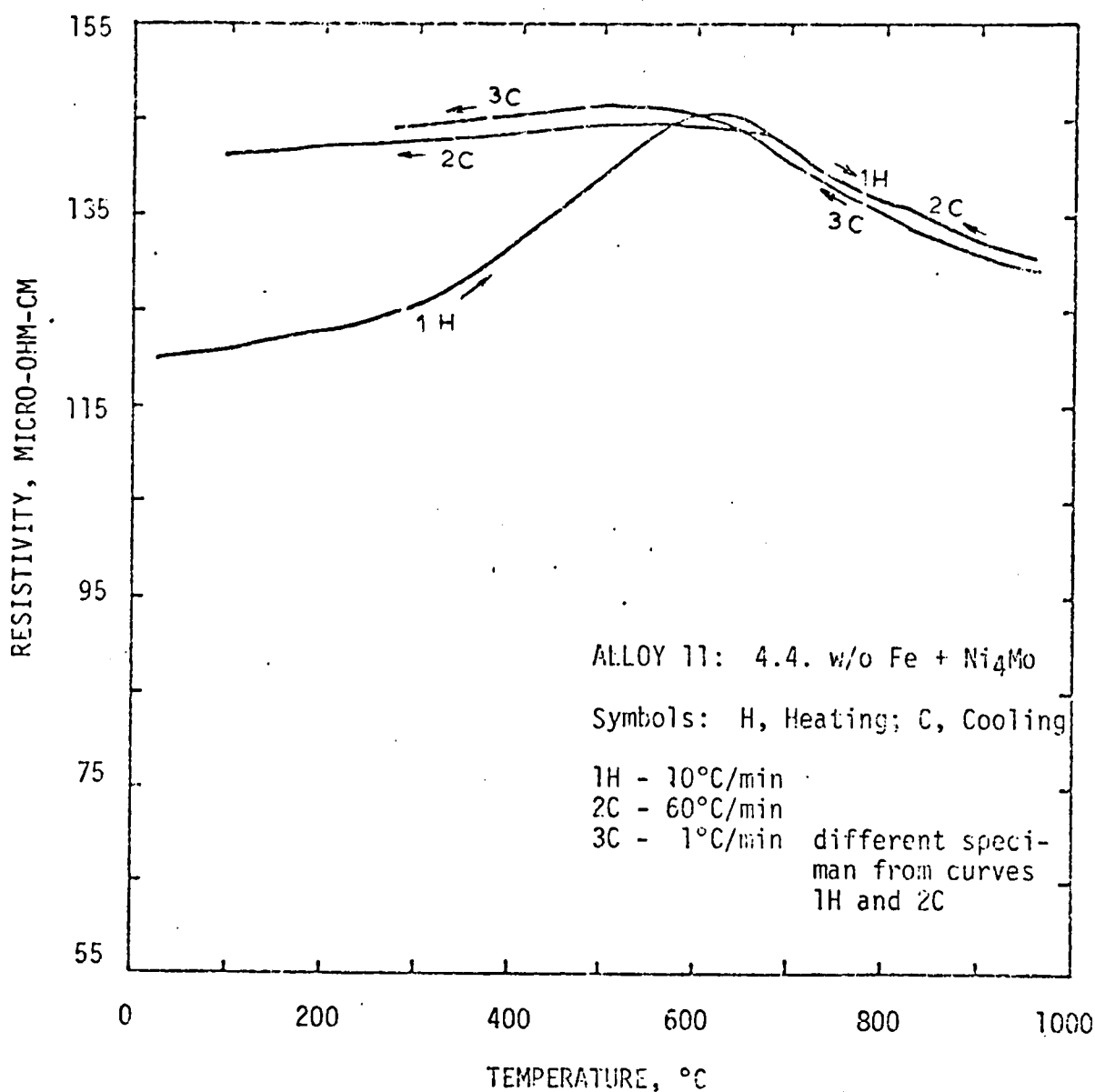


Figure II-8. Resistivity-temperature curves for Alloy 11 following indicated sequence of heating and cooling transformation. Initial condition - W.Q. form 950°C and swaged 55% RA.

Source: T. S. Lei, "The Effect of 0-8 Wt.% Iron on Transformations of Alpha Phase Ni-Mo-Fe Alloys With Ni:Mo Ratio Equal to 4:1", Ph.D. Dissertation, The University of Tennessee, (1979).

near 650°C due to the progressive return of SRO which had been destroyed by prior cold work. Above 650°C, there is a rapid increase in resistivity due to the onset of LRO in this temperature range. Near 850°C, LRO resistivity values attain equilibrium and at 868°C the ordering temperature, the resistivity increases sharply due to rapid loss of long range order. The decrease in resistivity above 868°C is attributed to SRO and SRO decreases with increasing temperature. This confirms the fact that the decrease in SRO is more effective in decreasing the resistivity than the increase in temperature is increasing it. These observations concur well with those of Chang (19).

Rapid cooling (curve 2C, 60°C/min, Figure II-7) results in higher resistivity values as the SRO state is retained below 868°C. Slow cooling (curve 4C, 1°C/min, Figure II-7) leads to spontaneous change to the LRO state in the temperature range 800-775°C, the resistivity changing from 143 to 120 micro ohm cm.

The resistivity-temperature curves of Ni-Mo-Fe alloys containing low amounts of iron show the same trends as the binary Ni_4Mo . However, from Table II-2 it can be seen that the resistivity values for alloys containing iron are higher than the binary Ni_4Mo . Besides increase in iron decreases the ordering temperature. From Figure II-8, Lei (10) concluded that about 4.41 wt.% Fe in Ni_4Mo was sufficient to suppress the ordering for alloys cooled at rates faster than 1°C/min.

It is significant to compare the resistivity-temperature characteristics of Lei's (10) Alloy 10 and Hastelloy B2. These alloys are comparable in iron contents, namely, 0.78 and 0.82 wt.% Fe

Table II-2. Selected resistivity values characterizing Ni-Mo-Fe alloys*.

Alloy → → Conditions	3 Ni ₄ Mo	19 Ni ₄ Mo	18 .35% Fe	13 .48% Fe	14 .74% Fe	15 .69% Fe	16 .73% Fe	10 .78% Fe
Cold reduced 54% at 25°C	119.2	120.2	121.3	121.2	120.7	122.4	118.6	123
Cooled, 1°C/min at 25°C	47.6	45.89	50.41	55.5	59.67	62.81	69.33	67
Cooled, 60°C/min at 25°C	146.5	143.5	141.2	143.5	141.0	144.0	138.4	146
W. Q. from 350°C at 25°C	138.7	138.4	138.1	137.9	137.6	138.8	135.5	137.7
Resistivity at 950°C at 950°C	133.	132.1	129.7	132.3	129.5	132.5	130.3	133
Temperature of								
TC	870°C	868°C	861°C	850°C	848°C	850°C	840°C	840°C
TS	802°C	795°C	790°C	786°C	777°C	778°C	767°C	760°C

Table II-2 (continued)

Alloy → + + Condition	7 1.94% Fe	8 3.04% Fe	11 4.41% Fe	12 6.35% Fe	17 8.43% Fe	B2 Hastelloy	Average
Cold reduced 54% at 25°C	120.2	120	119.9	119.0	116.8	120	119.6 ± 2.4 8.5
Cooled, 1°C/min at 25°C	77.73	93	141.6	140.5	138.5	130	
Cooled, 60°C/min at 25°C	143.5	143	140.6	-	-	148	
W. Q. from 950°C at 25°C	137.1	135.2	135.4	133.2	130.9	138	
Resistivity at 950°C at 950°C	130.3	129	130.5	129.2	129.10	133	130.4 ± 2.6 7.7
Temperature of							
TC	841°C	815°C					
TS	737°C						
Maximum ρ			620°C	610°C	600°C	600°C	

*Resistivity in micro ohm cm.

Source: T. S. Lei, "The Effect of 0-8 Wt.% Iron on Transformations of Alpha Phase Ni-Mo-Fe Alloys With Ni:Mo Ratio Equal to 4:1", Ph.D. Dissertation, The University of Tennessee, (1979).

respectively; while Alloy 10 contains less than 0.1 wt.% Cr, Hastelloy B2 contains 0.97 wt.% Cr. The results of the resistivity-temperature curves for these two alloys is shown in Figures II-9 and II-10. Alloy 10 on slow cooling ($1^{\circ}\text{C}/\text{min}$) shows a resistivity value of 68 micro ohm cm at room temperature, while Hastelloy B2 for the same cooling rate has a resistivity value of 128 micro ohm cm - a difference of nearly 200%. It is thus evident that chromium is responsible for this difference. The presence of chromium in Hastelloy B2 has increased the resistivity either by inducing an incomplete transformation to the LR0 state due to kinetic or thermodynamic factors or by further decreasing the degree of LR0 i.e the value of the parameter S. It is difficult to say conclusively which factor is responsible or whether both factors together contribute towards increasing the resistivity.

Very little microstructural work has been done on continuously cooled Ni_4Mo . Irani et al. (91) reported a foam structure in continuously cooled samples. They also observed that an increase in cooling rate from 3 to $5^{\circ}\text{C}/\text{min}$, resulted in a decrease in average domain size and also that the domains oriented themselves along certain crystallographic directions.

Isothermal kinetics in Ni_4Mo . Based on isothermal resistivity measurements Lei (10) reported that the TTT curve as shown in Figure II-11 of Ni_4Mo , is "C-Shaped", with the nose occurring at 775°C and 20 seconds. Snyder and Brooks (8) reported earlier that the microhardness tends to be a maximum of 410 DPN, after one hour at 775°C . Lei (10) also reported that the resistivity of Ni_4Mo reaches a low value of 48 micro ohm cm after aging for 10 hours at 850 and 800°C , 192 hours at

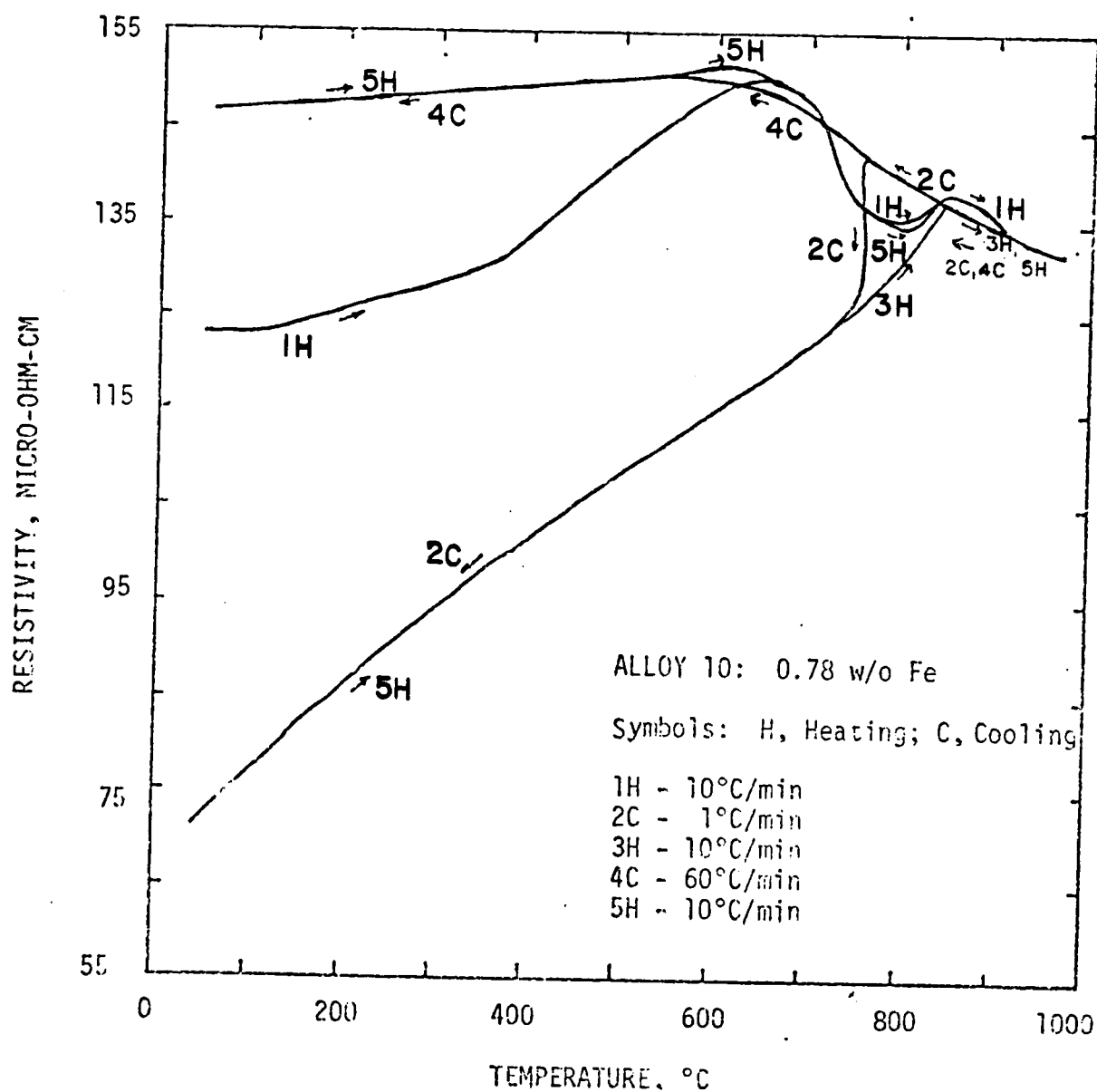


Figure II-9. Resistivity-temperature curves for Alloy 10 following indicated sequence of heating and cooling transformation. Initial condition - W.Q. form 950°C and swaged 55% RA.

Source: T. S. Lei, "The Effect of 0-8 Wt.% Iron on Transformations of Alpha Phase Ni-Mo-Fe Alloys With Ni:Mo Ratio Equal to 4:1", Ph.D. Dissertation, The University of Tennessee, (1979).

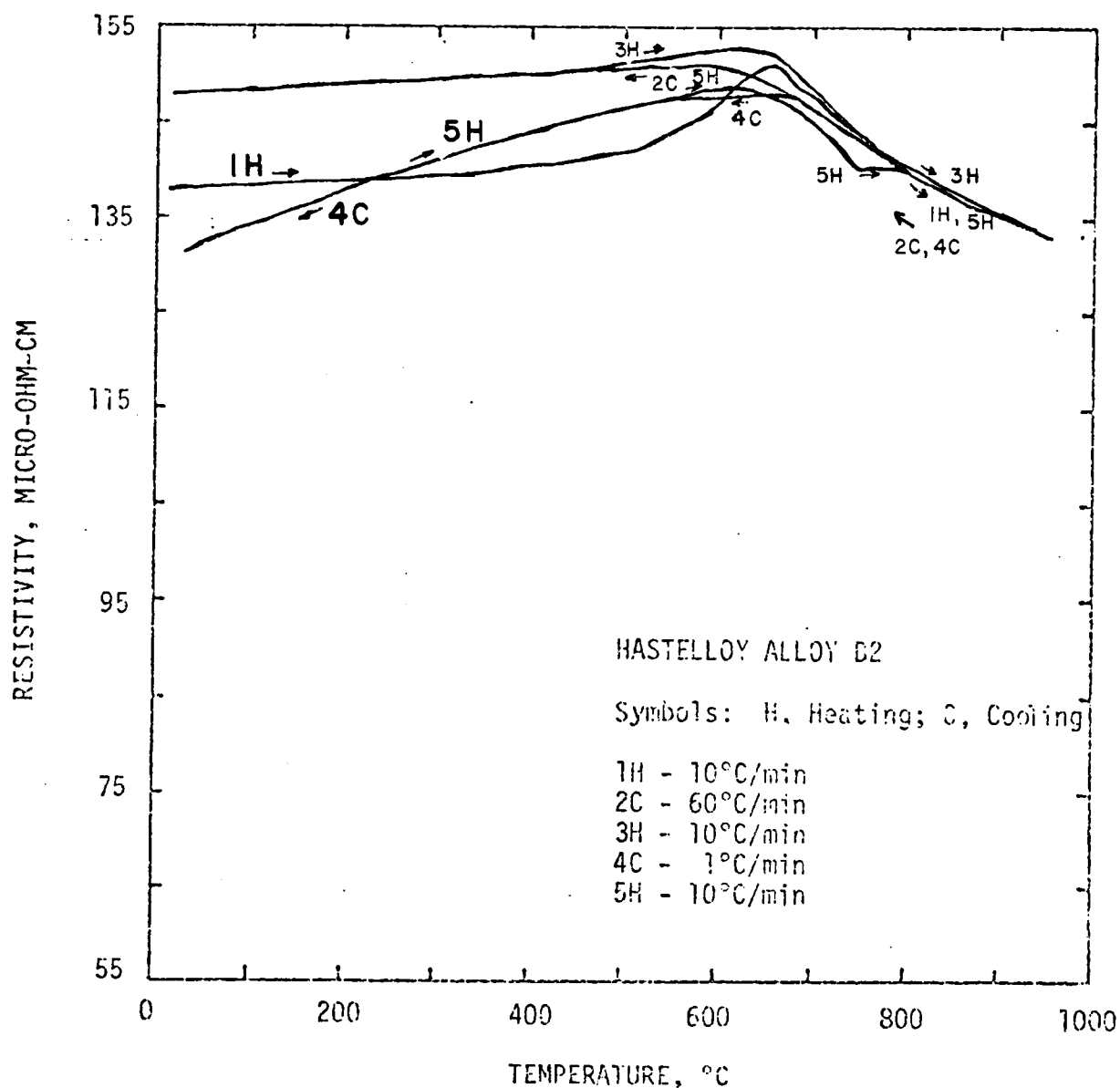


Figure II-10. Resistivity-temperature curves for Hastelloy B2 following indicated sequence of heating and cooling transformation. Initial condition - W.Q. form 950°C and swaged 55% RA.

Source: T. S. Lei, "The Effect of 0-8 Wt.% Iron on Transformations of Alpha Phase Ni-Mo-Fe Alloys With Ni:Mo Ratio Equal to 4:1", Ph.D. Dissertation, The University of Tennessee, (1979).

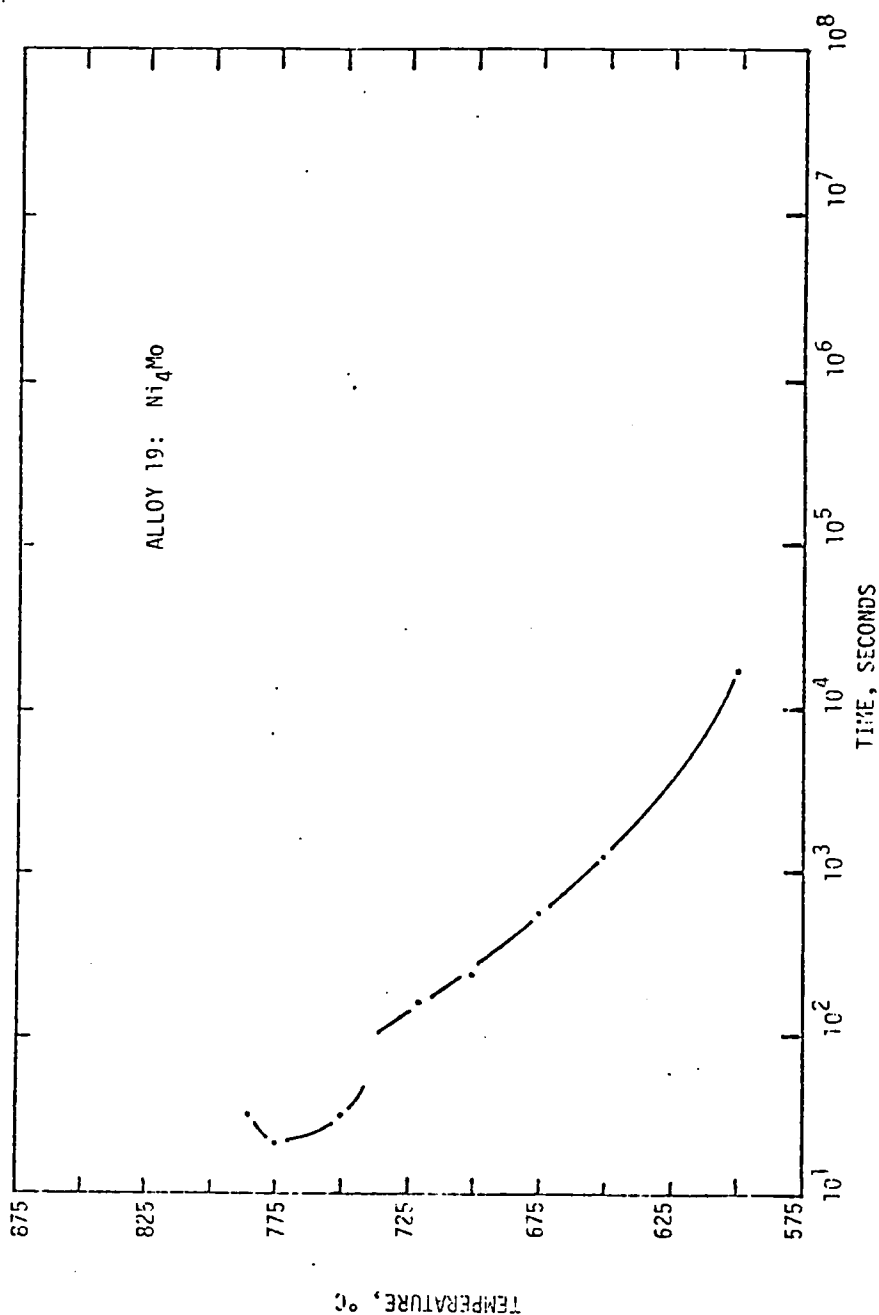


Figure II-11. Time-temperature dependence of beginning of the α -phase transformation of Alloy 19 based on isothermal resistivity measurements.

Source: T. S. Lei, "The Effect of 0-8 Wt.% Iron on Transformations of Alpha Phase Ni-Mo-Fe Alloys With Ni:Mo Ratio Equal to 4:1", Ph.D., Dissertation, The University of Tennessee, (1979).

700°C and 4500 hours at 600°C. The hardness vs aging time curves showed that at each of the higher temperatures, the hardness reached a maximum at different times and then decreased and finally converged to the same value after 2000 hours. This overaging effect was attributed to domain impingement followed by growth (coarsening), rendering dislocation movement easier. The hardness reached a maximum value of 410 DPN after 1 hour at 800°C, at 10 hours with 360 DPN at 850°C and at 192 hours with 390 DPN at 700°C. Aging at 600°C resulted in a continuous increase in hardness over the time period of 4500 hours with the final hardness still below that attained at higher temperatures.

Saburi et al. (83,84), from TEM observations concluded that the transition to LRO at 800°C takes place by a homogeneous nucleation and growth process. Partially ordered nuclei were observed under TEM after 5 minutes aging and domains impinged on each other after 30 minutes.

Chakravarti et al. (23) concluded that at 700°C ordering proceeded homogeneously. They proposed that at low temperatures, the frequency of nucleation is so high and the nuclei so small that the material is homogeneous i.e. impingement between domains is instantaneous and there is essentially no "two-phase" region between ordered nuclei and disordered matrix. Ling and Starke (85) concluded that at 700°C ordering proceeds homogeneously because of the gradual broadening and splitting of fundamental (420) lines into superlattice lines. However, they seem to have ignored the effects of SRO existing above T_c . The degree of order increases homogeneously inside the

domains and the LRO parameter follows a relation $S = 1 - \exp(-kt)$, (t =annealing time and k =constant), before reaching a value of 0.7. After $S=0.8$, increase in domain size occurs linearly and was attributed to elimination of domain boundaries due to domain growth. They also proposed that the rate of domain growth was analogous to rate of grain growth and satisfies the relation $D^n - D_0^n = kt$, where $n = 2.9$.

Ordering in nickel-molybdenum alloys containing less than 20 at.% Mo. Spruiell et al. (87) studied formation of Ni_4Mo in Nickel-Molybdenum alloys containing 23.4 and 25.8 at.% Mo using TEM in the temperature range 600-775°C. They observed particles of beta on aging and believed these to have formed by a homogeneous nucleation and growth process and then coarsened to a cube shaped, modulated morphology. This modulated morphology was concluded to have resulted from the strain field surrounding the particles and seemed to be enhanced by conditions which resulted in greater coarsening. The cube-shaped particles were found to possess a habit in which the cube faces were parallel to the $\{100\}$ planes of the f.c.c. alpha matrix. This has also been reported by Goodrum and Lefevre (88) and Nesbit and Laughlin (22) who observed that the precipitates became faceted on the $\{100\}$ planes and aligned in the $\langle 100 \rangle$ directions of the matrix. The particle sizes determined by Spruiell et al. (87) were found to be directly proportional to the cube root of time i.e. $D^3 - D_0^3 = kT$. This cube root relationship between particle size and time was also reported by Goodrum and Lefevre (88) in Ni-17 at.% Mo alloy aged at 700°C for 50 hours.

Nesbit and Laughlin (22) studied ordering in an Ni-16.7 at.% Mo alloy at 700 and 750°C using TEM. Prolonged aging at 700°C resulted in the precipitation of beta, faceted along the (100) and (010) planes. They concluded that at 750°C, a heterogeneous transformation occurs by a mechanism of homogeneous nucleation, while at 700°C a homogeneous transformation occurs by the mechanism of spinodal ordering.

Ordering kinetics in nickel-molybdenum ternary alloys.

Kiriyenko et al. (89) examined the influence of 2.09-2.39 at.% V and 1.34 at.% Nb on ordering kinetics in Ni-19 at.% Mo alloy at 700 and 800°C. They found that addition of V slowed down the ordering at 700°C and takes more than 100 hours. At 800°C, the reaction is slowed down no doubt, but after 7 hours a rapid increase in hardness was observed due to the formation of Ni_3Mo . This phase was not observed at 700°C. Niobium did not have as much of an effect as vanadium in slowing down the kinetics; this is perhaps because less of it was added.

Kiriyenko et al. (89) suggested that ordering becomes slow in these ternary alloys at high temperatures because diffusion of molybdenum atoms was reduced due to the development of vacancy complexes around vanadium atoms, as a result of which there is a change in the number of migrations which molybdenum atoms can make over the distances required for the formation of an ordered nucleus. They pointed out that the capacity of vanadium for formation of such complexes may be less marked at lower temperatures. Addition of vanadium to Ni_4Mo was proposed to alter the phase diagram, particularly in depressing the ordering temperature and perhaps expanding the $\alpha + \text{Ni}_3\text{Mo}$ region. The increased probability of stacking

faults in ternary alloys they claimed, could under certain circumstances act as basis for formation of Ni_3Mo .

Vlasova et al. (90) in their study of a $\text{Ni}_{78.6}\text{Mo}_{19}\text{V}_{2.4}$ alloy unlike Kiriyenko et al. (89) did not observe Ni_3Mo on aging at 800°C . This is probably because the aging times used by them were shorter (3 hours). At 700°C however, they observed Ni_4Mo , Ni_2Mo and DO_{22} phases.

Lei (10) studied the ordering kinetics in Ni-Mo-Fe alloys at 600, 700, 800 and 850°C using resistivity and hardness measurements. He found that the resistivity increases and hardness decreases with an increase in iron content over the composition limits and at temperatures and times for which the beta phase is indicated as present in Figure II-12. Kinetically iron slows down the ordering as is evident from the TTT curve in Figure II-13. However, it is not clear whether resistivity increases because iron atoms increase electron scattering in the LRO state just as foreign atoms do and /or decrease the degree of LRO or that the transformation is still incomplete at the times shown.

With increasing iron contents, the microstructure progressively changes from beta phase to alpha + beta + gamma, alpha + gamma, alpha + gamma + delta and alpha + delta as can be seen from Figure II-12. The increase in resistivity at 0.48 and 0.74 wt.% Fe has been associated with the partial decomposition of beta phase to alpha + gamma. At 1.94 wt.% Fe, the microstructure is alpha + gamma at 850°C and the high resistivity has been associated with the SRO alpha phase. In alloys of Ni_4Mo containing iron higher than these, a discontinuous precipitation of delta phase was observed at the higher

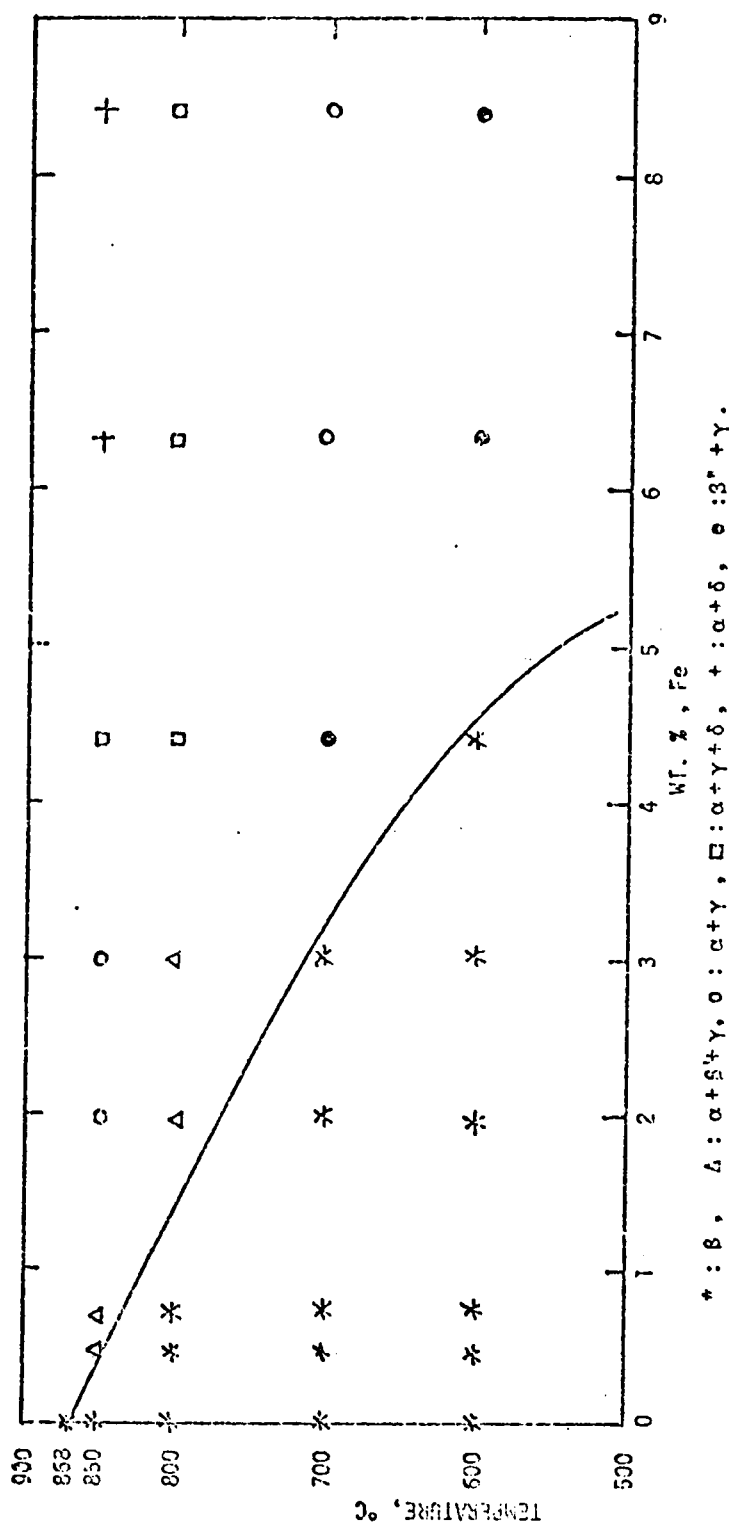


Figure II-12. Phase correspond to alloys after aging 4500 hours at 600 and 800°C and 2000 hours at 700 and 850°C.

Source: T. S. Lei, "The Effect of 0-8 Wt.% Iron on Transformations of Alpha Phase Ni-Mo-Fe Alloys With Ni:Mo Ratio Equal to 4:1", Ph.D. Dissertation, The University of Tennessee, (1979).

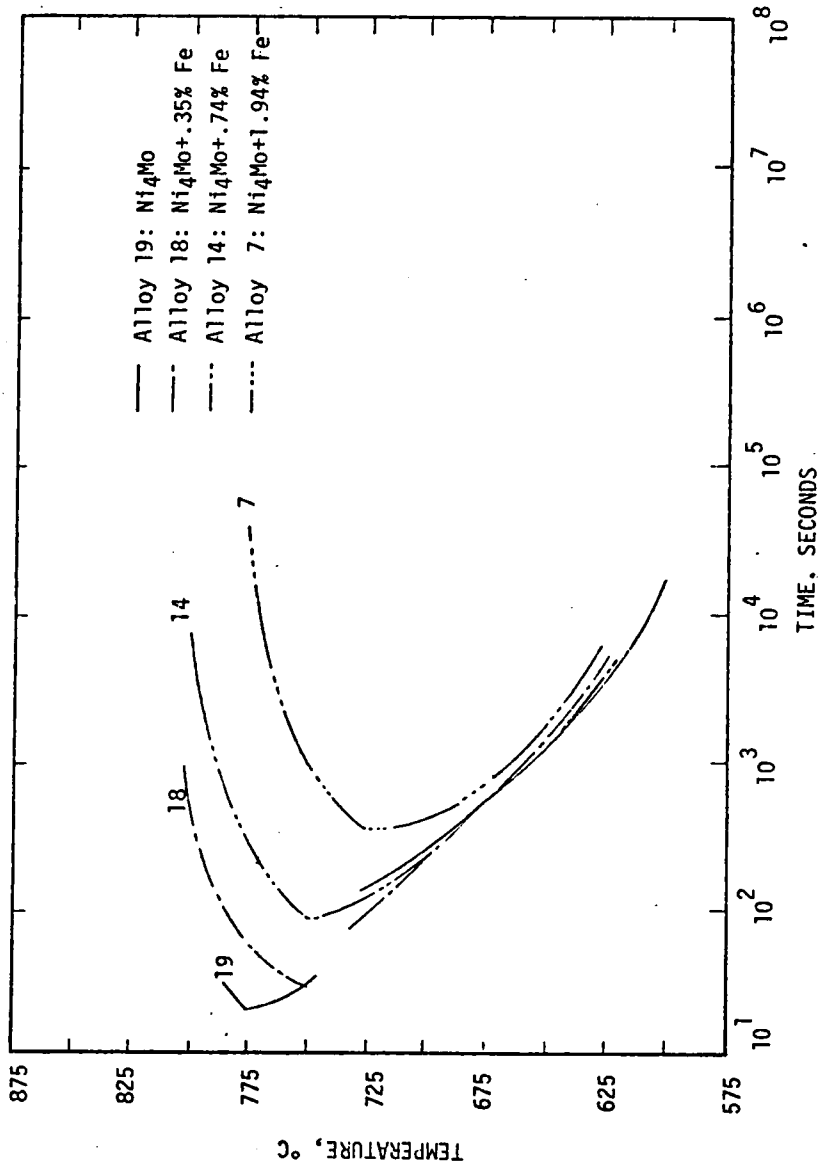


Figure II-13. Time-temperature dependence of the α -phase transformation of Alloy 19, 18, 14 and 7 based on isothermal resistivity measurements.

Source: T.S. Lei, "The Effect of 0-8 Wt.% Iron on Transformations of Alpha Phase Ni-Mo-Fe Alloys With Ni:Mo Equal to 4:1", Ph.D. Dissertation, The University of Tennessee, (1979).

temperatures. Tawancy (92) has also observed this at 900°C and 955°C in Hastelloy B. The water quenched alloy shows a decrease in resistivity with increasing iron. This means that the effect of iron is not confined to suppressing LRO alone. SRO increases resistivity and thus it is evident that iron decreases SRO.

Hastelloy B and B2 are commercial alloys which can be considered to be closely related to the Ni_4Mo composition. Alloy B has a nominal composition consisting of: Mo-28 wt.%, Fe-5 wt.%, Co-2.5 wt.%, Cr-1.0 wt.% max., C-0.05 wt.% max., Si-1.0 wt.% max., and balance Ni. Both these alloys have excellent corrosion resistance and mechanical properties and are well suited for equipment handling hydrochloric acid at all temperatures and concentrations.

There is no reported work on aging characteristics of Hastelloy B2, but there is some reported work on the physical metallurgy of Hastelloy B. Alloy B has a f.c.c. structure in the solution treated condition and undergoes structural changes on aging below the ordering temperature. Aging results in increase in yield strength and hardness, low creep rate, high stress rupture properties but a decrease in ductility (8).

Roan and Brooks (7) studied the mechanical properties and aging characteristics of this alloy at 705, 760, 815 and 900°C. A feather-like precipitate was observed at 900 and 815°C, which resulted in a slight increase in strength but extensive decrease in ductility. This was attributed to the Ni_3Mo phase. At 705 and 765°C, a Widmanstätten structure, presumably beta + gamma predominated. The strength obtainable at these temperatures was much higher than that at the higher temperatures.

Microstructural Features of the β Phase

One outstanding aspect which characterizes the ordered beta phase is the presence of a striated, Widmanstätten type structure. Guthrie and Stansbury (24) reported the appearance of these striations and presumed they were parallel to the $\{100\}$ planes of the alpha phase. Spruiell (93) used a two-surface trace analysis to show that at least in one set, these striations were parallel to the trace of twin planes which are $\{111\}$ planes in the alpha phase f.c.c. crystal. Chakravarti et al. (23) observed these striations in the early stages of ordering at 700°C in Ni_4Mo and showed that these were approximately parallel to the $\{112\}$ traces.

Irani et al. (91) also observed this lamellar, striated structure and proposed that it was a form of stress-relief to release some of the stresses as a non-cubic lattice replaces a cubic symmetry. They coined the term "Order Twin" for these striations. In contrast to the above results, they concluded that the order twins were parallel to the (101) planes of the alpha f.c.c. phase. In agreement with Irani et al (91), Saburi et al. (84) using a two-surface trace analysis argued that these striations were parallel to $\{110\}$ planes. They interpreted from TEM observations that the Widmanstätten structure observed under a optical microscope arose due to preferential etching of perpendicular twin boundaries. Snyder and Brooks (8) however, did not agree with this.

Lei (10) in agreement with Spruiell (93) showed that the striations were parallel to $\{111\}$ traces in the alpha phase. He argued from Figure II-14, that the striations in a single grain were parallel

to three or four differently oriented twin boundaries. Besides these striations, he reported the presence of long tapered striations which usually appeared at longer times of aging. These second type of striations were never parallel to the twin boundaries and usually made an angle of 45° with the twins. Using a single surface trace analysis he showed these to be parallel to $\{110\}$ f.c.c. planes. This is in agreement with the observations of Saburi et al. (84).

It is evident that the nature of these striations is enmeshed in controversy. None of the evidences presented so far have been unambiguously able to establish the source of these striations. It is conceivable that the composition, the time-temperature history of the alloy and in particular the etching reagent used, are all important factors and altering these could produce different results.

Lei (10) observed that at very long aging times, besides the $\{111\}$ and $\{110\}$ striations, a third morphology appears consisting of large patchy regions with wavy outlines. This is shown in Figure II-15 for an Ni_4Mo alloy aged for 2000 hours at 850°C . These patchy regions are also observed at 800°C after 384 hours, but not at 700 and 600°C . Lei (10) also observed that addition of iron to Ni_4Mo gradually changed the microstructure. Low amounts of iron did not alter the structure much. However, in these alloys (0.48 and 0.74 wt.% Fe) besides the $\{111\}$ and $\{110\}$ type striations, a third group of short, broader striations with six different orientations or variants was noticed after 48 hours. These were also said to be parallel to the $\{110\}$ of the alpha f.c.c. phase. In addition, a grain boundary reaction was noted which was determined by energy dispersive x-rays as consisting of alpha and gamma phases.

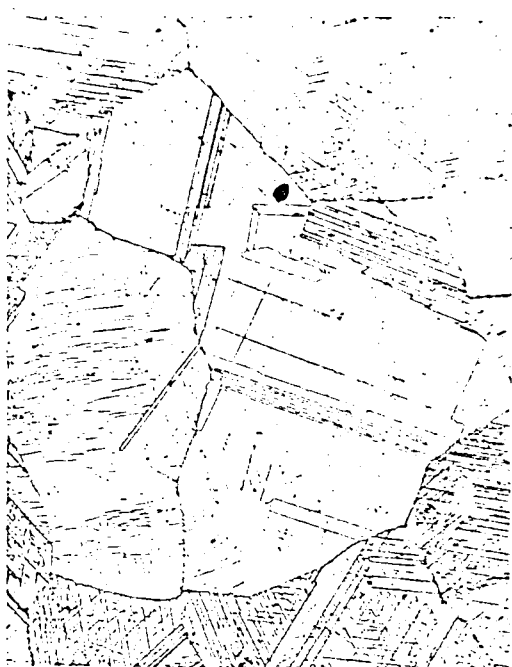


Figure II-14. Alloy 3 (29.07Mo-850C, 10HR). Striations associated with the β -phase. 200X.



Figure II-15. Alloy 3 (29.07Mo-850C, 2000HR). β domain growth. 200X.

Source: T. S. Lei, "The Effect of 0-8 wt.% Iron on Transformations of Alpha Phase Ni-Mo-Fe Alloys With Ni:Mo Ratio Equal to 4:1", Ph.D. Dissertation, The University of Tennessee, (1979).

Addition of larger amounts of iron profoundly affected the structure. Higher amounts of iron tended to stabilize the formation of gamma phase. Large amounts of the gamma phase were observed on aging at the higher temperatures even in alloys containing about 2 wt.% Fe. Figures II-16 and II-17 are microstructures obtained on aging a 4.41 wt.% Fe alloy at 800 and 700°C for 4500 and 2000 hours respectively. The microstructure in both cases shows predominantly gamma phase and delta phase along the grain boundaries. In $\text{Ni}_4\text{Mo} + \text{Fe}$ alloys located in the alpha+gamma+delta three phase region, a discontinuous precipitation of delta and gamma phases was observed. This was also observed by Tawancy (92) on aging Hastelloy B at 900 and 955°C.

The microstructural manifestations of Ni-Mo-Cr alloys are expected to be similar to that of the Ni-Mo-Fe alloys and hence the above observations can be used for comparison purposes.

Order Strengthening in Ni_4Mo

Strengthening due to ordering has been observed by a number of researchers (8,23,85,86,88,91). Most of these reports have drawn a relation between degree of LRO order, domain size, mechanical properties and fracture characteristics. Snyder and Brooks (8) found the 0.02% yield strength of Ni_4Mo to increase from 56,000 psi for the water-quenched alpha phase to 127,000 psi for material aged for 10 minutes at 775°C. The domain size was found to increase to 150°A from about 40°A. At the end of 186 hours at the same temperature, the domain size increased to about 3500°A but the yield strength dropped below that of the water-quenched alpha phase, evincing overageing effects. The fracture was observed to change from a transgranular to intergranular type.

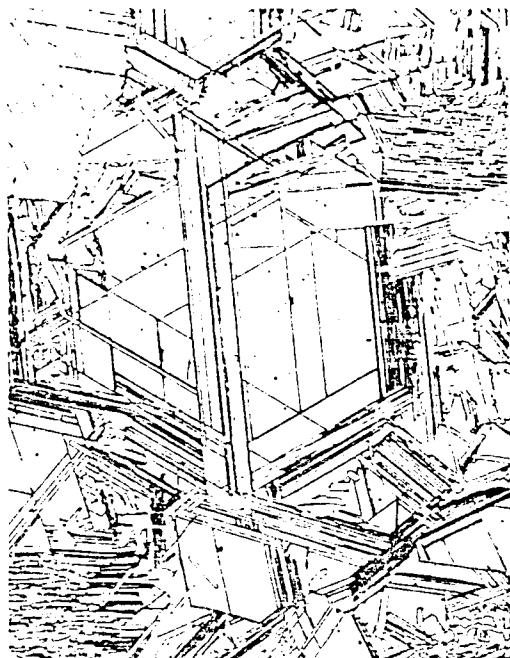


Figure II-16. Alloy 11 (27.91Mo, 4.41Fe-800C,4500HR). Widmanstätten γ in α matrix, $\alpha+\gamma+\delta$ secondary reaction. 200X.



Figure II-17. Alloy 11 (27.91Mo, 4.41Fe-700C,2000HR). Widmanstätten γ in β matrix. 200X.

Source: T. S. Lei, "The Effect of 0-8 wt.% Iron on Transformations of Alpha Phase Ni-Mo-Fe Alloys With Ni:Mo Ratio Equal to 4:1", Ph.D. Dissertation, The University of Tennessee, (1979).

Chakravarti et al. (23) attributed the strengthening mechanism at 700°C to the increase in domain size, the degree of order and stresses induced due to the tetragonality of the ordered phase. The decrease in ductility was attributed to either the development of dislocations in coplanar arrays or concentrated slip in the heterogeneous structure observed at grain boundaries at longer aging times.

Ling and Starke (85) measured the strains produced by ordering and proposed that high strength occurred at the later stages of ordering mainly due to the high density of dislocations generated from the strained coherent interface. The early stage hardening was supposed to occur due to domain hardening and/or partial order. A region of constant hardness was also observed and was explained by proposing that the strain generated by creation of new dislocations was counteracted by reduction in strain from the elimination of domain boundaries during domain growth.

Irani et al. (91) conducted hardness measurements at 800°C and on the basis of correlation with the microstructure, concluded that order twinning occurs before maximum hardness is attained.

Chen et al. (86) measured mechanical properties in Ni_4Mo with and without an accompanying stress and observed that the degree of order, domain size, yield strength and work hardening coefficient increase faster with aging for the stress-ordered samples than for the stress-free ones. However, the stress-free ordered samples showed higher maximum yield strength and work hardening coefficient and more pronounced overageing.

CHAPTER III

EXPERIMENTAL METHODS

Alloy Preparation

Seven alloys, containing 0 to 4 wt.% Cr were prepared. The alloy designations and corresponding compositions are listed in Table III-1. The alloys were prepared from a Nickel-Molybdenum master alloy, with additions of nickel to get a Ni_4Mo composition. Chromium was added in the form of 99.999% pure chips. Approximately 950 grams of each alloy were melted in a Balzers induction furnace under a refilled argon-hydrogen atmosphere at 45 cm pressure, degassed under vacuum and poured into water-cooled copper molds to produce cylindrical ingots 0.75 inches in diameter.

The cast alloys were homogenized at 1150°C for 100 hours in a high temperature furnace in dry hydrogen, furnace cooled, reheated to 950°C for 1 hour and water quenched to retain the soft f.c.c. (α) phase. The alloy ingots were subsequently swagged with intermediate anneals in argon at 950-1000°C, to rods 0.187 and 0.125 inch diameter. The larger rods were used for metallographic examinations and hardness tests and the smaller ones for electrical resistivity measurements.

Heat Treatments

Four inch long rods of both sizes were sealed in Vycor tubes under rough vacuum. The smaller rods were held at 950°C for 2 hours and the larger ones at 1250°C for the same time and water quenched on breaking the vycor capsules to retain the f.c.c. phase; the 1250°C treatment resulted in a grain size of about 2-3 mm. Samples for aging

TABLE III-1
Chemical Compositions of Alloys

Composition*	Alloys						
	NMCRO	NMCR6	NMCR3	NMCR1	NMCR2	NMCR4	NMCR5
Ni	70.94	70.48	70.18	69.86	68.49	67.36	68.16
Mo	28.77	28.70	28.67	28.68	28.29	28.29	28.07
Cr	0.10	0.41	0.54	0.74	2.08	2.97	3.84
Fe	0.10	0.10	0.10	0.10	0.10	0.10	0.10
Al	0.05	0.05	0.05	0.05	0.05	0.05	0.02
Co	0.10	0.10	0.10	0.10	0.10	0.10	0.10
Cu	0.03	0.03	0.03	0.03	0.02	0.02	0.02
Mg	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Mn	0.10	0.10	0.10	0.10	0.10	0.10	0.10
Si	0.02	0.02	0.02	0.02	0.02	0.02	0.02
V	0.01	0.01	0.01	0.01	0.01	0.01	0.01
W	0.10	0.10	0.10	0.10	0.10	0.10	0.10
Zr	0.01	0.01	0.01	0.01	0.01	0.01	0.01
C	0.005	0.003	0.006	0.003	0.006	0.008	0.005
B	0.002	0.005	0.002	0.002	0.003	0.003	0.006
P	0.006	0.004	0.004	0.005	0.004	0.004	0.004
S	0.002	0.002	0.002	0.002	0.003	0.002	0.002
Ni : Mo	4.032	4.015	4.001	3.981	3.957	3.892	3.969

*Composition in weight percent.

Note : Actual compositions of Fe, Al, Co, Mg, Mn, Si, V, W, B, P and S are less than the amounts indicated.

were cut from the solution treated rods and sealed in Vycor tubes under vacuum. Quarter-inch-long specimens from the 0.187 inch rods and one-inch-long specimens were cut from 0.125 inch rods.

The samples were aged in a four-in-one furnace assembly maintained at 600, 700, 800 and 850°C respectively. A six inch uniform temperature zone was established. The temperature which was periodically checked with a chromel-alumel thermocouple varied over time by $\pm 4^\circ\text{C}$. Groups of specimens of each alloy were introduced into the isothermal zone of each furnace. After aging at each temperature for times upto 4500 hours, the capsules were broken and the specimens water quenched to arrest further transformation.

For aging times upto ten hours, a salt bath furnace was used. The specimens were immersed directly into the bath and then water quenched.

Optical Metallography and Hardness Measurements

The aged specimens, 0.25"x0.125", were mounted in Buehler's epoxide resin. After curing at room temperature for 12-24 hours, the surface was ground to remove any possible oxide layer, then mechanically rough and fine ground, and finally rough and fine polished using conventional techniques for metallographic examination. Both manual and automatic polishing techniques were used during the various stages of polishing.

Hardness measurements were made on polished metallographic specimens using a Tukon Hardness Tester with a 136° apex angle diamond pyramid indenter and 10 kg load. Usually the hardness was measured after the third stage of rough polishing and again checked after the

last stage of fine polishing. Five impressions were read, averaged to yield a Diamond Pyramid Hardness Number, DPN. The machine was calibrated often with standard hardness blocks.

For metallographic examination the etchant used was a mixture of one part solution of CrO_3 and three parts 20% HCl. The CrO_3 stock solution was prepared by gradually mixing 30 gms of CrO_3 with 300 ml boiling water. The specimens were etched by swabbing for a time ranging from 3 to 8 seconds. Etched specimens were examined under an optical and a scanning electron microscope at a series of magnifications.

Electrical Resistivity Measurements

The electrical resistivity measurements were made with equipment developed in the department over the years and adapted more recently to computer control.

Manual measurements at room temperature. The resistivity, ρ , of the rod sample was calculated from Resistivity, $\rho = 0.785Vd^2/IL$, where, d = diameter of rod, L = sample length along axis, V = voltage drop across L , and I = current passed through rod.

The diameter of the rod was measured with a micrometer at a number of points along the length of the rod and the average computed. The sample length was defined by the span between two knife edges which were glued to the cut ends of a quartz cylinder. Three knife edge standards, 7.685 ± 0.003 , 2.5438 ± 0.0005 , and 0.3848 ± 0.000 cms. respectively were used. The resistivity was measured by mechanically fixing the rod to the top of the knife edges, ensuring that proper contact was made and connecting the ends of the rod to a

precision controlled current source in series with a calibrated standard resistor. With a controlled current of about 1 ampere passing, the voltage drop, V , across the knife edges was measured with a digital voltmeter. Readings were taken with the current in the forward and then the reverse direction and the values averaged to cancel thermal emf effects.

Resistivity measurements at elevated temperatures. The resistivity equipment was interfaced with a PDP-15/35 digital computer to measure the resistivity of samples over wide ranges of heating and cooling rates, or isothermally for periods more than a day. The computer equipped with analog-to-digital converters, digital-to-analog converters and relay switching, permitted both resistivity measurement and temperature control with great flexibility. FORTRAN IV language was used in programming.

The resistivity of the alloy rod was first determined manually at room temperature. Then two Pt-13%Rh, thermocouple wires were spot welded on the sample about 7 mm apart, near the center of the specimen. The actual distance between the wires was calculated by repeating the steps used in manual measurement. Knowing the resistivity at room temperature, the length between the wires could be calculated from $L = 0.785Vd^2/I\rho$. Subsequently two platinum thermocouple wires, were welded adjacent to the Pt-13%Rh wires respectively. The length of the rod sample used was 4 inches.

Current (0-90 amperes) to resistively heat the rod specimen was provided through welded nickel strips at each end. These strips were welded to one-quarter-inch diameter nickel rods about ten inches long

and then to the same size copper rods which passed to the cold end of the equipment. These rods were part of a specimen support assembly which was suspended vertically in a 2.5 inch diameter ceramic tube, lined with 0.01-inch-thick nickel as a reflector to reduce heat loss. This arrangement along with ceramic sheathed nickel and copper rods, ceramic tube for thermocouples and ten nickel radiation shields gave acceptably low heat loss. All leads passed through vacuum tight seals in the wall of the specimen chamber which was maintained at a vacuum of 5×10^{-5} Torr or lower.

A block configuration of the electrical resistivity measuring system is shown in Figure III-1. The specimen is shown schematically in a horizontal position at the bottom of the figure. The three functions of the PDP-15/35 computer are represented at the top. Information to the computer included values of the parameters for the particular run, amplified thermocouple voltages, and the voltage drop along the power supply. Information fed through computer operated switches in the several multiplexers and provided input to temperature control algorithms with output response to the 90 ampere, 6 volt, specimen power supply. Operator communication to the computer was carried out with a keyboard terminal. Calculated values of the resistivity, specimen temperatures, and other information on the operation of the system were output to the terminal and/or magnetic tape and x-y plotter.

The computer operates through user written FORTRAN programs called TASKS, which are requested either by the user or by other tasks. A flow chart of the programs used to monitor the resistivity

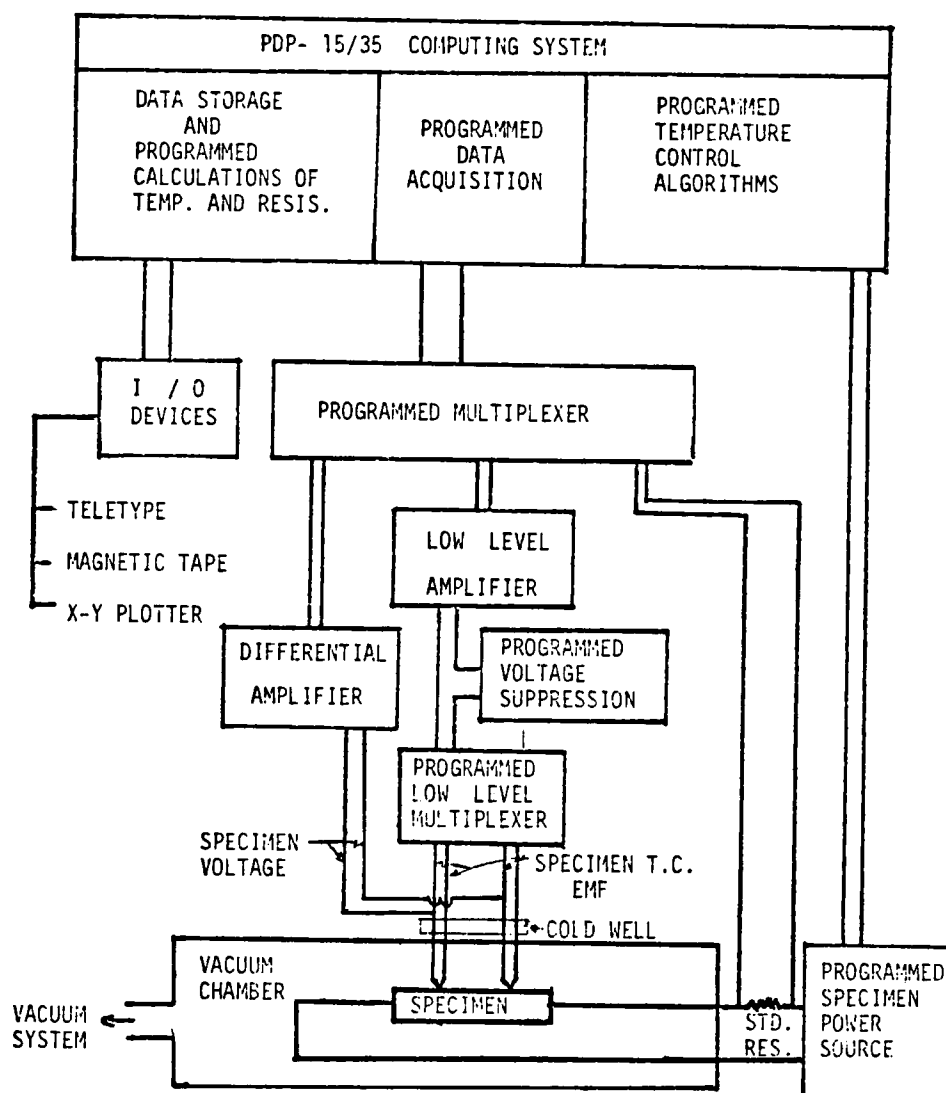
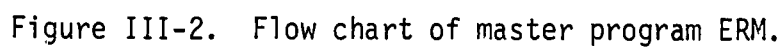


Figure III-1. Block diagram of operational devices for electrical resistivity measurements.

equipment and process both input and output data is shown in Figure III-2. The function of each program is also stated in Appendix A. A master program called ERM receives user instructions such as specimen dimensions and the time-temperature history desired and then monitors the entire run. Upto five uninterrupted heating-cooling and/or isothermal runs could be made. A set of three system commons permits continuous interchange of information between ERM and supervised tasks and between tasks.

Five values of temperature were sampled from a designated thermocouple every 0.1 seconds with an averaged sample taken every 2 seconds. During the thermocouple sampling period, the power was momentarily interrupted to reduce signal noise from the high D.C. current through the specimen to which the thermocouples were attached. The time elapse between voltage-drop sampling (along sample and standard resistor) was chosen arbitrarily to yield enough data points to define the temperature or time dependence of the resistivity; the interval ranged from 5 seconds to 10 minutes.

Heating rates upto $30^{\circ}\text{C}/\text{min}$ and cooling rates from $60^{\circ}\text{C}/\text{min}$ to $0.1^{\circ}\text{C}/\text{min}$ could be programmed. Cooling rates at low temperatures were limited by the physical capability of the system to remove heat by radiation. The values for the proportional - integral - derivative (PID) parameters used in the control algorithm were determined through preliminary programs directed towards studying the output response of the power supply and in particular determining the time constant for a series of power/current settings. The values of the PID parameters which gave the best temperature control were used. Temperatures were



controlled within $\pm 0.5^{\circ}\text{C}$ during isothermal runs. During continuous heating or cooling, the deviation of the temperature from the programmed time-temperature relationship was $\pm 2^{\circ}\text{C}$ below 800°C and $\pm 3^{\circ}\text{C}$ above 850°C .

The sample heat treatments and experimental observations are summarized in Table III-2. All specimens were subjected to optical metallography, hardness and resistivity measurements. A few specimens as indicated at the bottom the table, received X-ray diffraction and scanning electron microscopic analysis.

TABLE III-2

Summary of heat treatments and experimental observations made on all alloys

Alloy		NMCRO	NMCR6	NMCR3	NMCR1	NMCR2	NMCR4	NMCR5
Wt. % Cr		<0.1	0.41	0.54	0.74	2.08	2.97	3.84
600°C	0.16 hr	R	RH	RH	RH	RH	RH	RH
	1	R	RH	RH	RH	RH	RH	RH
	10	R	RH	RH	RH	RH	RH	RH
	16	R	RH	RH	RH	RH	RH	RH
	24	R	RH	RH	RH	RH	RH	RH
	48	X	X	X	X	X	RH	RH
	96	R	RH	RH	RH	RH	RH	RH
	192	R	RH	RH	RH	RH	RH	RH
	384	R	RH	RH	RH	RH	X	X
	840	R	RH	RH	RH	RH	RH	RH
	2000	R	X	RH	RH	RH	RH	RH
	4500	X	R	X	X	X	X	X
700°C	0.16 hr	R	RH	RH	RH	RH	RH	RH
	1	R	RH	RH	RH	RH	RH	RH
	10	R	RH	RH	RH	RH	RH	RH
	16	R	RH	RH	RH	RH	RH	RH
	24	R	RH	RH	RH	RH	RH	RH
	48	X	X	X	X	X	RH	RH
	96	R	RH	RH	RH	RH	RH	RH
	192	R	RH	RH	RH	RH	RH	RH
	384	R	RH	RH	RH	RH	X	X
	840	R	RH	RH	RH	RH	RH	RH
	2000	R	RH	RH	RH	RH	RH	RH
	4500	SX	SX	SX	SX	SX	SX	SX
800°C	0.16 hr	R	RH	RH	RH	RH	RH	RH
	1	R	RH	RH	RH	RH	RH	RH
	10	R	RH	RH	RH	RH	RH	RH
	16	R	RH	RH	RH	RH	RH	RH
	24	R	RH	RH	RH	RH	RH	RH
	48	X	X	X	X	X	RH	RH
	96	R	RH	RH	RH	RH	RH	RH
	192	R	RH	RH	RH	RH	RH	RH
	384	R	RH	RH	RH	RH	X	X
	840	X	RH	RH	RH	RH	RH	RH
	2000	R	RH	RH	RH	RH	RH	RH
	4500	SX	SX	SX	SX	SX	SX	SX
850°C	0.16 hr	R	RH	RH	RH	RH	RH	RH
	1	R	RH	RH	RH	RH	RH	RH
	10	R	RH	RH	RH	RH	RH	RH
	16	R	RH	RH	RH	RH	RH	RH
	24	R	RH	RH	RH	RH	RH	RH
	48	X	X	X	X	X	X	X
	96	R	RH	RH	RH	RH	RH	RH
	192	R	RH	RH	RH	RH	RH	RH
	384	R	RH	RH	RH	RH	RH	RH
	840	R	RH	RH	RH	RH	RH	RH
	2000	R	RH	RH	RH	RH	RH	RH
	4500	SX	SX	SX	SX	SX	SX	SX

R - Optical + Resistivity;
X - "R/RH" + X-Ray;

RH - "R" + Hardness
SX - "X" + SEM

CHAPTER IV

RESULTS AND DISCUSSIONS

The results of this research are presented in the form of plots, tables and photomicrographs. The results of resistivity measurements made on the different alloys is presented first. This includes results of continuous heating, cooling and isothermal holds on alloys in various initial states including cold work. This is followed by the section on long time aging hardness, resistivity and microstructural characteristics. In closing, a summarizing section on the effect of chromium on the morphology and stability of phases is presented.

Results of Resistivity

Effect of cold working on water-quenched alloys. The resistivities of alloys water quenched and cold reduced 28%, 45%, 68% and 77% RA are shown in Table IV-1. Also shown in the table are the chromium content and the nickel:molybdenum ratio of the different alloys. The values are represented graphically in Figure IV-1 for the Ni_4Mo alloy, the highest chromium containing (3.84 wt.%) alloy and a hypothetical average composition alloy.

The resistivity decreases with an increase in cold work upto 68% RA, beyond which there is a slight increase. The higher chromium alloys show the same trend but have lower resistivities than the binary alloy. The largest decrease in resistivity after 68% cold work occurs in the Ni_4Mo and the lower chromium alloys and is on the average 25.37 micro-ohm-cm. The least decrease occurs in the 3.84 wt.%

TABLE IV-1

Resistivity of Alloys Water-Quenched from 950°C

Alloys	Wt.% Cr	At % Ni:Mo	W.Q.	Resistivity*			
				28% RA	44% RA	68% RA	77% RA
NMCR0	<0.1	4.032	144.5	135.1	129.6	120.1	124.4
NMCR6	0.41	4.015	144.4	133.66	130.25	119.22	123.16
NMCR3	0.54	4.001	144.12	122.43	127.43	118.61	122.6
NMCR1	0.74	3.981	144.0	133.2	126.9	118.0	122.1
NMCR2	2.08	3.957	142.85	132.86	125.9	117.2	120.78
NMCR4	2.97	3.892	139.5	130.35	124.9	116.7	121.2
NMCR5	3.84.	3.969	132.46	129.9	123.95	115.8	123.04

*Resistivity in micro-ohm-cm. at room temperature.

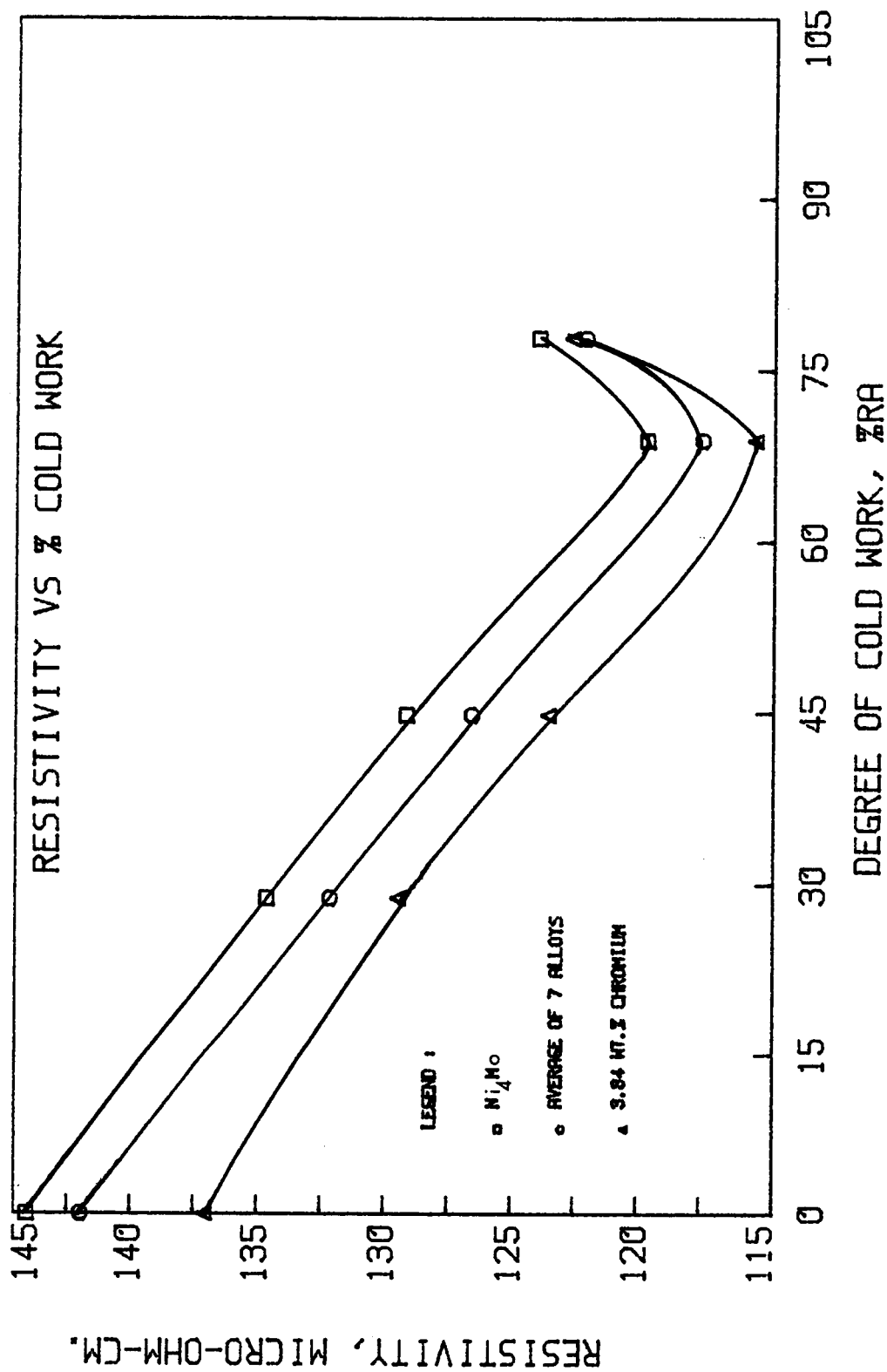


Figure IV-1. Effect of cold work on short range order resistivity.

Cr alloy and is 21.66 micro ohm cm. Reference to the average composition alloy, indicates that the first 28% RA decreases the resistivity by 9.8 micro ohm cm, the next 13% RA by 5.6 micro ohm cm, the additional 23% RA in the third stage by 9.1 micro ohm cm. and the final 9% RA causes a 4.6 micro ohm cm increase in resistivity.

The results suggest that cold work of about 68% RA significantly reduces the short range order that exists in alloys quenched from elevated temperatures. This is consistent with the "K-State" type of SRO which exists in Ni_4Mo alloys at high temperatures and retained in the water quenched condition. This has also been observed by Lei and Stansbury (10) and Chang (19). Cold working destroys the SRO with almost the same effectiveness in all alloys. The fact that alloys containing chromium had lower resistivity implies that there is less short range order in these alloys. The slight increase in resistivity beyond 68% RA is interpreted as arising from the increased defect concentration due to cold work becoming more effective in increasing resistivity than the reduction in SRO is in decreasing it.

Continuous heating and cooling. Results of resistivity measurements of the Ni_4Mo alloy during continuous heating and cooling is shown in Figure IV-2. These curves are typically those produced by the computer-controlled resistivity measuring equipment developed in the department. The temperature and computed resistivity were usually plotted on an x-y plotter during a run or by retrieving data stored in magnetic tapes. The plots were subsequently digitized with a Houston Instrument digitizer and replotted on a HI-Plot digital plotter with the aid of a PDP-11/03 computer.

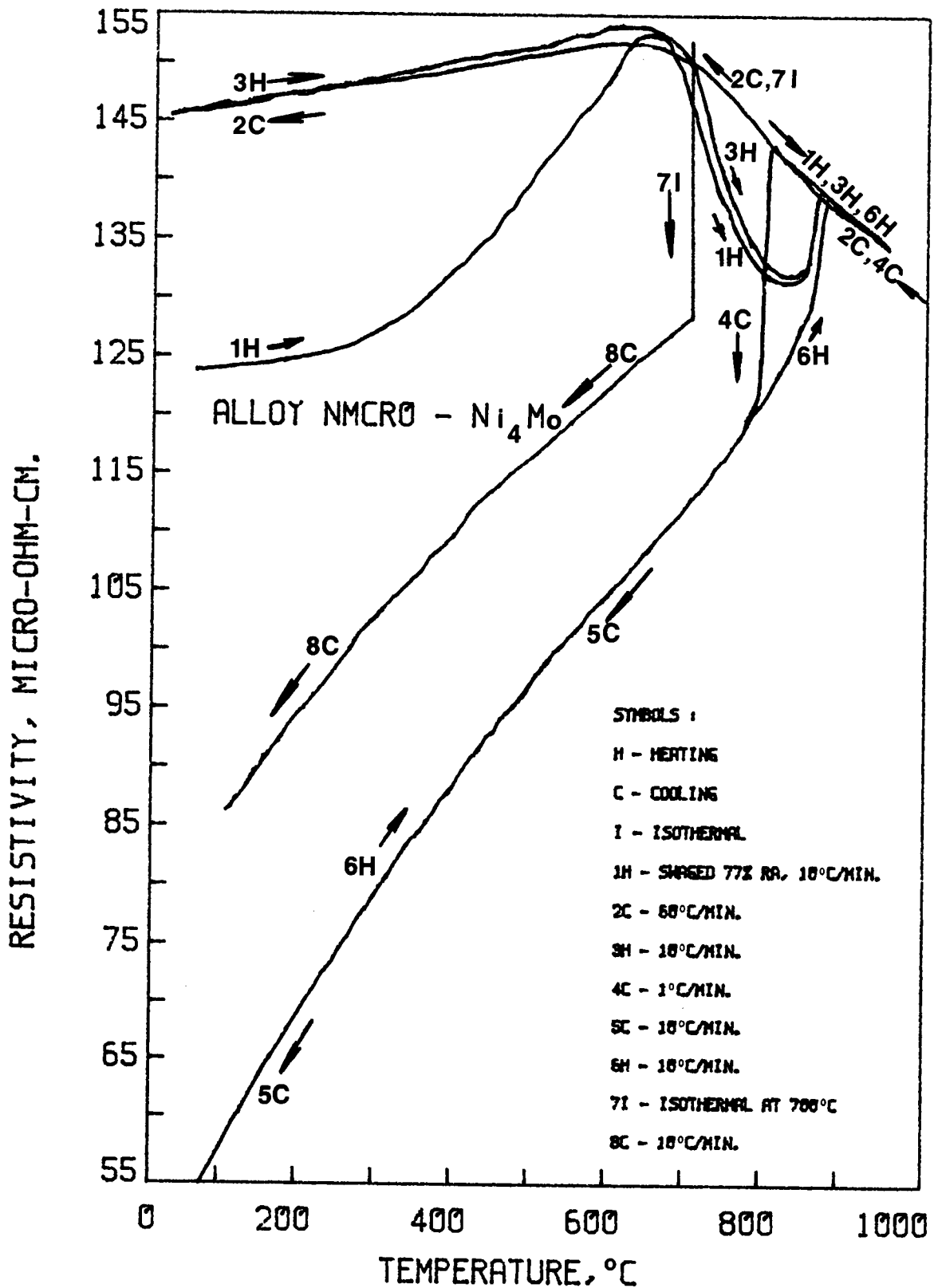


Figure IV-2. Resistivity as a function of temperature for Alloy NMCRO on continuous heating, cooling and isothermal runs.

In Figure IV-2, the symbols H, C and I designate heating, cooling or isothermal runs; the numbers 1,2...., denote the sequence of runs. During heating the rate was usually maintained at $10^{\circ}\text{C}/\text{min}$ to 950°C . During runs to determine the order-disorder transformation temperature, the rate was maintained at $1^{\circ}\text{C}/\text{min}$ in its vicinity. The fastest cooling rate of about $60^{\circ}\text{C}/\text{min}$ was obtained by "free cooling". However, this rate could not be maintained below 500°C . This was not a limitation because the low atom mobilities at the lower temperatures inhibit the ordering process and not the resistivity. For the sake of brevity, the cooling rate of $60^{\circ}\text{C}/\text{min}$ is referred to as "Fast Cooling", while a cooling rate of $1^{\circ}\text{C}/\text{min}$ or $10^{\circ}\text{C}/\text{min}$ is referred to as "Slow Cooling" or "Medium Cooling".

In Figure IV-2, curve 1H, resulting from heating the initially 77% RA cold swaged Ni_4Mo alloy, shows that resistivity increases linearly to about 300°C with a slope of $0.021 \text{ micro ohm cm}/^{\circ}\text{C}$ due to increasing thermal scattering of electrons. This is followed by a non-linear rapid increase in resistivity to 650°C due to progressive return of SRO which had been destroyed by plastic deformation. If the linear portion of the curve is interpolated, the SRO contribution to the resistivity above 300°C can be estimated. Above 650°C , the onset of long range order leads to rapid decrease in resistivity. Near 850°C , LRO resistivity attains its equilibrium value and then rises sharply as the ordering temperature (868°C) is approached. Above 870°C , the resistivity again decreases as the degree of SRO decreases with increasing temperature. Thus it is evident that the decrease in SRO is more effective in decreasing the resistivity than the increase

in temperature is in increasing it. These results are in excellent agreement with those of Lei (10) and Chang (19). It should be noted that measurements have not been made at higher temperatures to determine if the rate of decrease of SRO continues to decrease the resistivity by overcompensating the increase due to thermal scattering for temperatures to the melting point.

Curve 2C in Figure IV-2 represents data for a sample "fast cooled" from above 950°C. This cooling rate which is about 60°C/min is rapid enough to retain the SRO state with a resistivity of 146 micro ohm cm at room temperature. On cooling, the resistivity initially increases to about 152 micro ohm cm at 650°C and then slowly decreases to the value at room temperature with a temperature coefficient of resistivity α , equal to 0.011 micro ohm cm/°C. The initial increase is due to increase in SRO which continues down to about 650°C. Below 650°C, the rate of increase of SRO decreases until the amount of SRO is effectively "frozen-in" due to insufficient atom mobilities.

The following heating curve, 3H, shows that the resistivity coincides with the previous curve 2C, to 300°C, and then has a higher resistivity to 650°C due to additional SRO which occurs by virtue of adequate atom mobility. Above 650°C, the behavior is similar to that of curve 1H. Curve 4C results from slow cooling with a rate of 1°C/min from 950°C to 700°C. The resistivity increases initially on cooling to about 800°C, and then rapidly drops in the temperature range 800-775°C with the initiation of long range order. This cooling rate is sufficiently slow to allow complete transformation to the long range ordered state. Curve 5C is a continuation of curve 4C from 700°C to

room temperature at a cooling rate of $10^{\circ}\text{C}/\text{min}$. At room temperature, the LRO value of resistivity is 48 micro ohm cm which contrasts markedly with the "water-quenched-in" SRO state value of 144 micro ohm cm, the "Free Cooled" SRO state value of 146 micro ohm cm and the cold worked state value of 124 micro ohm cm.

The resistivity-temperature relationship on reheating the long range ordered Ni_4Mo alloy is represented by curve 6H. The resistivity values are essentially similar to 775°C with curve 5C. Beyond 775°C , the resistivity increases with a higher gradient to 850°C , after which there is a more rapid increase as the ordering temperature is approached. Above the ordering temperature, the curve is reproducibly similar to curves 1H and 3H. The long range to short range order transformation occurs at $868 \pm 2^{\circ}\text{C}$ which is in exact agreement with the results of Guthrie and Stansbury (24) and Lei (10).

The following curve 7I represents an isothermal anneal at 700°C . The sample was initially held for 5 minutes at 950°C , to obtain a fully alpha matrix and then rapidly cooled to 700°C . At the end of 3 hours at 700°C , the resistivity drops from about 150 micro ohm cm at the start of the hold to 129 micro ohm cm, after which the sample was medium cooled to room temperature (curve 8C).

Reference to curve 6H shows that the equilibrium value of the long range ordered state at 700°C is 110 micro ohm cm. The fact that 3 hours holding at 700°C results in a resistivity of 129 micro ohm cm, is indicative of a partially ordered state. Much longer holding times should result in a resistivity corresponding to the equilibrium value. One aspect of the resistivity-temperature relationship is particularly

noteworthy. In the heating curve 6H (Figure IV-2) it is noticed that at 868°C , the resistivity rises sharply from 130 to 140 micro ohm cm and then decreases. This marks the transition from long range to short range order. Although there are data points shown in the steeply increasing section, there is no basis for the resistivity of the LRO state to have the same value as the SRO state at T_c . Rather, a discontinuous i.e first order change would be expected at 868°C . In fact, curve 2C represents the SRO state. The difference between the two curves at any temperature is the difference in resistivity of the two states. The two states may exist in equilibrium at 868°C . At lower temperatures the SRO state should transform to LRO and is in fact observed (curve 4C). Normally, the change would occur over a temperature range on continuous cooling. In this case the change is almost isothermal due to a, by chance, balance between heat evolved by the transformation and heat losses from the specimen. In any case, the resistivity is very sensitive in this temperature range to heating and cooling rate, resulting in a thermal hysteresis.

Lariko et al. (94) have pointed out that ordering is a phase transformation of the first kind if with a slow heating rate, the ordering of the alloy takes place reversibly, but with a marked hysteresis and also qualitatively if the high temperature disordered phase can be retained by rapid cooling. They also pointed out that systems in which the disordered phase could be retained by rapid cooling were face centered cubic. The resistivity-temperature response in Ni_4Mo alloys as shown in Figure IV-2 displays this behavior. Moreover, the short range ordered phase has a face centered cubic

structure. These features concur with the hypothesis of Lariko et al. (94) and strengthen the arguments adduced in the preceding paragraph that, ordering in Ni_4Mo on continuous cooling is a phase transformation of the first kind i.e. a heterogeneous transformation.

In Figure IV-2, first, comparison between curves 5C and 8C evinces that the difference in resistivity between the completely ordered and partially ordered states becomes larger the lower the temperature. This is because the long range ordered state has a higher temperature coefficient of resistivity than the short range ordered state. Second, there is a negative deviation of resistivity in the long range ordered state above about 480°C . This is not properly understood. The SRO resistivity of both Cu_3Au (38) and Ni_4Mo decreases with an increase in temperature. However, in the long range ordered state, Cu_3Au displays a positive deviation in resistivity on heating (15) while Ni_4Mo shows a negative deviation. A positive deviation in resistivity could possibly arise due a change from a state of perfectly ordered to imperfectly ordered domains. This does not seem to be the case in Ni_4Mo .

The difference in transformation behavior between Ni_4Mo and alloys containing chromium is shown by comparing their resistivity values under the following conditions:

- 1.) As cold reduced 68% RA.
- 2.) Water quenched from 950°C .
- 3.) Rapidly cooled from 950°C to 25°C at $60^\circ\text{C}/\text{min}$.
- 4.) Slow cooled from 950°C to 25°C at $1^\circ\text{C}/\text{min}$.

In addition it is significant to compare the temperatures at which sharp changes in slope occur on heating and cooling. These results are summarized in Table IV-2 and Figure IV-3. Several consistent changes in resistivity as a function of chromium content are evident.

First, the resistivity in the SRO state decreases with an increase in chromium content and since SRO increases resistivity in this system, this suggests decreased short range order existing in chromium containing Ni_4Mo alloys compensating for the normal increase expected on additional solid solution alloying. Second, irrespective of the cooling rate employed to retain SRO, and the physical condition of the alloy, the slopes of the lines representing the effect of chromium are the same. This implies that regardless of the degree of SRO (indicated by differences in resistivity caused by differently imposed conditions), increase in chromium content decreases this degree quantitatively to the same extent.

As pointed out in the preceding paragraph, the degree of short range order appears to be dependent on the cooling rate from 950°C . From Figure IV-3, alloys cooled at a rate of $60^\circ\text{C}/\text{min}$ in vacuum have a higher resistivity than ones water quenched i.e. more rapidly cooled. The increase in resistivity on cooling rapidly from 950°C is due to SRO which is "frozen in" at different temperatures depending on the cooling rate and therefore more SRO can occur in the vacuum cooled ($60^\circ\text{C}/\text{min}$) alloy than the water quenched one. Hence the water quenching leads to lower values of resistivity. Although the temperature of 950°C is low relative to the melting temperature, the

TABLE IV-2

Typical Values of Resistivity* of Ni-Mo-Cr Alloys

Alloy	NMCRO	NMCR6	NMCR3	NMCR1	NMCR2	NMCR4	NMCR5
Conditions	Ni ₄ Mo	0.41% Cr	0.54% Cr	0.74% Cr	2.08% Cr	2.97% Cr	3.84% Cr
W.Q. from 950°C	140.6	135.0	139.5	136.2	136.4	133.3	134.2
Cold reduced 68% RA	120.1	119.2	118.5	118.0	117.7	116.7	115.8
Cooled 60°C/min. from 950°C	146.4	144.5	144.0	145.0	145.0	142.5	142.5
Cooled 1°C/min. from 950°C	50.0	53.0	58.5	61.0	84.0	132.5	144.5
<u>Ordering Temperature</u>							
On heating, °C	870	865	850	845	825	—	—
On cooling, °C	800	795	785	770	725	—	—

*Resistivity in micro-ohm-cm. at room temperature.

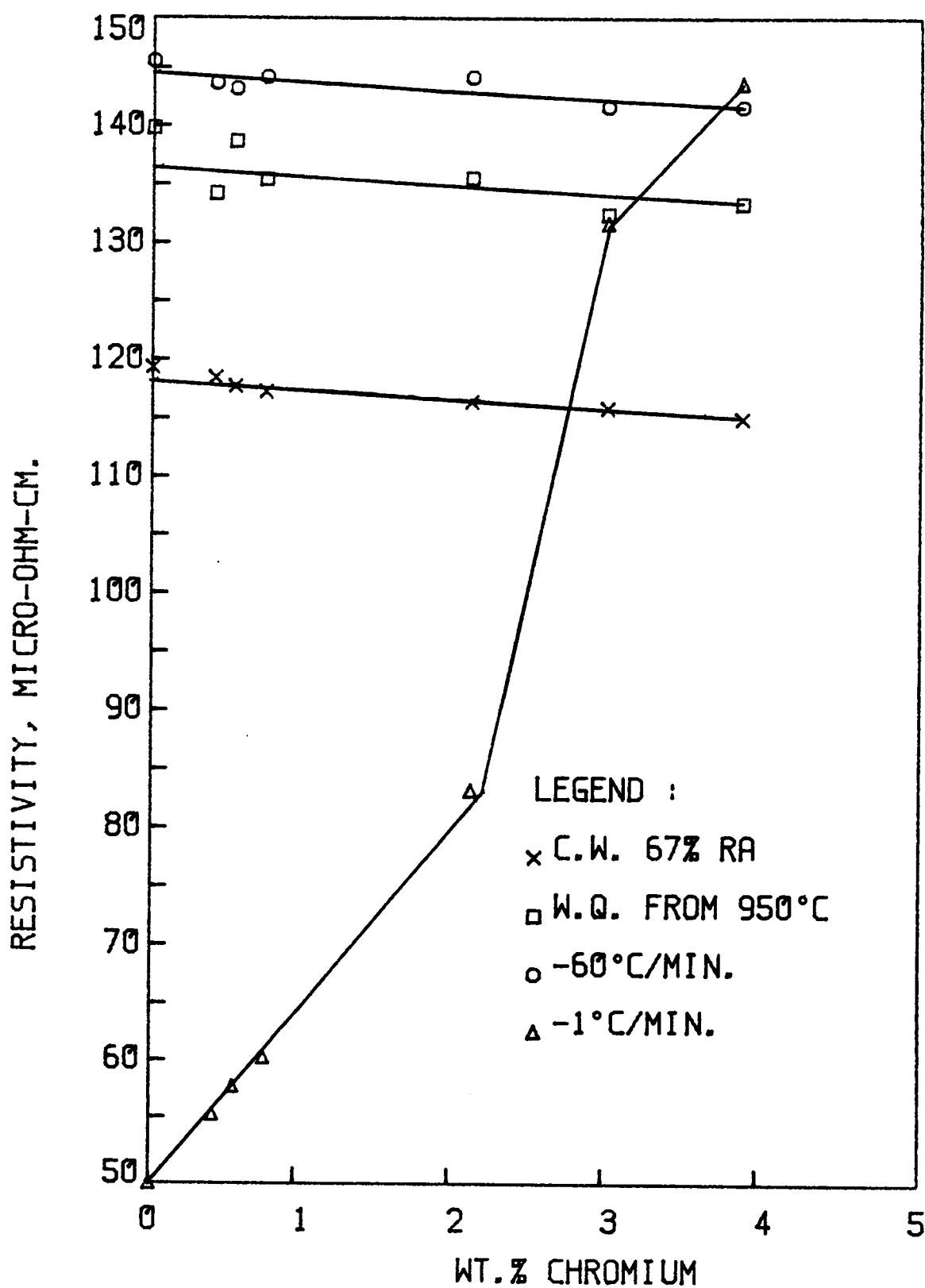


Figure IV-3. Resistivity as a function of chromium content under different indicated conditions.

effect of vacancies (on resistivity) and how their presence is influenced by cooling rate should be considered.

A third influence of chromium shown in Figure IV-3 in alloys slowly cooling at a rate of $1^{\circ}\text{C}/\text{min}$ from 950°C is the increase in room temperature resistivity with an increase in chromium content. This increase is slight to 0.74 wt.% Cr, beyond which there is a sharper rise. Additionally from Figure B-5 in Appendix B it can be seen that about 3 wt.% chromium is sufficient to suppress long range ordering in alloys cooled at rates faster than $1^{\circ}\text{C}/\text{min}$ from above the ordering temperature. In $\text{Ni}_4\text{Mo} + \text{Fe}$ alloys under the same conditions, similar behavior is exhibited only in alloys containing more than 4 wt.% Fe (10). This indicates that chromium is more effective than iron in slowing the kinetics of ordering.

It is not clear as to whether chromium increases the resistivity by enhancing electron scattering in the LRO state just as foreign atoms do and/or decrease the degree of LRO or that the transformation is incomplete within the time range of cooling. At least in alloys containing to 0.74 wt.% Cr the increase appears to be solely due to increased electron scattering, while in those containing 2.08 wt.% and above Cr, both increased scattering and decreased degree of long range order are contributory.

A final feature observable in Table IV-2 is the decrease in ordering temperature with increase in chromium. The ordering temperature, at least in cases obtainable, was observed to be relatively insensitive to the heating rate. However, on cooling the ordering temperature is depressed on the average in every alloy

(except the 2.97 wt.% and 3.84 wt.%) by about 70°C and the degree of depression decreases with a decrease in cooling rate. This decrease in ordering temperature with chromium is an important factor and will be shown to be consistent with hardness, resistivity and microstructural observations of long time isothermally aged alloys.

Effect of cold work on long range ordering kinetics. Isothermal resistivity measurements under computer control were conducted primarily to study the effect of prior cold work on the kinetics of long range ordering. The measurements were made on a single Ni₄Mo alloy namely, NMCR6 containing 0.41 wt.% Cr, at 700°C, on specimens cold worked 0%, 22%, 68% and 77% RA.

The temperature control algorithm was programmed to rapidly heat the specimen (to avoid loss of cold work) to ten degrees below the desired aging temperature within one minute, to prevent overshooting. A reset to the desired temperature brings the temperature into control at $\pm 0.4^\circ\text{C}$ within ten to twenty seconds. The time of isothermal transformation was initiated when the specimen reached the desired aging temperature for the first time. The temperature of 700°C was chosen because it is high enough to induce substantial rates of ordering and still low enough to prevent (at least initially) loss of cold work and enable detection of its influence if any, on the kinetics.

The resistivity was observed to initially rise due to return of the cold work-destroyed short range order and then to begin to decrease. Regardless of the actual resistivity values of the differently cold worked specimens, the first drop in resistivity after

the initial increase occurred at the same time namely, 4 minutes. However, the specimen containing no cold work showed a decrease in resistivity in only 20 seconds from the start of aging. This implies that this incubation time probably increases very rapidly for very small amounts of cold work.

The decrease in resistivity on aging is due to the onset of long range order. Although an increase in the degree of cold work does not seem to influence the time of initiation of ordering, the value of resistivity itself is lower the greater the amount of cold work. For example, after aging 8 hours the 0%, 22%, 68% and 77% RA cold worked specimens had resistivities of 123.96, 122.88, 122.77 and 113 micro ohm cm respectively. The change in resistivity is rather marked beyond 68% RA.

Since varying amounts of cold work on the alloy result in different start and end-of-run resistivities, it is difficult to quantify the data in its present form, to obtain a proper kinetic meaning. Rather it would be more meaningful to transform the resistivity results into fractional change in resistivity. This fractional change can be considered as analogous to conventional concepts of fraction volume transformed of parent phase and can be determined from the relation:

$$f = (\rho_i - \rho(t)) / (\rho_i - \rho_e)$$

where, f = fractional change in resistivity, ρ_i = initial high resistivity, $\rho(t)$ = resistivity at time t and ρ_e = approximate equilibrium value of resistivity at a given temperature as given by the continuous heating/cooling resistivity-temperature curve. The

approximate equilibrium resistivity for the alloy studied (NMCR6) at 700°C is 113 micro ohm cm (Figure B-1, Appendix B).

The results of the fractional change in resistivity as a function of time for specimens cold worked to different degrees is illustrated in Figure IV-4. In each case, in about twenty minutes, the value of f increases to about 0.3. In the initial stages (upto 200 minutes), while the f values are comparably the same for specimens cold worked 0%, 22% and 68% RA, the 77% RA specimen at equivalent times has substantially higher values. Although cold working upto 68% RA does not seem to substantially influence the ordering rate in the initial stages, subtle differences can be discerned on reexamining actual values of f . On replotting f values on an expanded scale (Figure IV-5), it can be seen that in the 22%, 68% and 77% RA samples there is an initial fall in f due to short range order. In addition, the specimens cold worked 22% and 68% RA had lower f values than the cold work-free specimen, being lowest in the 68 %RA sample, for times upto 200 minutes. For times between 200 and 400 minutes, with the exclusion of the 77% RA sample, the 22% RA specimen had the highest f value followed by the 68% RA specimen and lastly the cold work-free specimen. Reference to Figures IV-5 and -6 shows that for times beyond 400 minutes, values of f increase almost linearly upto 68% RA beyond which there is an exponential rise. In the 77% RA specimen the ordering rate is substantially higher than the other specimens for all times beyond 20 minutes, so much so that it is virtually complete in about 8 hours. In the other samples, the ordering is not complete even after 15 hours.

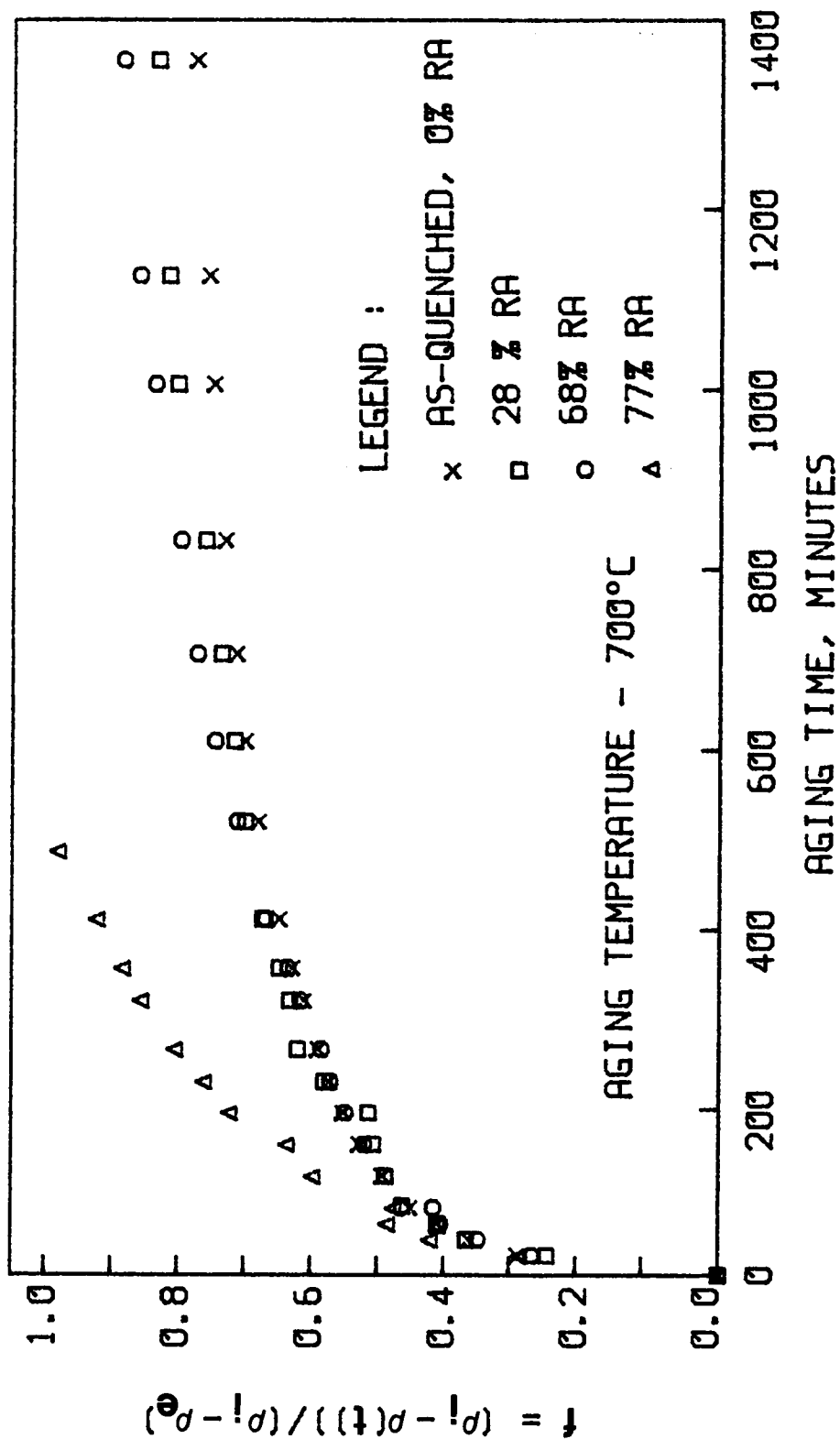


Figure IV-4. Fractional change in resistivity, f , as a function of time for Alloy NMCR6 on aging at 700°C.

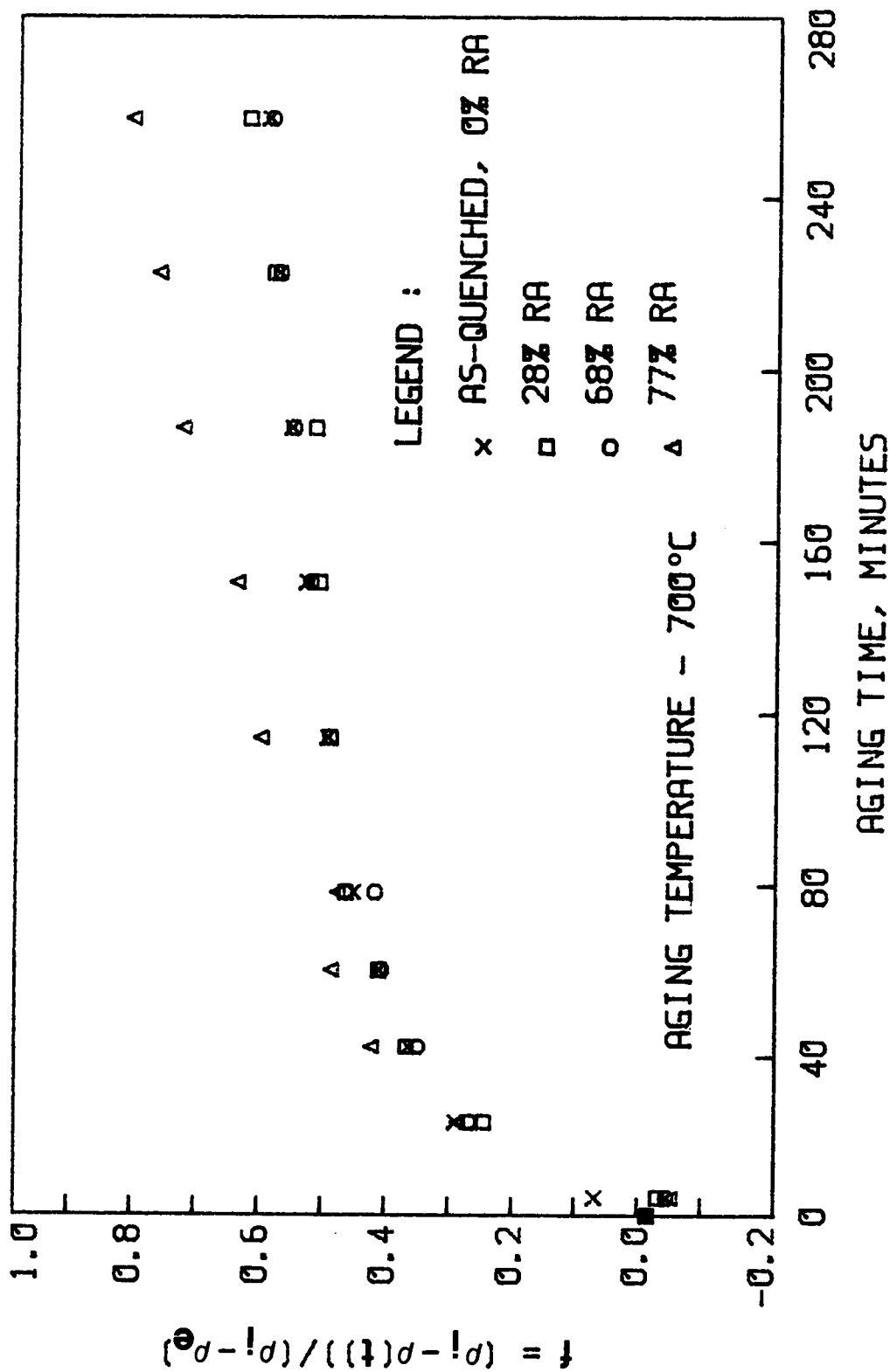


Figure IV-5. Fractional change in resistivity, f , as a function of time for Alloy NMCr6 on aging at 700°C.

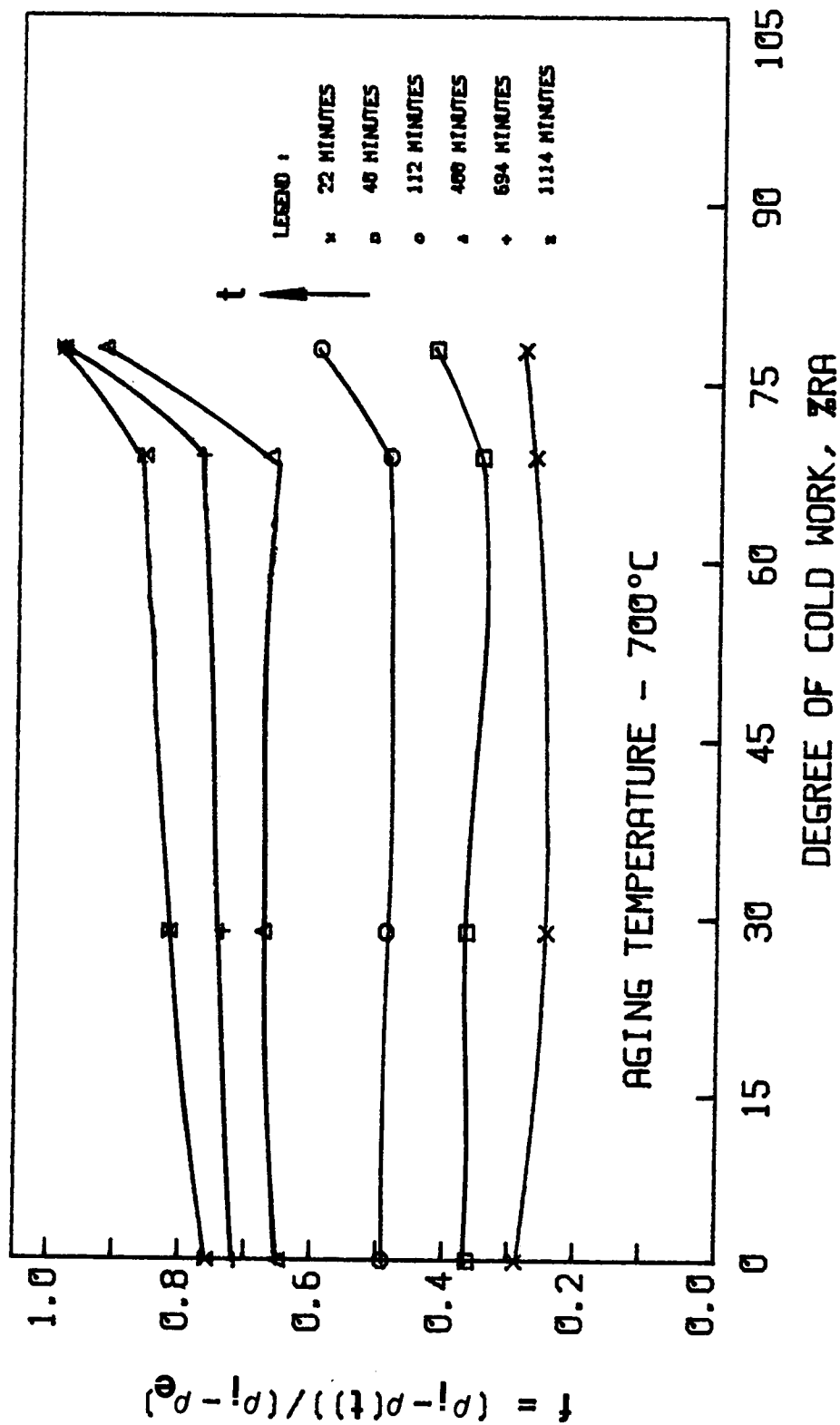


Figure IV-6. Fractional change in resistivity, f , as a function of degree of prior cold work for Alloy NMCr6 on aging at 700°C for various times.

Davies and Funes (95) reported no effect of cold work on ordering rate of Au_3Cu . However, the cold worked specimens showed a larger antiphase domain size. They related this to the higher vacancy concentration brought about by dislocation movement in the cold worked specimen. Stable ordered nuclei were said to form at the center of the dislocation network where the motion of vacancies occurs with least elastic interaction. In this research it is seen that cold working does increase the rate of ordering, at least in the later stages.

The resistivity changes resulting from cold work upto 68% RA indicate that there are two combatting factors contributing to the resistivity in the initial stages of ordering, namely, the decrease caused by long range order and the increase caused by recovery of short range order. It can be recalled from Figure IV-1 in page 66 that about 68% RA substantially reduced the resistivity and hence the SRO existing in water quenched alpha phase and cold working beyond this increased the resistivity. On this basis it is evident that in alloys cold worked to 68% RA, some SRO has to be recovered before substantial rates of long range ordering can be realised on isothermal aging. This is probably the reason for the slower kinetics evinced by cold worked specimens in comparison to the non-cold worked specimen in the initial stages of aging and additionally supports the microdomain concept of short range order in Ni_4Mo . The higher rates of ordering in the later stages of aging can then be explained by enhanced nucleation in a higher dislocation density strained matrix. In the 77% RA specimen, though some SRO is recovered initially, its effect is overshadowed by

accelerated heterogeneous nucleation of long range order at dislocations and other defect sites provided by a much more defect-enriched matrix and results in an overall increased rate of ordering at nearly all times. If the vacancy concept of Davies and Funes (95) is accepted, then the vacancy concentration in the 77% RA should be higher than that in the other specimens and should result in considerable enhancement in nucleation rate, which projected in terms of ordering rate is in fact observed. This argument if anything, strengthens the propounded hypothesis.

Thus although the concept of homogeneous ordering in Ni_4Mo and low chromium alloys at 700°C is strengthened in the light of the these observations, presence of dislocations acting as sites for nucleation cannot be ignored. At 700°C and perhaps at temperatures below this, the ordering in cold worked Ni_4Mo can be effectively described as a homogeneous reaction occurring by a process of heterogeneous nucleation.

Long Time Isothermal Aging

The resistivity and hardness for alloy NMCR6 containing 0.41 wt.% Cr on aging at 600, 700, 800 and 850°C is illustrated in Figures IV-7 and -8. The results for all the other alloys are given in Appendix C for resistivity and Appendix D for the hardness. The behavior of the Ni_4Mo alloy is very similar to that shown by the 0.41 wt.% Cr alloy.

From Figure IV-7, the resistivity drops from an initial value of 140 micro ohm cm to 128, 74 and 80 micro ohm cm at 700, 800 and 850°C respectively within 10 minutes. Subsequent aging results in a further

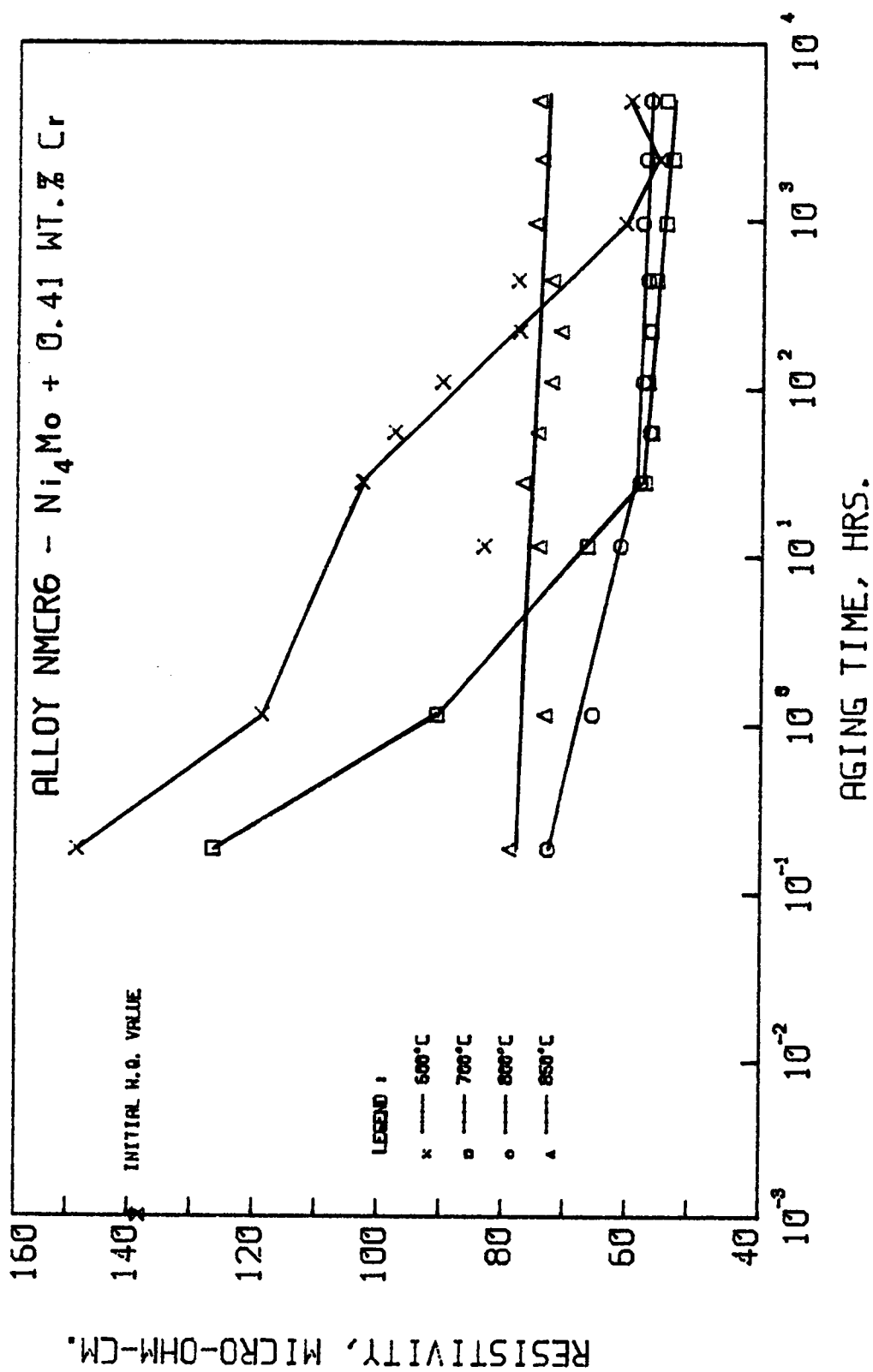


Figure IV-7. Resistivity as a function of aging time for Alloy NMCR6 at 600, 700, 800 and 850°C.

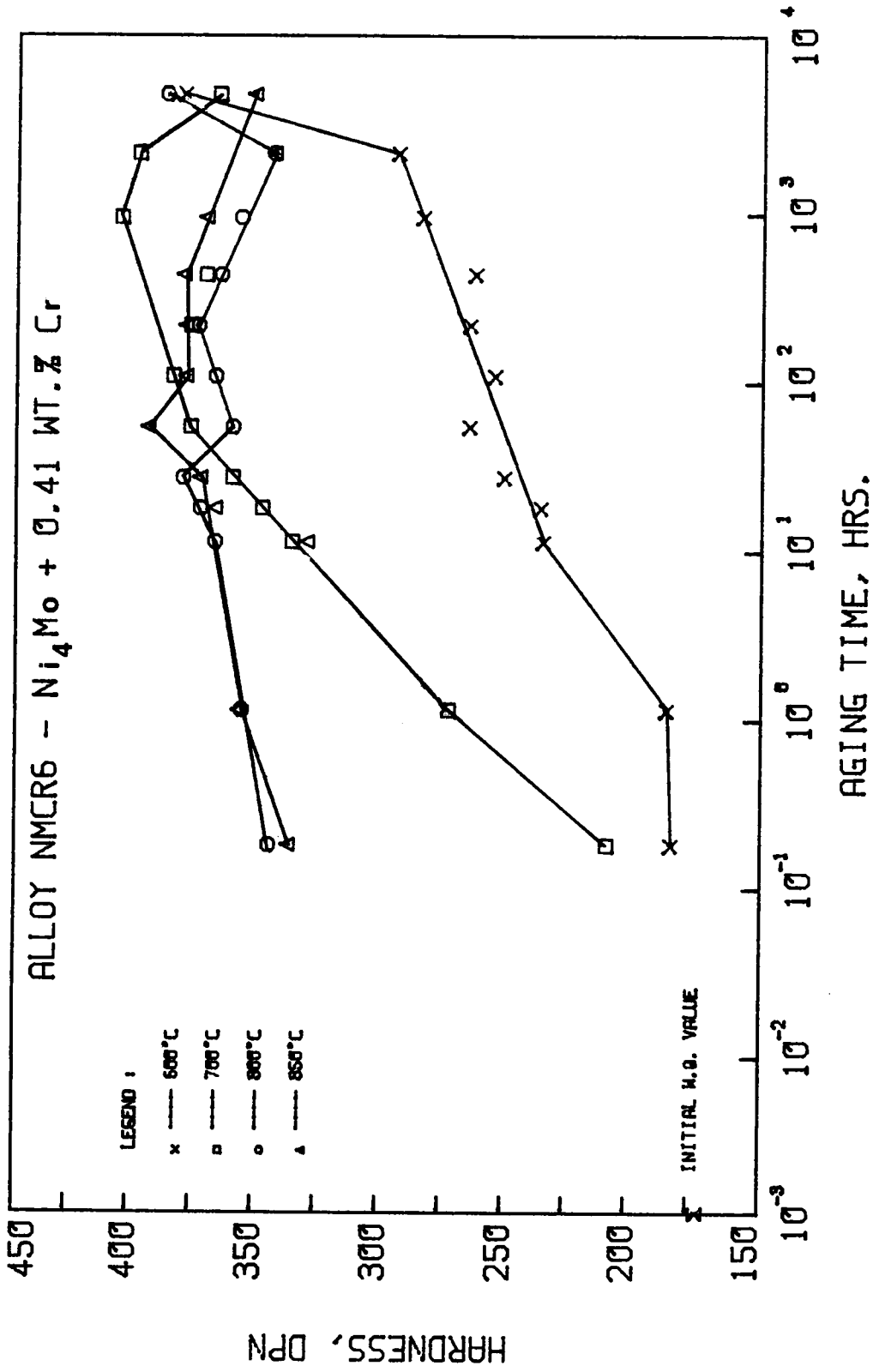


Figure IV-8. Hardness as function of aging time for Alloy NMCR6 at 600, 700, 800 and 850°C.

decrease in resistivity with the values remaining constant at 55 micro ohm cm at 700 and 800°C and 75 micro ohm cm at 850°C at the end of 4500 hours. At 600°C, the ordering reaction is much slower, the resistivity decreasing continuously throughout the aging period with a value of 61 micro ohm cm at the end of 4500 hours.

Figure IV-8 shows that the hardness has increased from 170 DPN to about 340 DPN within 10 minutes at 800 and 850°C but only slightly at 600 and 700°C. With increasing time, there is slight increase in hardness at the higher temperatures and continued increase at the lower temperatures, with some indication of overaging (peak in the curve) at all temperatures but 600°C. The hardness values tend to converge after 4500 hours. The interpretation of these maxima will be discussed under the section on "Microstructural Features on Aging".

The results of resistivity and hardness at the various aging temperatures are consistent with the temperature dependence concept of conventional nucleation and growth processes. This is demonstrated in Figure IV-9 for the 0.41 wt.% Cr alloy aged for 24 hours at 600, 700, 800 and 850°C. It is evident that kinetically the reaction is most rapid at 800°C, slightly slower at 700 and 850°C and slowest at 600°C. Thus 800°C or in the vicinity thereof, should correspond to the peak in the nucleation rate for this alloy. Actually for Ni_4Mo , the peak has been found to occur at about 775°C (8,10).

From the resistivity results on continuous heating, the temperature of ordering for the 0.41 wt.% Cr alloy was determined to be 865°C. At 850°C, fifteen degrees below the ordering temperature, the Gibbs free energy difference is small but diffusion is high. At

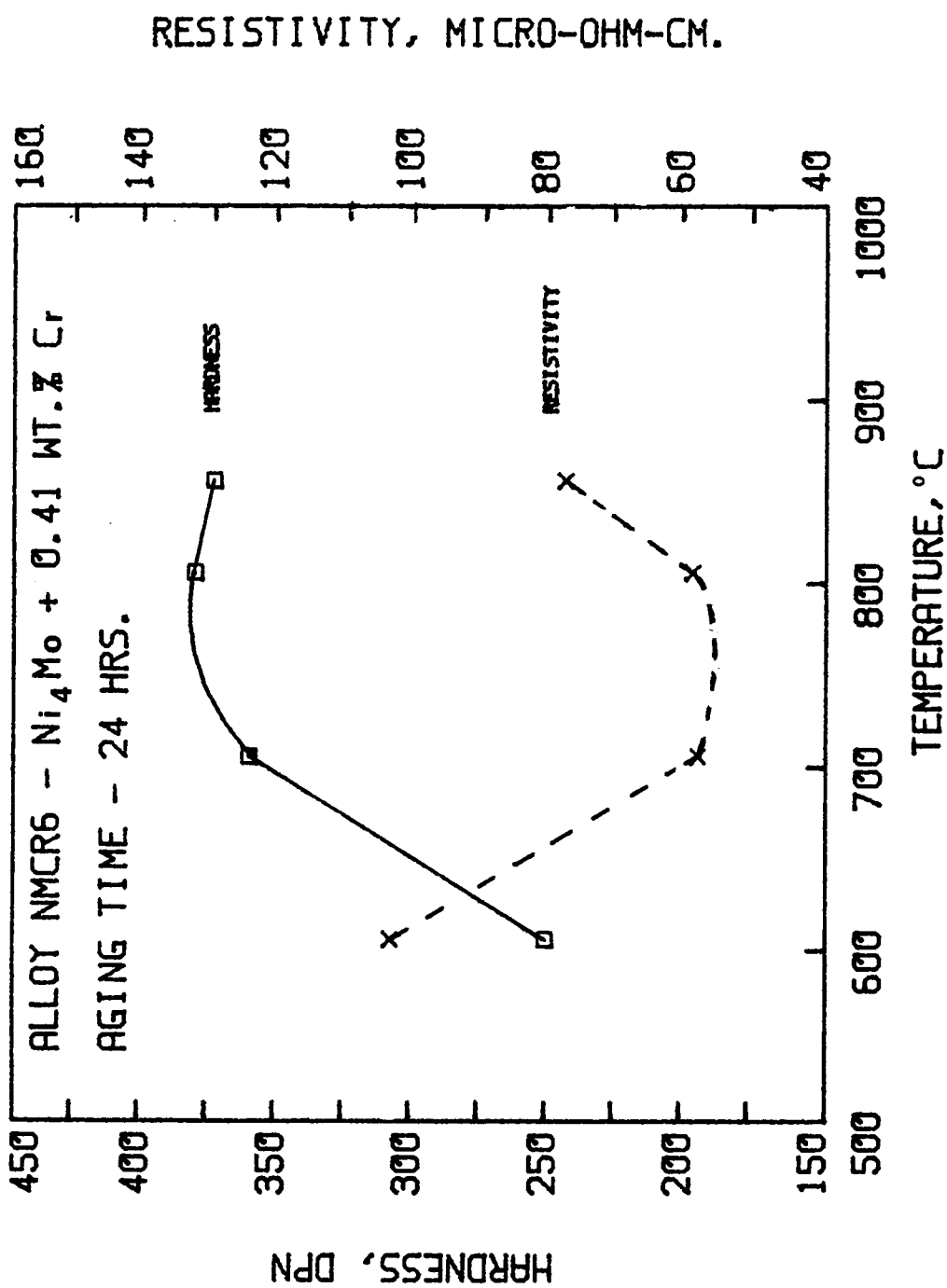


Figure IV-9. Temperature dependence of hardness and resistivity for Alloy NMCR6 aged for 24 hours.

800°C, both the driving force and diffusion are high and so is the ordering rate. At 700°C, the driving force is larger, but somewhat annulled by decreased diffusion. At 600°C, the rate of ordering is effectively inhibited by insufficient atom mobilities. The above arguments thus explain, the observed temperature dependence of the ordering process.

Figures IV-10 and -11 illustrate hardness and resistivity as a function of chromium content on aging 10 minutes at 600, 700, 800 and 850°C. Alloys of Ni_4Mo containing 0.54 wt.% Cr (NMCR3) and 0.74 Wt.% (NMCR1) respond similarly to the 0.41 wt.% Cr alloy (NMCR6) alloy on aging. There are however, fine differences. The hardness values can be seen to decrease slightly while the resistivity values increase slightly. At the end of 4500 hours the values are 58 and 60 micro ohm cm respectively. On occasion, rather anomalous decrease in hardness and increase in resistivity were observed at 850°C in both alloys. It is known from the resistivity-temperature results on continuous heating that these two alloys had approximate ordering temperatures of 850 and 845°C respectively (Table IV-2, page 74). Thus any fluctuation in the furnace temperature could change the transformation to the forward or backward direction depending on whether the actual temperature is below or above the ordering temperature.

A significant difference in the ordering behavior occurs in alloys NMCR2, NMCR4 and NMCR5, namely, 2.08, 2.97 and 3.84 wt.% Cr respectively. As can be clearly seen in Figures IV-10 and -11, the ordering rate of Ni_4Mo is greatly decreased in these alloys. While the lower chromium alloys possess high hardness and low resistivities,

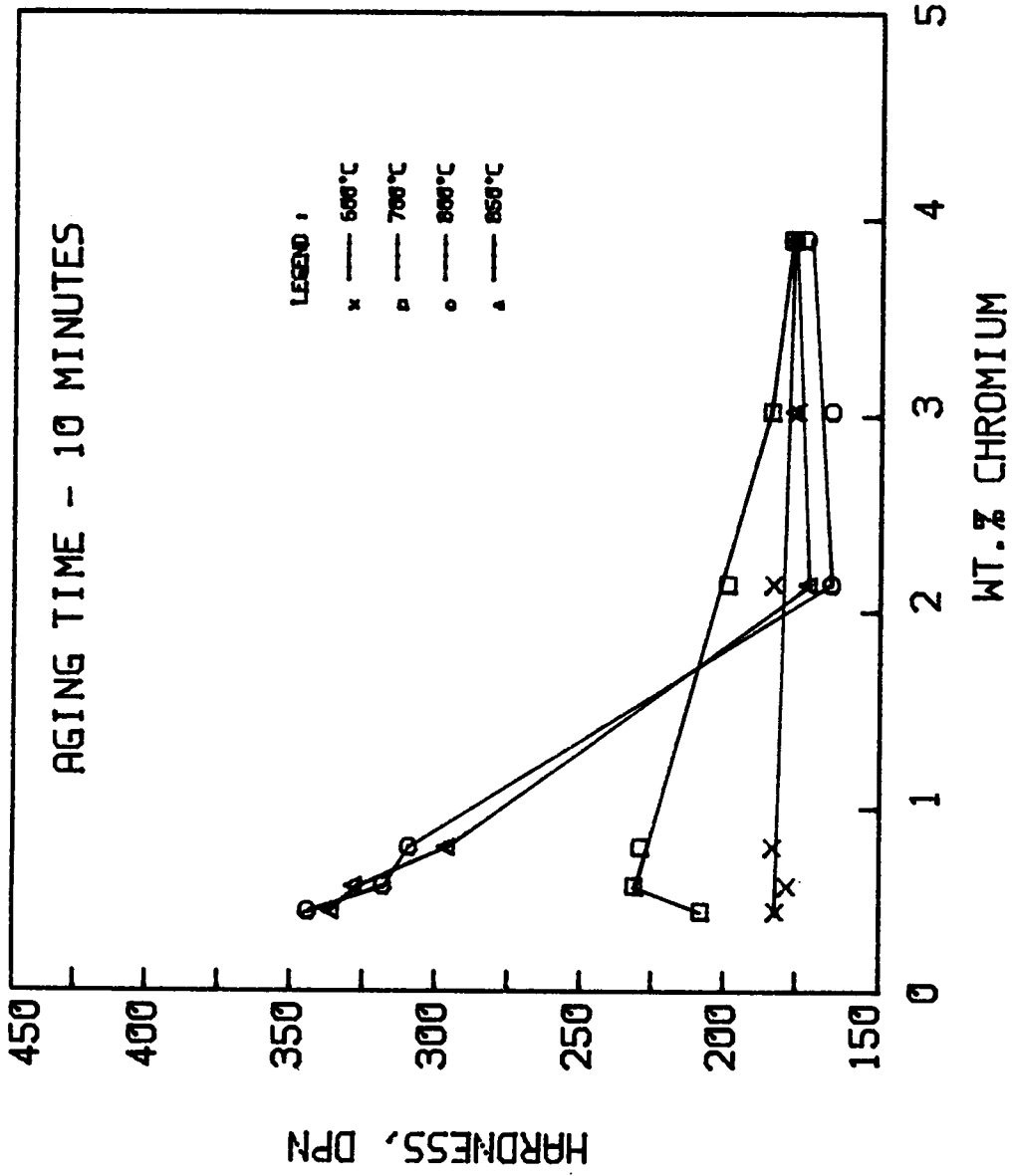


Figure IV-10. Hardness as a function of chromium content on aging ten minutes at 600, 700, 800 and 850°C.

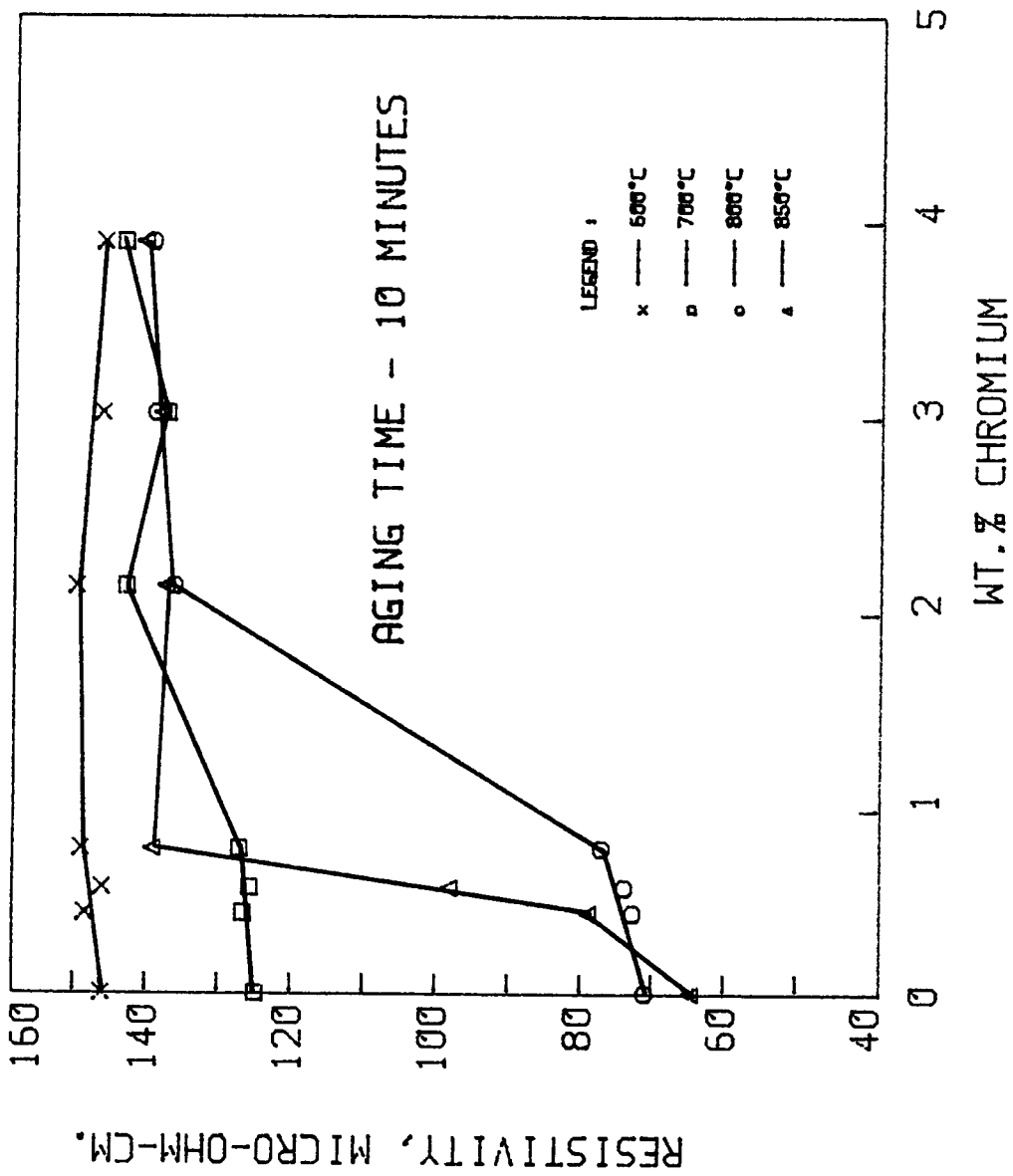


Figure IV-11. Resistivity as a function of chromium content on aging ten minutes at 600, 700, 800 and 850°C.

these three alloys show little or no change from the water quenched values after 10 minutes aging at 600, 700, 800 and 850°C. At 700°C, this trend continues upto 10 hours in the 2.08 and 2.97 wt.% Cr alloys and to 48 hours in the 3.84 wt.% Cr alloy. In comparison, the reaction is slower at the other three temperatures.

At 850°C, in each of the above three alloys, little or no change from the water quenched state hardness and resistivity is observed on aging. This indicates that the ordering reaction has been suppressed due to either depression of the ordering temperature and/or alteration of phase boundaries. Resistivity results on continuous heating and cooling clearly show that the ordering temperature has been depressed.

In this range of chromium content (2.08 wt.% and above), the kinetic processes occur most rapidly at 700°C and slower at both 800 and 600°C. This is shown clearly in Figure IV-12 for the 2.97 wt.% Cr alloy aged for 16 hours at each of the four temperatures. At the end of 4500 hours at 700°C in each of the three alloys, the hardness attains a value of nearly 450 DPN, the highest observed among any of the seven alloys studied.

The hardness and resistivity values show that for the 2.08 wt.% Cr alloy, the ordering rate is higher at 800°C than that at 600°C, while for the 2.97 and 3.84 wt.% Cr the converse is true. The 2.08 wt.% Cr alloy shows a maximum in hardness, then a drop, followed by further increase at 700 and 800°C. The 2.97 and 3.84 wt.% Cr alloys show such a relationship only at 700°C (Figures D-3 to D-5, Appendix D). From resistivity measurements on continuous heating and cooling, the ordering temperature of the 2.08 wt.% Cr alloy was established

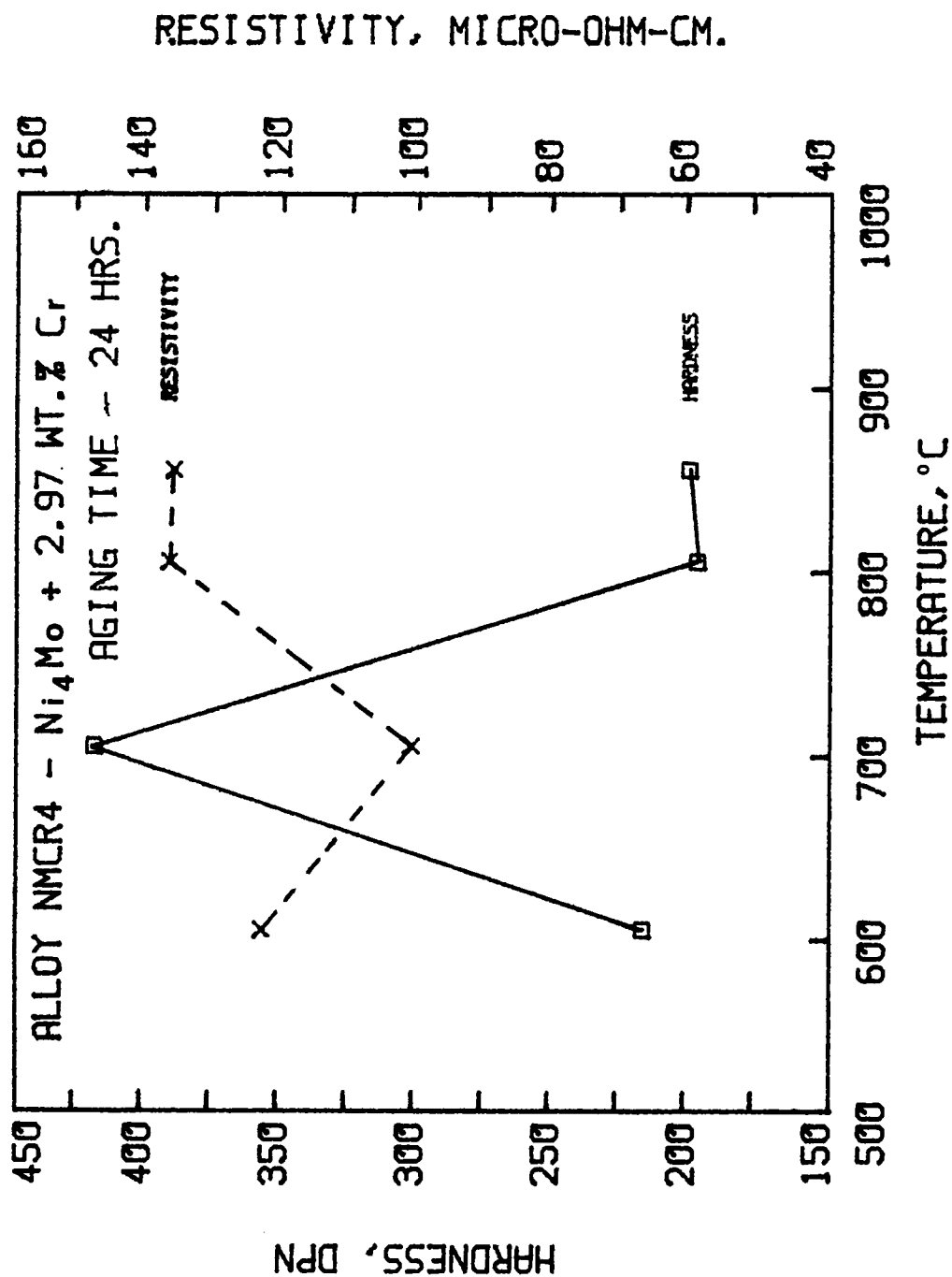


Figure IV-12. Temperature dependence of hardness and resistivity for Alloy NMCR4 aged for 24 hours.

near 825°C; these results suggest that the ordering temperature is further decreased in the higher chromium alloys.

The hardness and resistivity data correlate quite well. At the end of 4500 hours for each of the above three high chromium alloys, the resistivity tends to converge at 600 and 700°C to the same value of 80, 89 and 97 micro ohm cm respectively. At 800°C after 4500 hours, the resistivity is slightly higher namely 89, 102 and 102 micro ohm cm for the 2.07, 2.97 and 3.84 wt.% Cr alloys respectively.

All the above features observed this far, will be shown in the following section to be associated with definite microstructural changes.

Microstructural Features on Aging

The microstructures resulting from long time aging and observed optically are shown in Figures IV-14 through IV-50. Each micrograph is identified with respect to the alloy designation, chromium content, aging conditions and magnification. Also included in each caption is a brief description of the nature of phase/phases present. The etchant used consisted of one part chromium trioxide solution to three parts 20% hydrochloric acid. Details of the etching procedure are given in Chapter III under "Optical Metallography and Hardness Measurements" on page 56. The nature of the starting microstructure in all alloys will be discussed followed by a description of phases in individual alloys.

α phase. All the Ni_4Mo + (0-4) wt.% Cr alloys solution treated at 1250°C for 2 hours followed by water quenching showed a single phase structure. A typical structure illustrated in Figure IV-14, shows a clean, inclusion-free material, possessing annealing twins

within large equiaxed grains with a grain size of about 2-3 mm. This phase will be referred to as the alpha phase.

The nearest neighbor atomic distance for nickel is $2.492 \text{ \AA}$ while that for chromium is $2.498 \text{ \AA}$. Thus chromium is not expected to substantially alter the lattice parameter of the alpha phase. From Figure IV-13, the lattice parameter of the alpha phase Ni_4Mo is seen to increase with an increase in chromium content. The lattice parameter for the Ni_4Mo alloy was found to be $3.61 \text{ \AA}$, which is very close to the value of $3.608 \text{ \AA}$ reported by Guthrie and Stansbury (24). The 3.84 wt.% Cr alloy has a lattice parameter equal to $3.621 \text{ \AA}$ evincing that the increase in the alpha phase lattice parameter, is much more than that predictable from a nearest neighbor atomic distance consideration. The hardness of all alloys in the water quenched alpha phase condition ranged from 166 to 175 DPN. No particular trend in hardness with chromium content was observed.

Alloys NMCRO (28.77 wt.% Mo) and NMCR6 (28.7 wt.% Mo, 0.41 wt.% Cr). Since these two alloys have similar microstructures, they are discussed together. The microstructure of NMCR6 aged for 16 hours at 850°C is shown in Figure IV-15. The hardness and resistivity are 370 DPN and 75 micro ohm cm, which indicates a highly long range ordered Ni_4Mo structure, the beta phase. Two distinct features can be observed. First, the matrix in the center grain appears to consist of a fine mottled structure. Second, striations are present in every grain. The striations are of two distinct kinds: The first type appears as straight lines and is parallel to annealing twin boundaries, which are traces of $\{111\}$ planes in f.c.c. structures; the

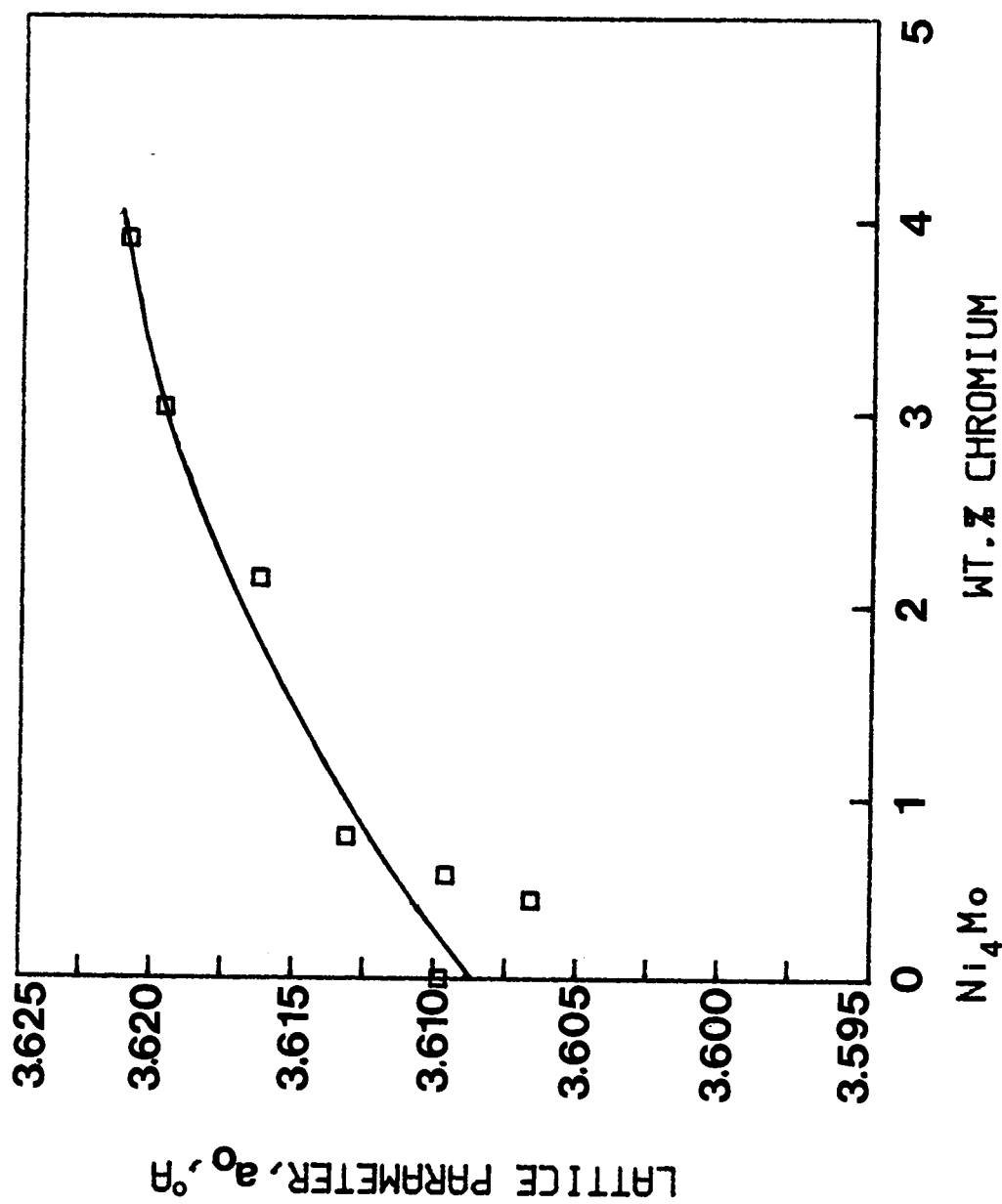


Figure IV-13. Lattice parameter of the alpha phase Ni_4Mo as a function of chromium content.

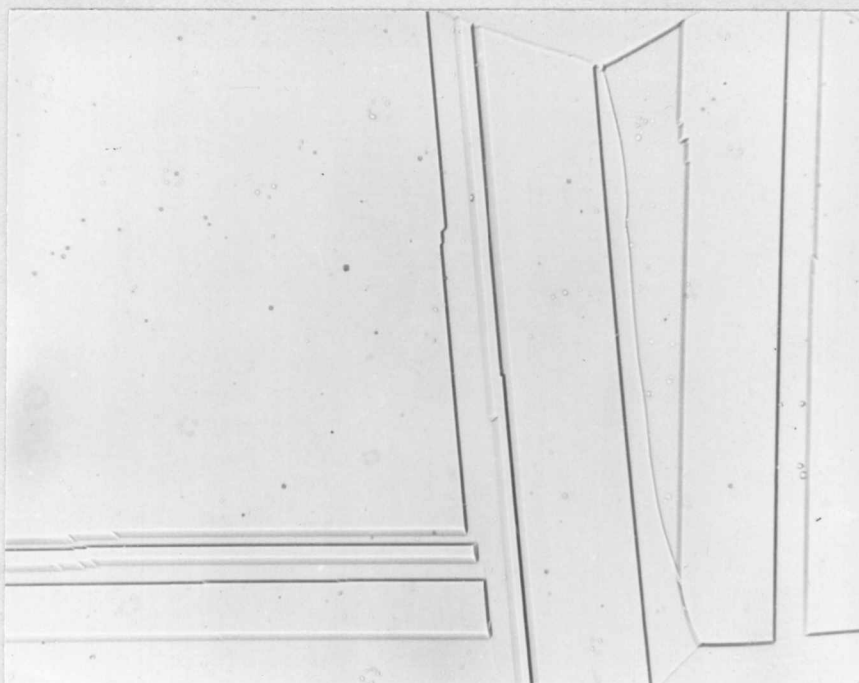


Figure IV-14. Alloy NMCR2 (2.08% Cr, 1250°C, W.Q.). Typical inclusion-free microstructure of the α phase. 200X.

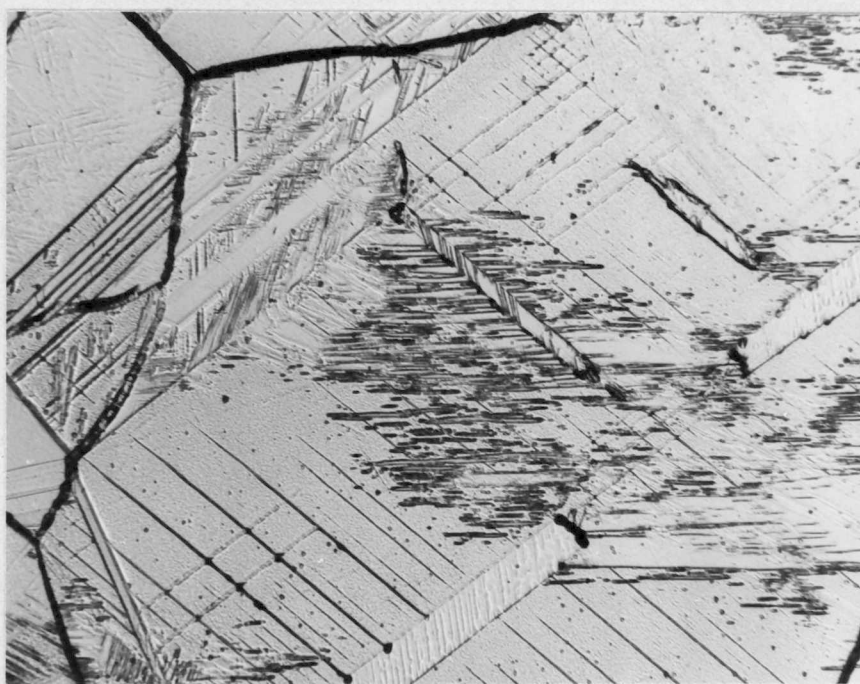


Figure IV-15. Alloy NMCR6 (0.41% Cr, 850°C, 16 HRS.). Striations associated with the β phase. 200X.

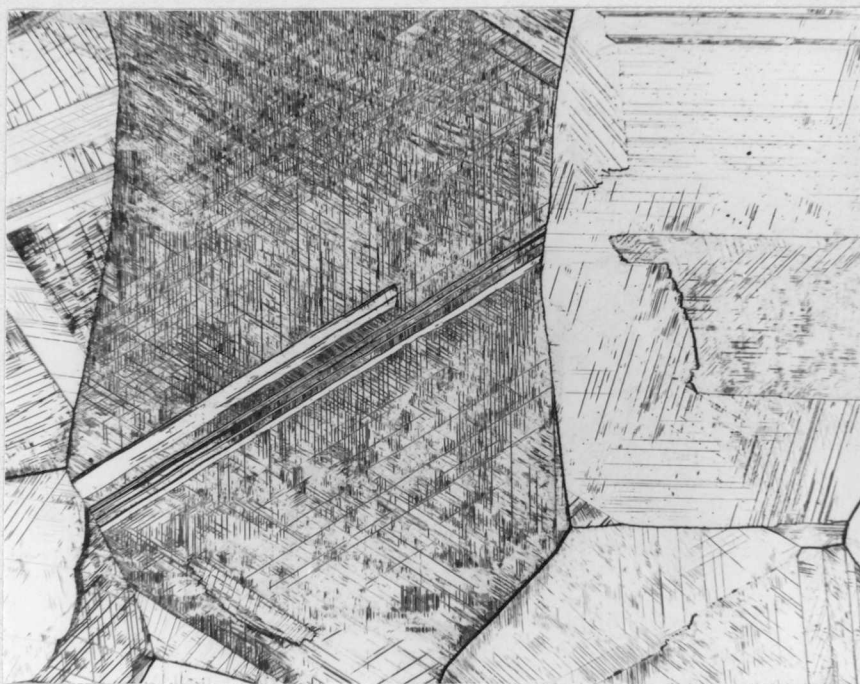


Figure IV-16. Alloy NMCr6 (0.41% Cr, 800°C, 16 HRS.). Striations associated with the β phase. 100X.

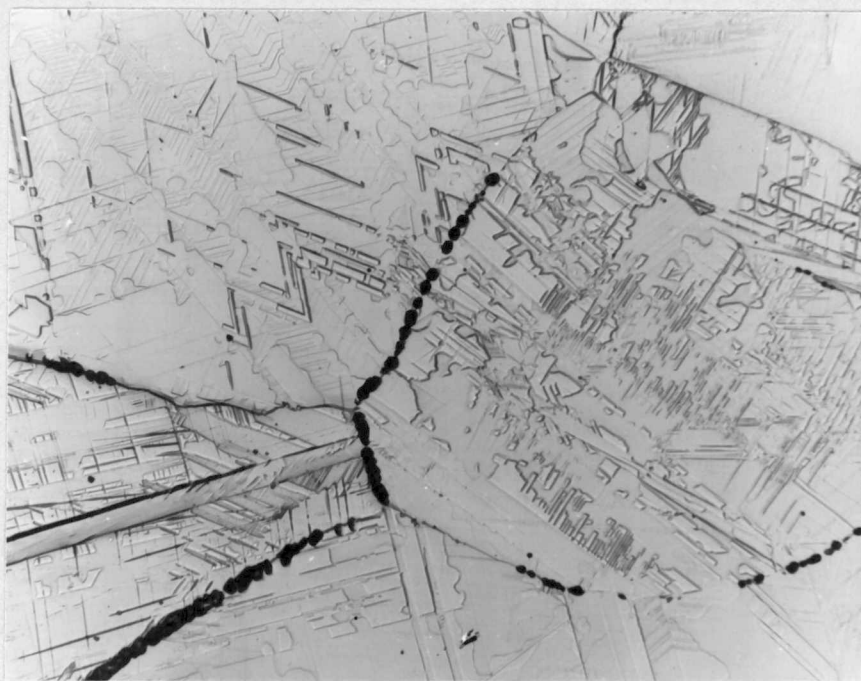


Figure IV-17. Alloy NMCrO (Ni_4Mo , 850°C, 4500 HRS.). β domain growth. 200X.

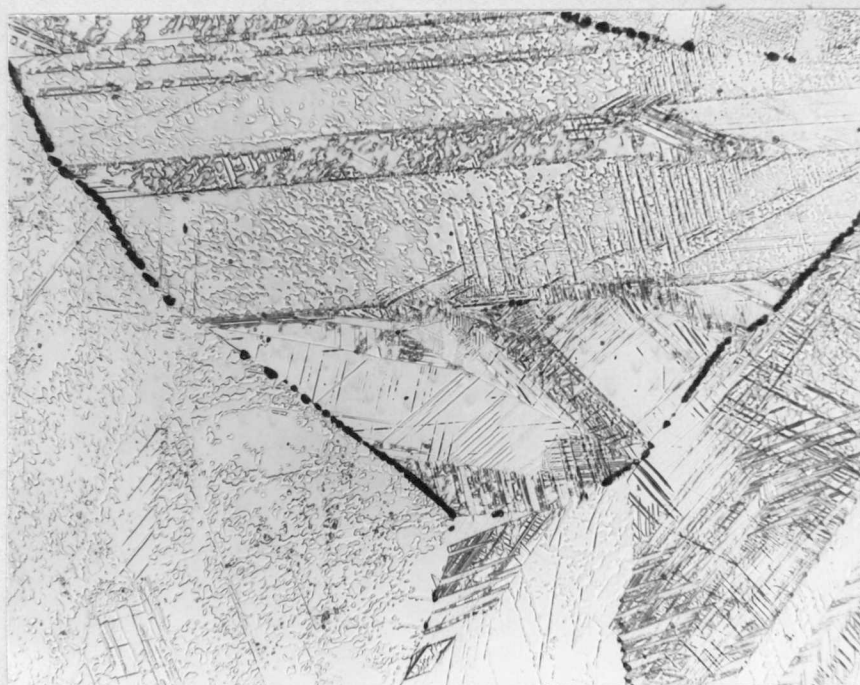


Figure IV-18. Alloy NMCRO (Ni₄Mo, 800°C, 4500 HRS.). β domain growth. 200X.



Figure IV-19. Alloy NMCRO (Ni₄Mo, 700°C, 4500 HRS.). Tapered striations in a β matrix. 200X.

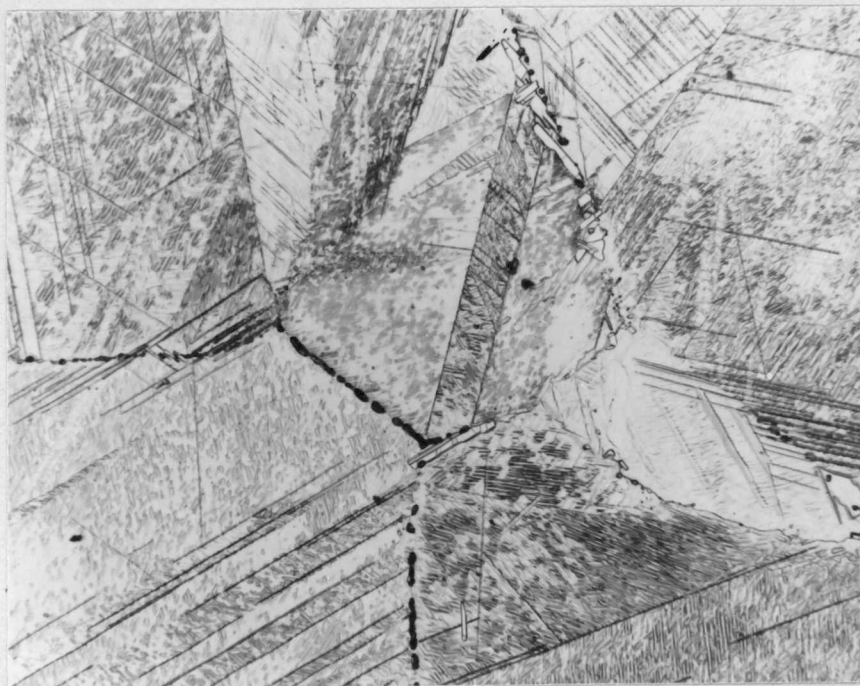


Figure IV-20. Alloy NMCR6 (0.41% Cr, 850°C, 4500 HRS.). β domains matrix, secondary $\alpha + \gamma$ G.B. reaction and δ particles at grain boundaries. 200X.

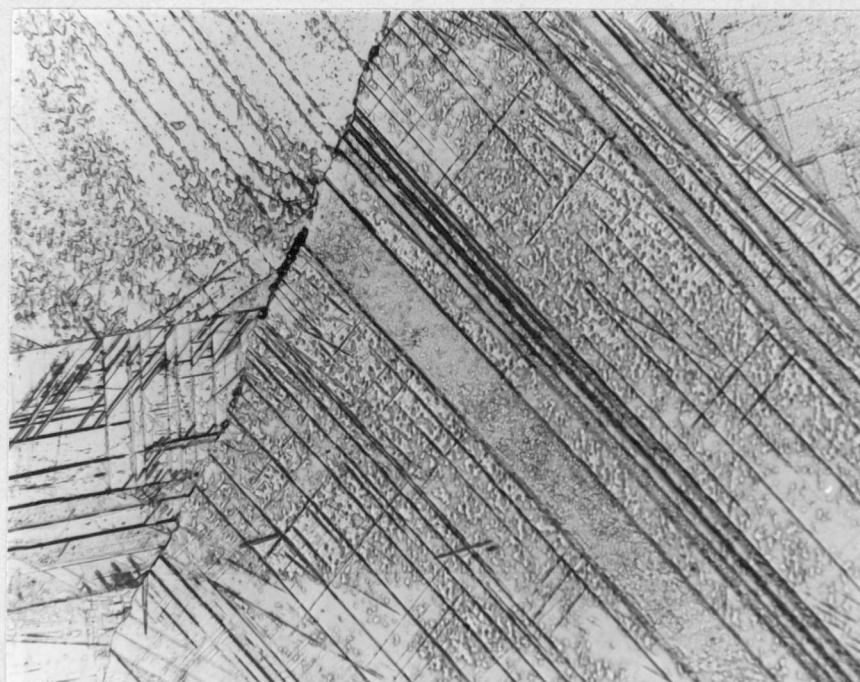


Figure IV-21. Alloy NMCR6 (0.41% Cr, 800°C, 4500 HRS.). β domain growth. 200X.



Figure IV-22. Alloy NMCR6 (0.41% Cr, 700°C, 4500 HRS.). Striations in a β matrix and secondary $\alpha + \gamma$ grain boundary reaction. 200X.

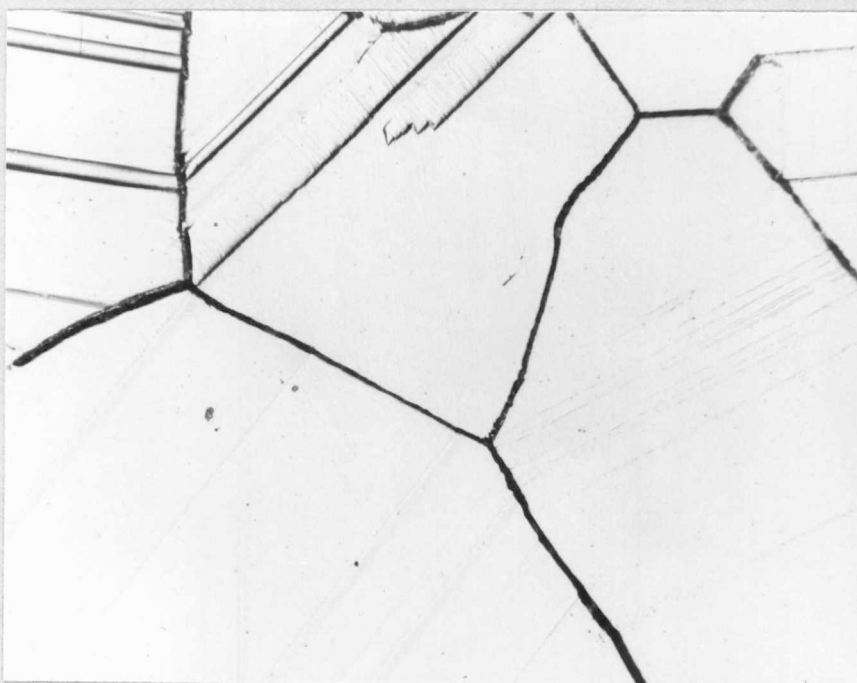


Figure IV-23. Alloy NMCR6 (0.41% Cr, 600°C, 2000 HRS.). Striations associated with the β phase and grain boundary migration. 200X.



Figure IV-24. Alloy NMCR3 (0.54% Cr, 850°C, 4500 HRS.). Wavy β domains, secondary $\alpha + \gamma$ G.B. reaction and δ phase along grain boundaries. 200X.

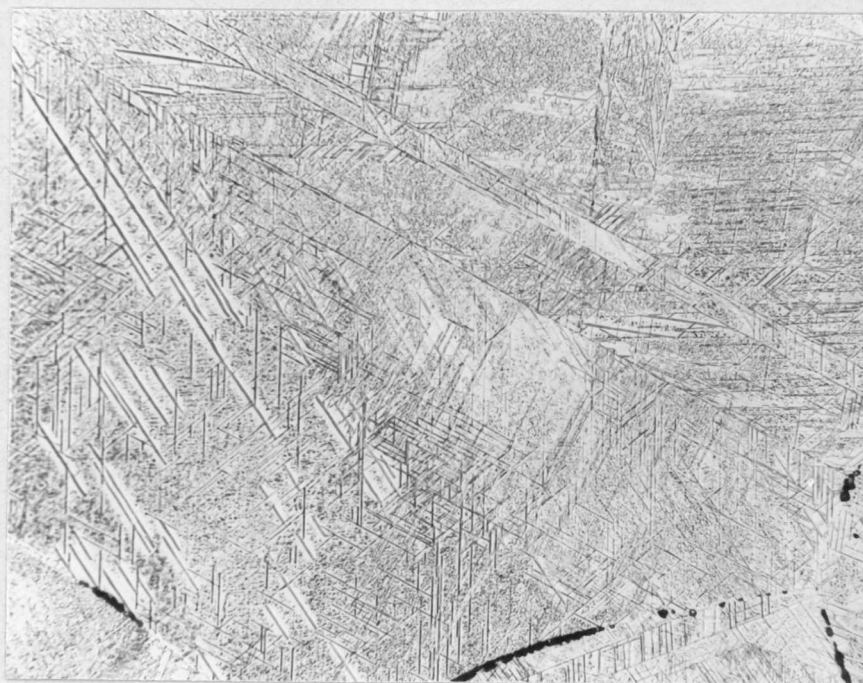


Figure IV-25. Alloy NMCR3 (0.54% Cr, 800°C, 4500 HRS.). Widmanstätten γ plates in a striated β matrix. 200X.

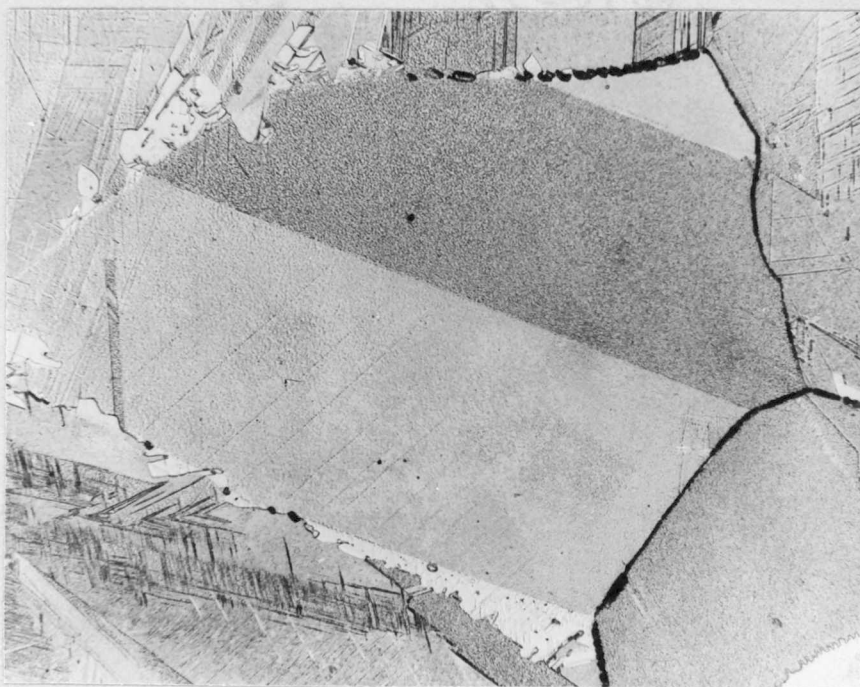


Figure IV-26. Alloy NMCR3 (0.54% Cr, 700°C, 4500 HRS.). Striations in a β matrix and secondary $\alpha + \gamma$ grain boundary reaction. 200X.

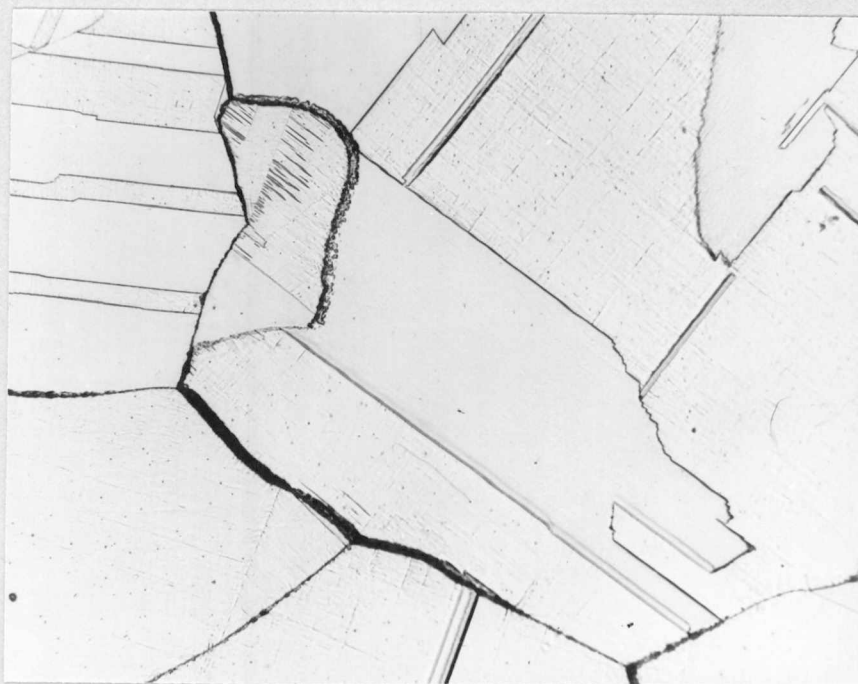


Figure IV-27. Alloy NMCR3 (0.54% Cr, 600°C, 4500 HRS.). Striations associated with the β phase and grain boundary migration. 200X.

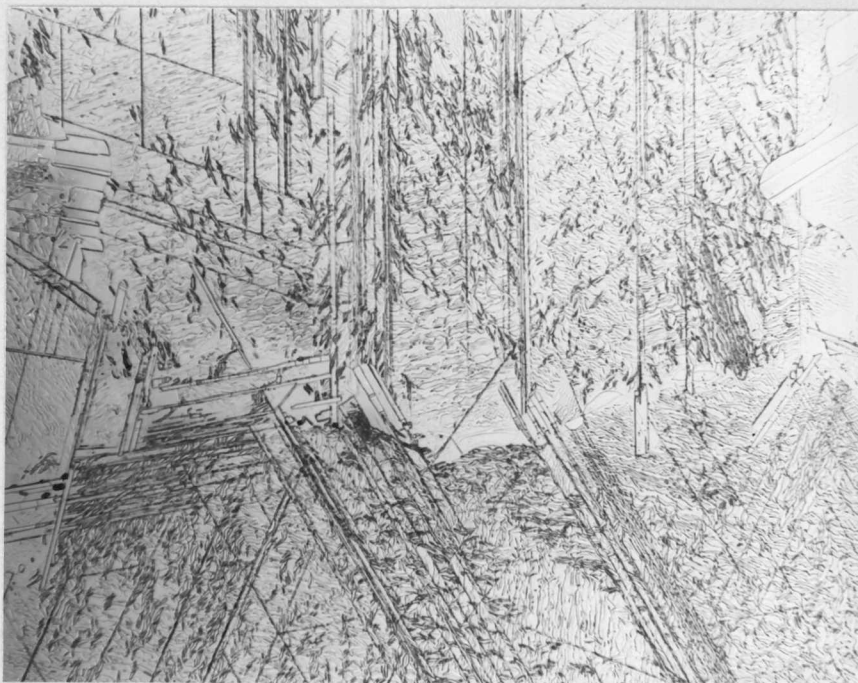


Figure IV-28. Alloy NMCR1 (0.74% Cr, 850°C, 4500 HRS.). Wavy β domains, secondary $\alpha + \gamma$ G.B. reaction and δ phase along grain boundaries. 200X.

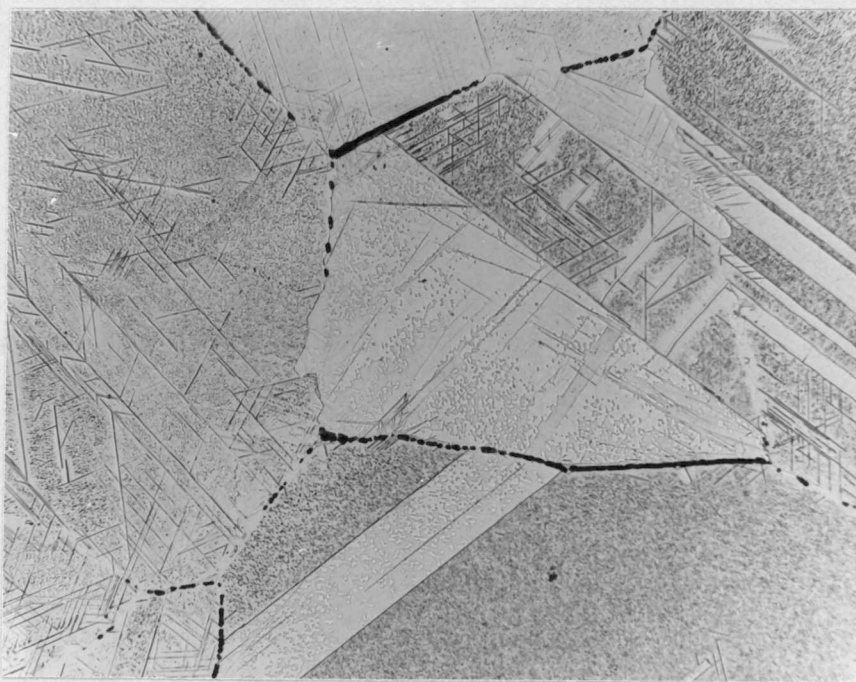


Figure IV-29. Alloy NMCR1 (0.74% Cr, 800°C, 4500 HRS.). Widmanstätten γ plates in a striated β matrix. 200X.

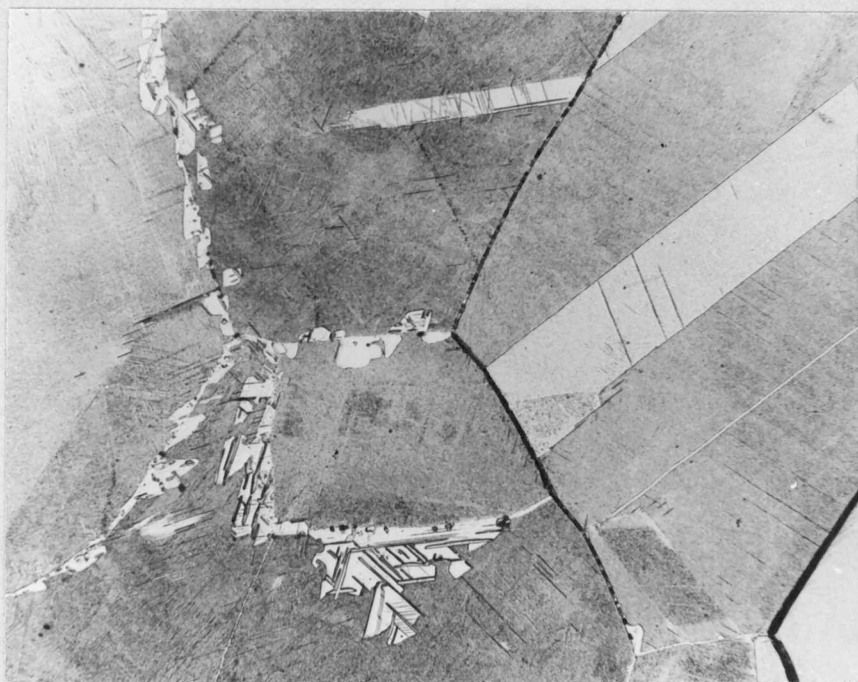


Figure IV-30. Alloy NMCr1 (0.74% Cr, 700°C, 4500 HRS.). Striations in a β matrix and secondary $\alpha + \gamma$ grain boundary reaction. 200X.

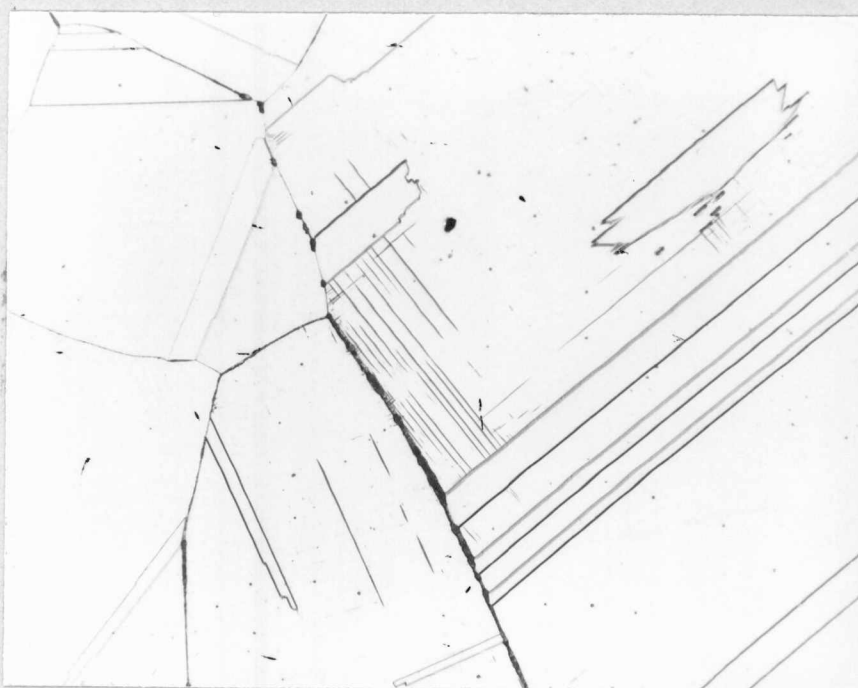


Figure IV-31. Alloy NMCr1 (0.74% Cr, 600°C, 4500 HRS.). Striations associated with the β phase and grain boundary migration. 200X.

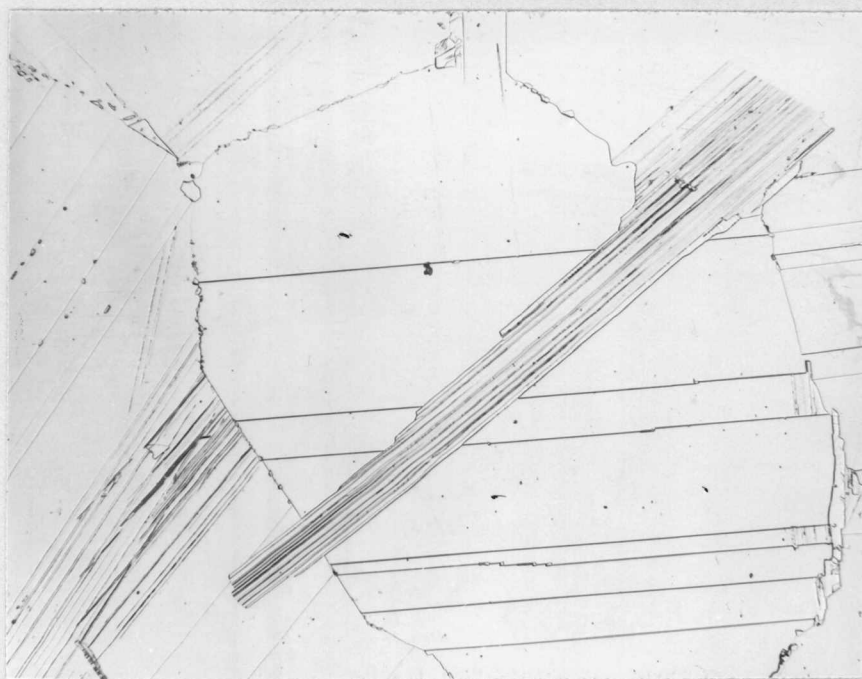


Figure IV-32. Alloy NMCR2 (2.08% Cr, 850°C, 4500 HRS.). Lamellar $\alpha + \gamma$ plates in α matrix and δ particles along grain boundaries. 200X.

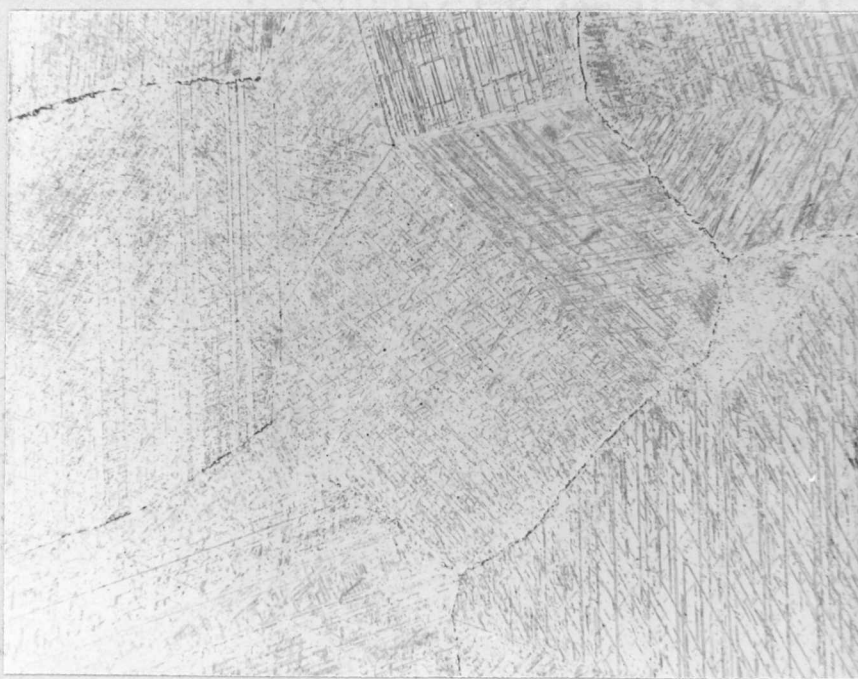


Figure IV-33. Alloy NMCR2 (2.08% Cr, 800°C, 16 HRS.). Segmented Widmanstätten plates associated with the β phase in α matrix. 200X.

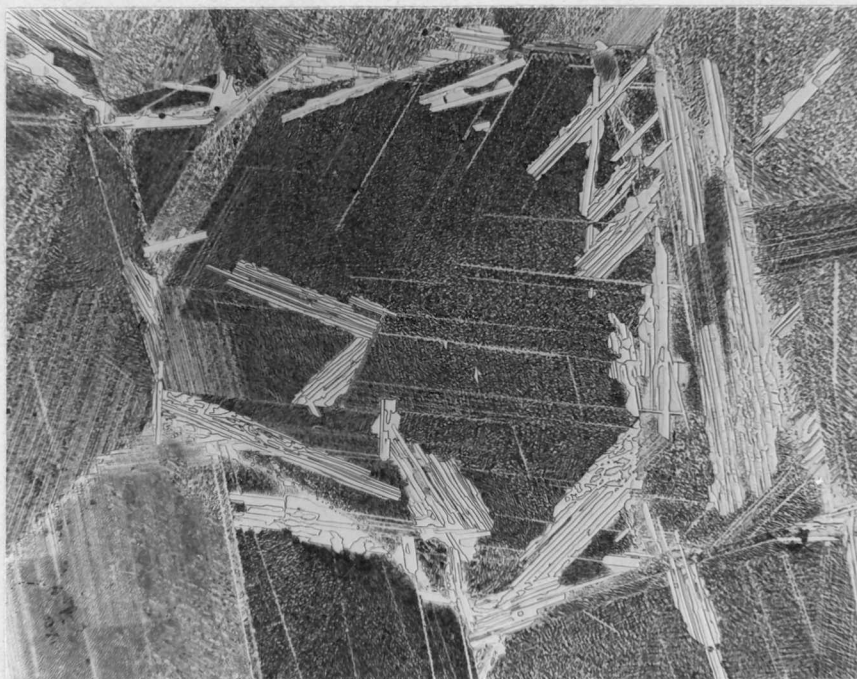


Figure IV-34. Alloy NMCR2 (2.08% Cr, 800°C, 4500 HRS.). Massive, lamellar $\alpha + \gamma$ plates in β matrix. 200X.



Figure IV-35. Alloy NMCR2 (2.08% Cr, 700°C, 4500 HRS.). Isolated γ plates in β matrix. 200X.

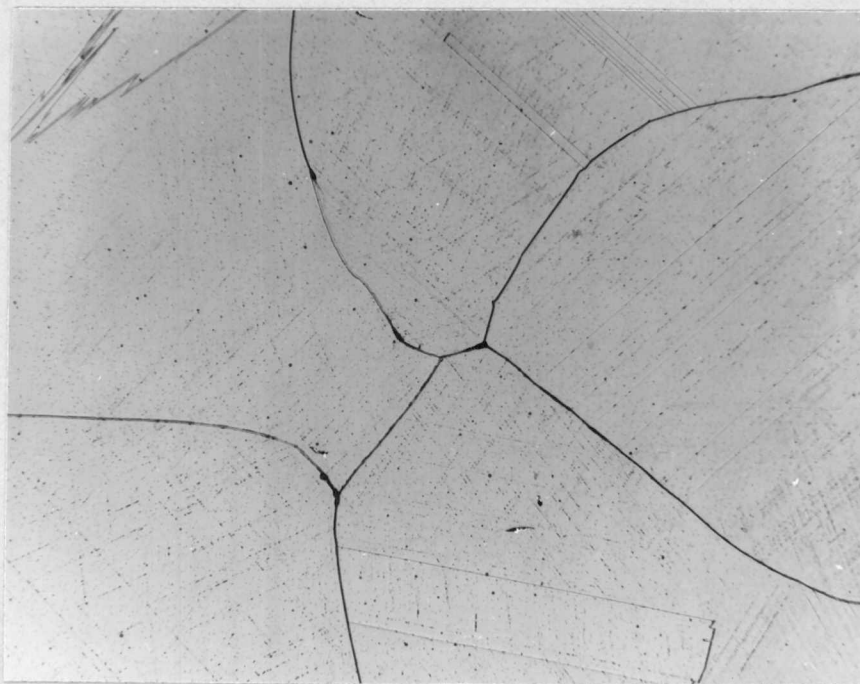


Figure IV-36. Alloy NMCR2 (2.08% Cr, 600°C, 4500 HRS.). Segmented Widmanstätten plates associated with the β phase. 200X.

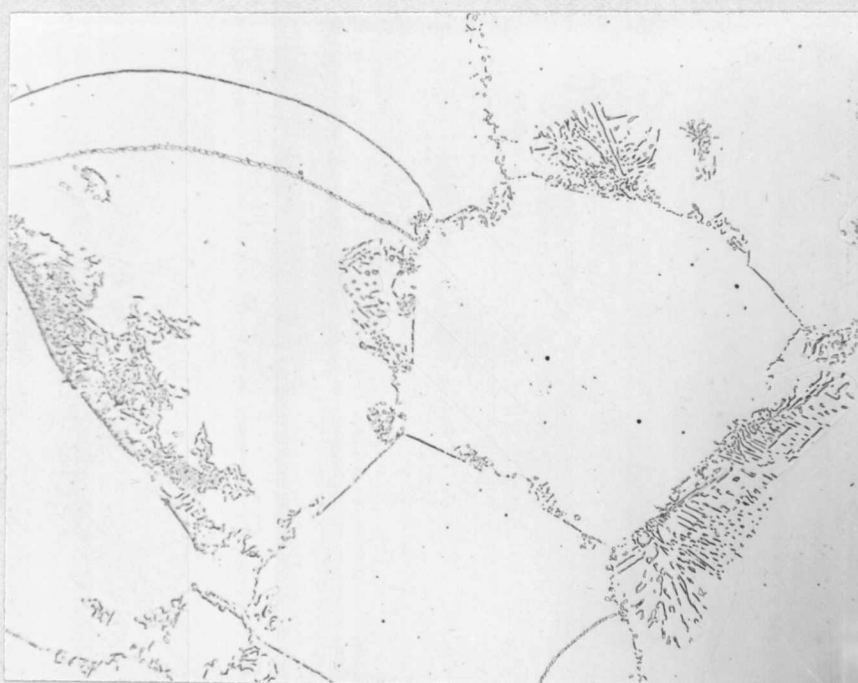


Figure IV-37. Alloy NMCR4 (2.97% Cr, 850°C, 192 HRS.). Discontinuous Precipitation of δ and γ phases in α matrix. 200X.

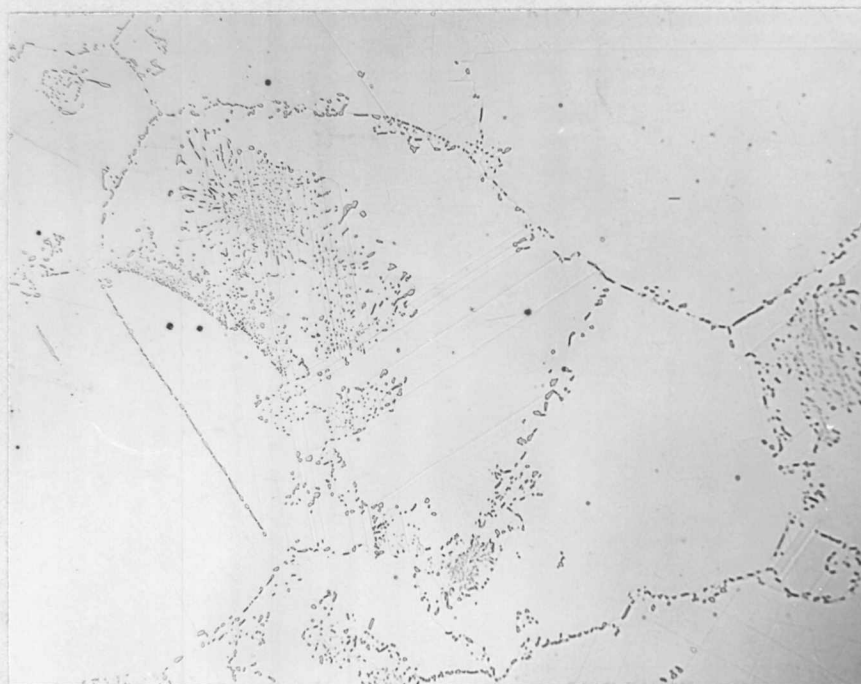


Figure IV-38. Alloy NMCR4 (2.97% Cr, 850°C, 4500 HRS.). Spreading of discontinuous reaction regions of δ and γ phases in α matrix. 200X.

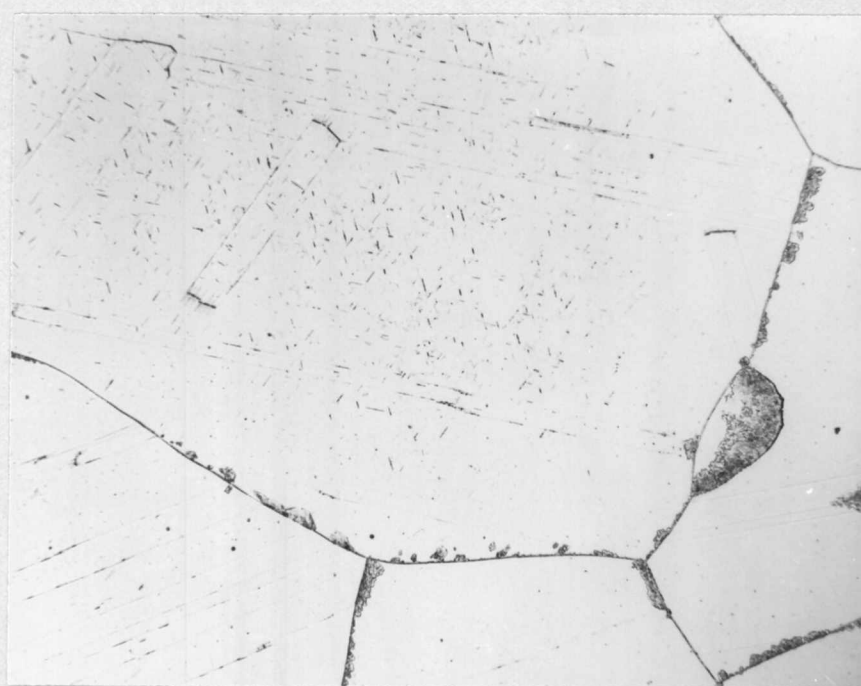


Figure IV-39. Alloy NMCR4 (2.97% Cr, 800°C, 16 HRS.). Segmented Widmanstätten plates associated with the β phase. 200X.

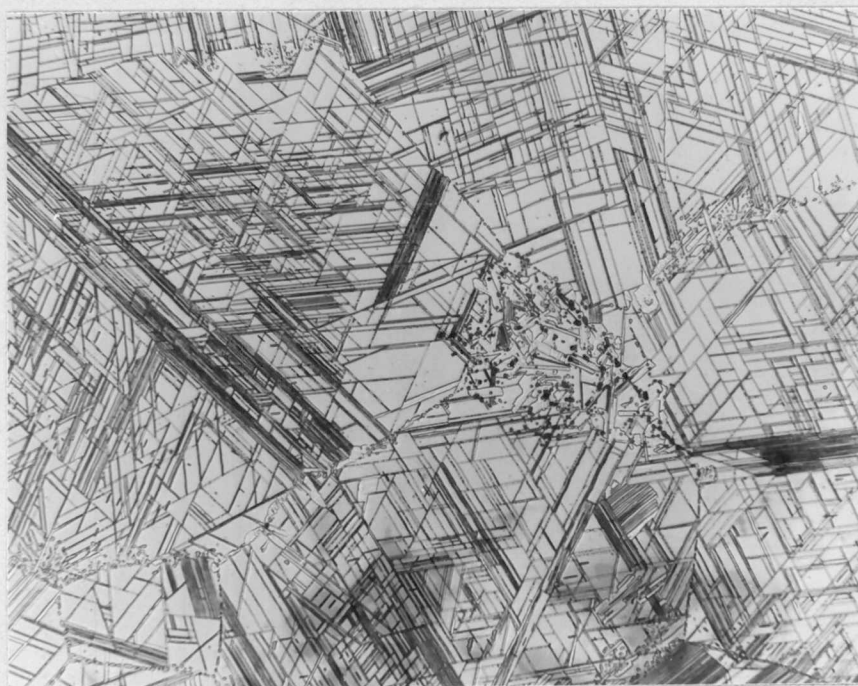


Figure IV-40. Alloy NMCR4 (2.97% Cr, 800°C, 2000 HRS.). Widmanstätten γ and δ phases in α matrix and δ particles along grain boundaries. 200X.

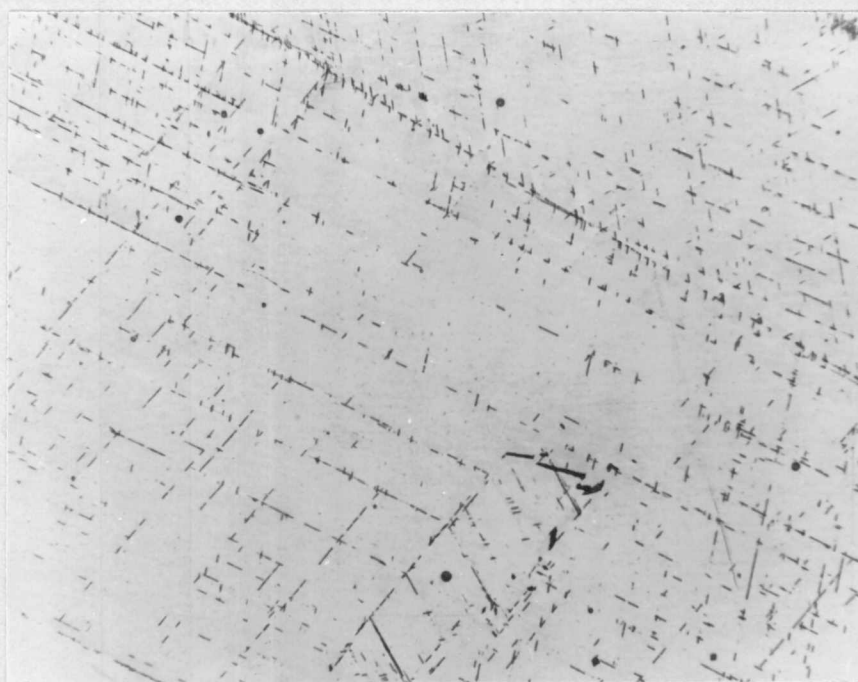


Figure IV-41. Alloy NMCR4 (2.97% Cr, 700°C, 16 HRS.). Segmented Widmanstätten plates associated with the β phase in α matrix. 500X

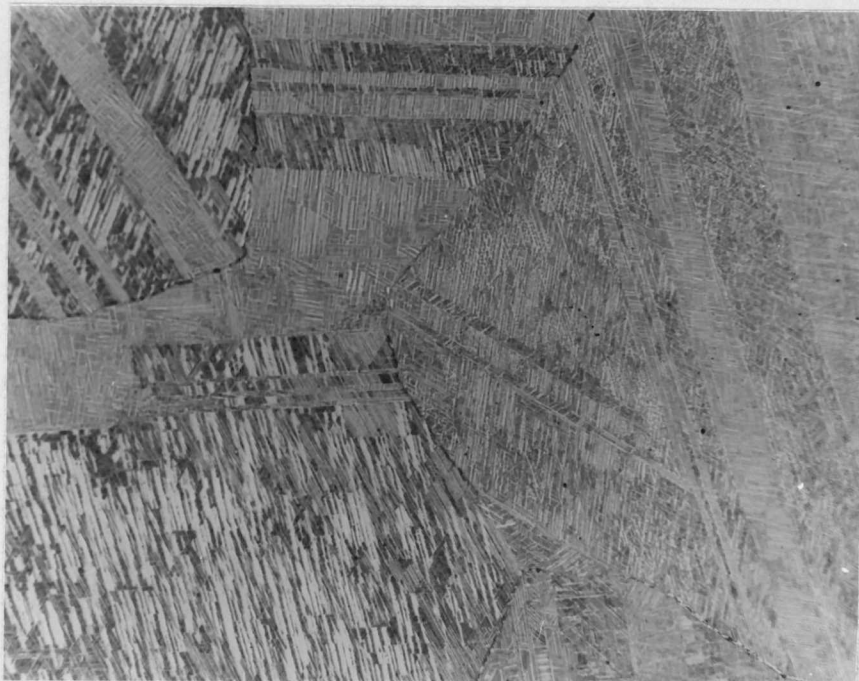


Figure IV-42. Alloy NMCR4 (2.97% Cr, 700°C, 4500 HRS.). Widmanstätten γ plates in β matrix. 200X.

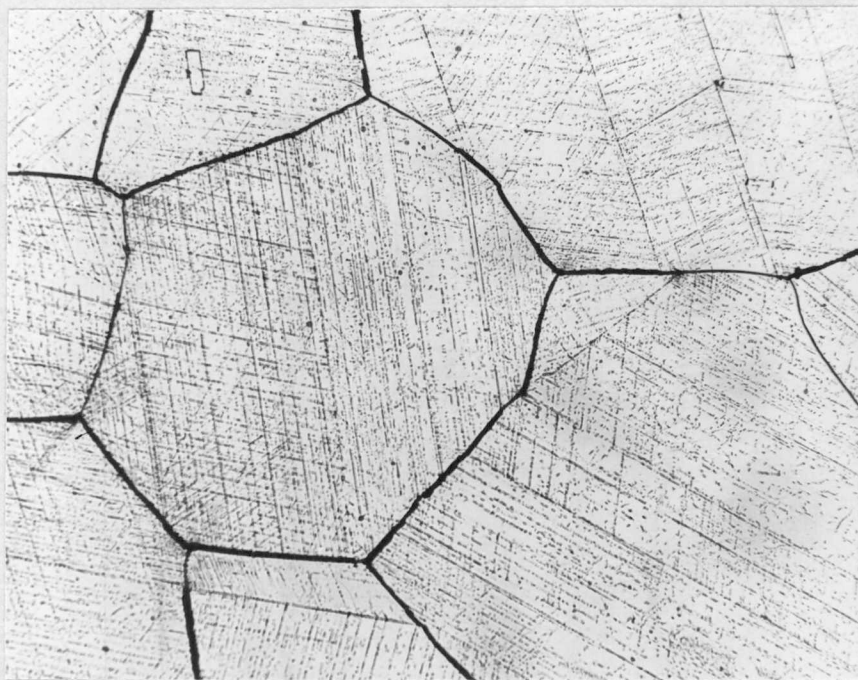


Figure IV-43. Alloy NMCR4 (2.97% Cr, 600°C, 4500 HRS.). Segmented Widmanstätten plates associated with the β phase. 200X.

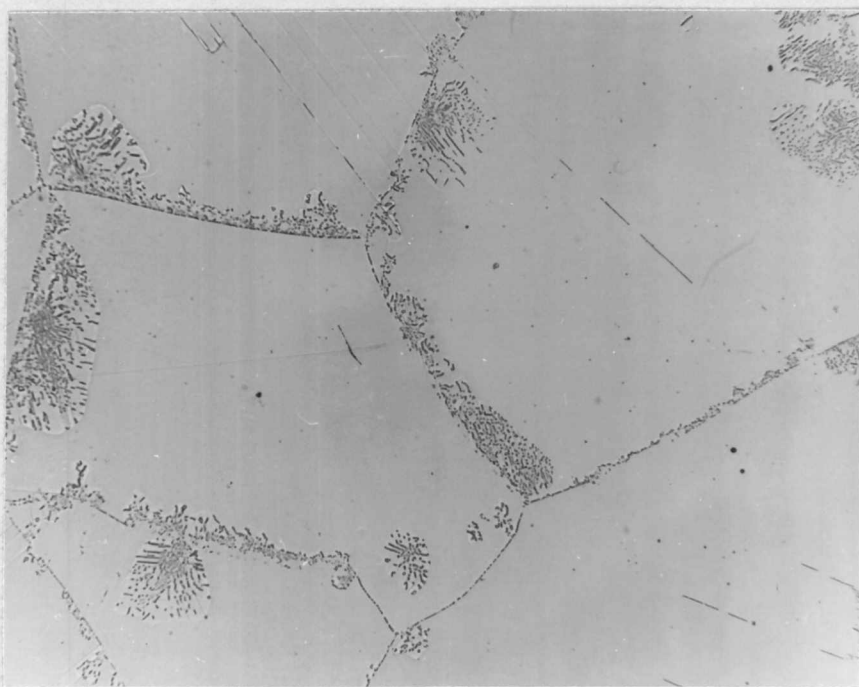


Figure IV-44. Alloy NMCR5 (3.84% Cr, 850°C, 192 HRS.). Discontinuous Precipitation of δ and γ phases in α matrix. 200X.

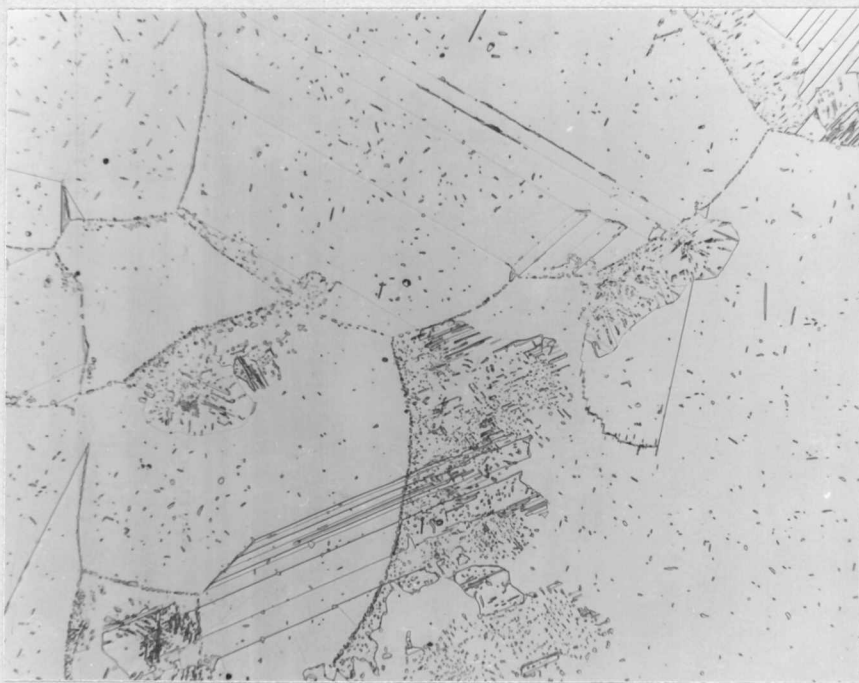


Figure IV-45. alloy NMCR5 (3.84% Cr, 850°C, 4500 HRS.). Uniform δ and γ associated with discontinuous reaction in α matrix. 200X.

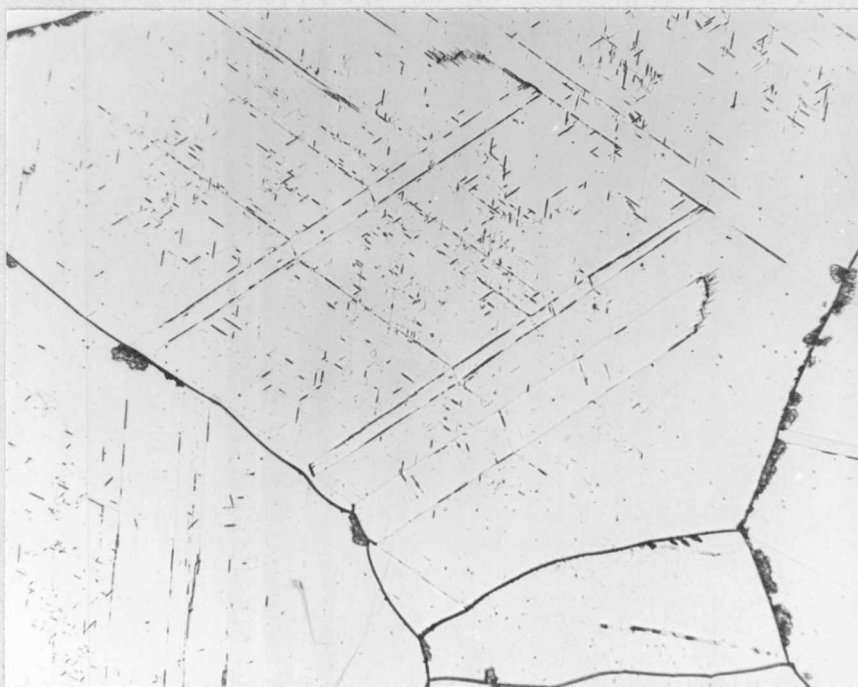


Figure IV-46. Alloy NMCR5 (3.84% Cr, 800°C, 16 HRS.). Segmented Widmanstatten plates associated with the β phase in α matrix. 200X

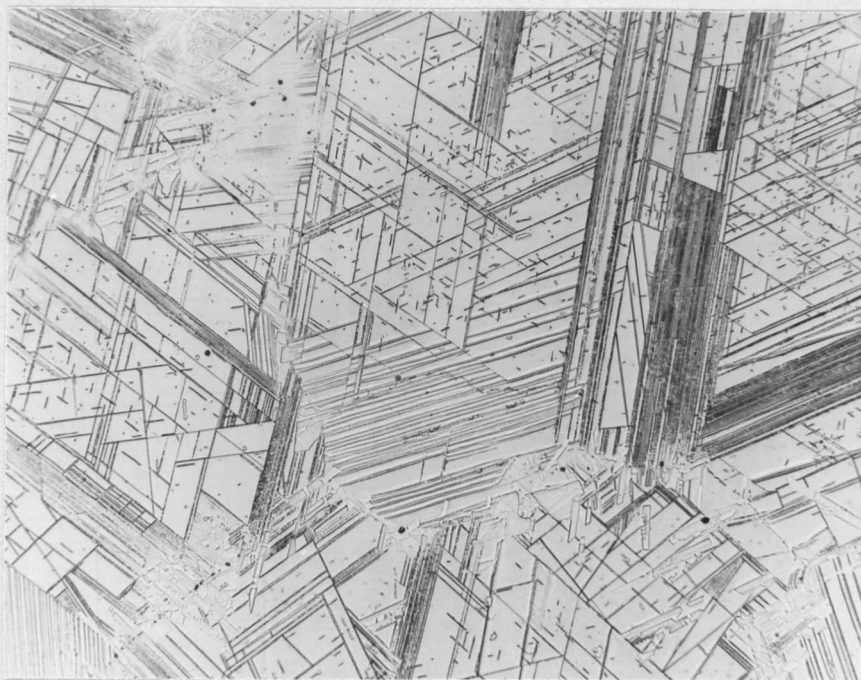


Figure IV-47. Alloy NMCR5 (3.84% Cr, 800°C, 4500 HRS.). Widmanstatten γ and δ in α matrix, secondary γ plates and δ at grain boundaries. 200X.



Figure IV-48. Alloy NMCR5 (3.84% Cr, 700°C, 16 HRS.). Segmented Widmanstätten plates associated with the β phase in α matrix. 200X.

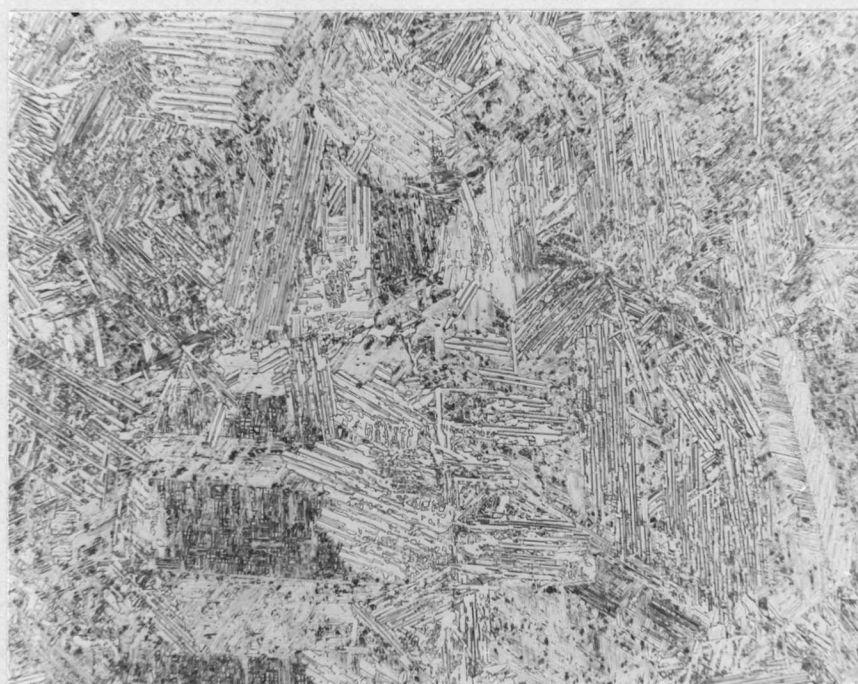


Figure IV-49. Alloy NMCR5 (3.84% Cr, 700°C, 4500 HRS.). Lamellar γ plates in β matrix. 200X.



Figure IV-50. Alloy NMCR5 (3.84% Cr, 600°C, 2000 HRS.). Segmented Widmanstätten plates associated with the β phase. 200X.

second type, also visible in the center grain in Figure IV-15 is never parallel to twin boundaries and appears as irregular tapered bands.

The straight striations have the same characteristics as those reported by Guthrie and Stansbury (24), Spruiell (93) and Lei (10). Spruiell (93) using a two-surface trace analysis established these as traces of $\{111\}$ f.c.c. planes. Lei (10) observed these to be parallel to more than one twin boundary and arrived at the same conclusion. In this research, these striations can be seen in the center grain in Figures IV-15 and -16 to be oriented in three different directions, each one parallel to an annealing twin boundary. These are hence identified as $\{111\}$ f.c.c. striations.

Using a single-surface trace analysis Lei (10) established the second type of striations as parallel to $\{110\}$ f.c.c. planes. In this research this fact is confirmed by the following two observations in the center grain of Figure IV-15. First, two of the annealing twins are roughly perpendicular, indicating that the orientation of the grain is very close to a $\langle 001 \rangle$. Second, the tapered striations make an angle of 45° with twin boundaries. These striations will be referred to as $\{110\}$ f.c.c. striations.

The $\{111\}$ striations begin appearing in just 10 minutes on aging at 850°C and 800°C and after 10 hours at 700°C . The striations are slightly finer at 800 and 700°C , which could be only an etching effect. This is shown in Figure IV-16 for alloy NMCR6 aged for 16 hours at 800°C . With an increase in aging time the $\{111\}$ striations decrease in number, especially with the onset of the $\{110\}$ striations and the mottled beta matrix which becomes more distinct with time,

eventually developing into resolvable β domains. This is shown in Figure IV-17 and -18 for alloy NMCRO (Ni_4Mo composition) aged for 4500 hours at 850 and 800°C respectively. In Figure IV-17, in the upper grain, the β appears as large amoeba-shaped regions with irregular boundaries. Each patchy region is presumably an individual domain of the beta phase. These patchy domains are also observed at 800°C (Figure IV-18), but not at 700°C (Figure IV-19). Moreover, comparison between Figures IV-17, -18 and -19 reveals that the size of the domains decreases with a decrease in temperature (from 850 to 700°C). This is consistent with the temperature dependence of nucleation and growth processes. The dark clutter of precipitates at the grain boundary were determined by SEM as holes. Also tremendous grain boundary migration can be observed in Figures IV-17, -18 and -19.

Microstructures of alloy NMCR6 (0.41 wt.% Cr) aged for 4500 hours at 850, 800 and 700°C are shown in Figures IV-20, -21 and -22 respectively. The microstructure is essentially that of the Ni_4Mo alloy (under the same conditions), but subtle differences exist. For example, fewer patchy beta domains are present at 850°C. The size of the domains at 850 and 800°C are smaller than those shown in Figures IV-17 and -18 for the Ni_4Mo alloy, indicating that even small amounts of chromium tend to decrease domain growth. The beta domains observed in general in Figure IV-20, tend to be elongated.

X-ray diffractometer methods to identify different phases present proved unprofitable owing to the small size of the specimens and concomitant large grain size. Though a splitting of fundamental lines into superlattice lines was observed, the results were not very

reproducible. As a result SEM analysis was conducted to determine through energy dispersive x-rays (EDAX) the local identity of phases.

Besides the presence of the characteristic beta phase, two additional features can be observed at the grain boundaries in Figures IV-20 and -21. One is the presence of light etching precipitates along the grain boundaries and the second is a broad Widmanstatten plate type phase either growing along the boundary or into the grain. The former was identified by SEM as highly molybdenum-rich particles relative to the matrix and is identified as the delta phase. The latter was slightly richer in molybdenum than the matrix and is identified as the gamma phase. A light, clear region usually exists around the Widmanstatten plates and is presumably the alpha phase. The grain boundary delta phase was observed at relatively early times while the gamma phase did not appear till prolonged times of aging. These features will be discussed in more depth by means of SEM micrographs.

At 700°C, after 4500 hours the beta domains are finer than those at 850 and 800°C as shown in Figure IV-22. Also a rather sharp grain boundary reaction resulting in extensive migration can be observed. The migrated regions appear to consist of striations surrounded by light regions. The former was identified by SEM as gamma and the latter as alpha.

After aging alloy NMCR6 for 4500 hours at 600°C, the hardness and resistivity were 383 DPN and 57 micro ohm cm., which based on data at higher temperatures indicates a completely long range ordered beta structure. However, as shown in Figure IV-23, the microstructure does

not have the characteristic features of the beta phase. There is some boundary migration and closer examination reveals what appears to be the presence of faint {111} striations. Presumably beta domains are not observable optically because of their fineness resulting from the low temperature. Study of the morphology of these domains will require transmission electron microscopy.

Alloys NMCR3 (28.67 wt.% Mo, 0.54 wt.% Cr) and NMCR1 (28.68 wt.% Mo, 0.74 wt.% Cr). These two alloys have markedly similar structures under all the aging conditions and are hence discussed together. The hardness and resistivity behavior are slightly different from the binary Ni_4Mo alloy and alloy NMCR6 (0.41 wt.% Cr). However, the microstructural differences observed in alloy NMCR6 relative to the Ni_4Mo alloy are more pronounced in these two alloys.

Broadly the features observed are the same; both the {111} and {110} f.c.c. striations are observed at the three higher temperatures. However, the {111} striations disappear completely in about 10 hours at 800 and 850°C and 840 hours at 700°C. At each of these three temperatures the maximum in hardness occurs before the disappearance of the {111} striations. After 4500 hours at the two higher temperatures, striations resembling these appear but it is difficult to identify these conclusively as being {111} striations because Widmanstätten gamma phase looks similar. The mottled matrix beta also appears sooner at 850 and 800°C and grows on further aging but at a decreased rate as compared to Ni_4Mo and 0.41 wt.% Cr alloys. In addition, much more reaction occurs at the grain boundaries and at relatively shorter times.

Microstructures of alloy NMCR3 and NMCR1 aged at 850, 800, 700 and 600°C for 4500 hours are shown in the set of Figures IV-24 to -27 and Figures IV-28 to -31 respectively. The similarity between the microstructures at equivalent temperatures is evident.

Figures IV-24 and -28 show that after 4500 hours at 850°C both alloys, unlike the binary, show no patchy beta domains. Instead, in slight contrast to the 0.41 wt.% Cr alloy, the domains have a doe-eye or flame-shaped morphology with six orientations as shown by the upper grain in Figures IV-24 and -28. Also much more grain boundary reaction can be observed. Particles of delta phase are present along the grain boundaries. Also increased formation of gamma plates as a secondary reaction surrounded by alpha phase occurs and is more in the 0.74 wt.% Cr alloy. These plates form along and away from the grain boundary. Evidently a reaction of type $\beta \rightarrow \alpha + \gamma$ occurs. A third feature shown in the lower grain in Figures IV-24 and -28 is the presence of closely grouped striations. Although not clearly resolvable in these figures, frequently gamma plates occurred among these striations, suggesting that the grouped striations are an intermediate step in the formation of the gamma plate phase. These grouped striations will be referred to as γ' .

Both 0.54 and 0.74 wt.% Cr alloys after aging at 800, 700 and 600°C, show the same characteristics of the beta phase as the binary and the 0.41 wt.% Cr alloys. As can be seen from Figures IV-25 and -29, on aging at 800°C for 4500 hours, both alloys show patchy domain growth and some grain boundary migration. The patchy domains however, are smaller than equivalent ones in the binary and 0.41 wt.% Cr

alloys. A few additional features not present in the binary can be seen. For example, in the center grain of Figure IV-25 and left grain in Figure IV-29, many of isolated Widmanstatten gamma plates surrounded by a halo are present. These plates appeared initially in both alloys after 384 hours and are usually oriented in only one direction in each grain. Adjacent to the halo alpha region many blocky particles can be seen. The molybdenum content of these particles is uncertain, some measurements indicating the same molybdenum as the matrix beta and others that the molybdenum content was closer to that of the gamma phase. These particles generally, were seen to lie along domain boundaries. The gamma plates appear to form by consuming these, suggesting that they occur as an intermediate step. For lack of more substantial evidence, the reason for this morphology is unknown at the present time. The gamma plates are not as massive as those occurring at 850°C. The grain boundary reaction is also less and little δ phase was observed at the grain boundaries.

At 700°C, in both alloys, as shown in Figures IV-26 and -30, no patchy domain growth can be seen. Instead the beta matrix is very fine and hardly resolvable. Extensive grain boundary reaction accompanied by migration is observed. Within these boundary reaction zones, Widmanstatten striations of gamma surrounded by alpha phase are present and movement of the boundary into the grain appears to occur at the expense of the matrix beta.

At 600°C, after 4500 hours the hardness and resistivity correspond to that of the beta phase, but the microstructures in Figures IV-27 and -31 show only few striations. No domains are

observed presumably due to their fineness. However, in consistence with the binary alloy, the structure in both alloys is identified as beta phase.

Alloy NMCR2 (28.29 wt.% Mo, 2.08 wt.% Cr). The morphology of this alloy appears as a transition between the 0.74 wt.% Cr and the 2.97 wt.% Cr alloys. First, throughout the aging period at 850°C, the resistivity corresponds to that of the water-quenched alpha phase. The microstructure as seen in Figure IV-32 for a sample aged for 4500 hours at 850°C, is predominantly alpha phase. However, a grain boundary reaction (which commences at early times) resulting in the formation of delta particles is seen. In addition, in the center grain of Figure IV-32, a massive lamellar morphology consisting of alternate alpha and gamma phases (determined by SEM) is observed to extend from one grain boundary, through the grain, into the opposite boundary. At the right end, closely grouped γ' striations can also be seen and it is evident that the lamellar gamma plates form from these.

Figure IV-33 shows that after 16 hours at 800°C, segmented {111} striations in addition to the grain boundary delta phase are present. The striations are not continuous but are broken up into small Widmanstatten plates oriented in three directions, each parallel to a twin boundary. Row of these lie parallel to a twin boundary, suggesting growth on {111} planes in a $\langle 111 \rangle$ direction. With aging, these plates are superseded by the formation of the mottled beta matrix. After aging 4500 hours at 800°C, the microstructure as seen in Figure IV-34, consists of wavy beta domains with numerous massive, lamellar gamma plates around the grain boundaries. No patchy

beta domains are observed apparently because of inhibited growth rates caused by addition of chromium. The gamma plates appear initially after 384 hours. Besides grouped γ' striations (lower corner Figure IV-34), a new type of thin long Widmanstatten striations can also be seen in the center grain. These striations have three different orientations, each parallel to a twin boundary and were identified using SEM as also being the gamma phase. The beta domains appear similar to the ones formed at 850°C in the lower chromium alloys (Figures IV-24 and -28) and have six distinct orientations.

At 700°C, after 4500 hours, the hardness and resistivity are 419 DPN and 75 micro ohm cm respectively. The microstructure as shown in Figure IV-35 consists of many individual gamma plates in a very fine mottled beta matrix. Most of the microstructures at early times, were obscured by a tenacious oxide film formed by the etchant and hence it was difficult to discern details. Some delta phase was found at grain boundaries.

Hardness and resistivity data at 600°C indicates that the reaction is still not complete after 4500 hours. In Figure IV-36, the structure is seen to consist of segmented $\{111\}$ striations in presumably a matrix of β and very little α .

Alloys NMCR4 (28.28 wt.% Mo, 2.97 wt.% Cr) and NMCR5 (28.07 wt.% Mo, 3.84 wt.% Cr). With a few exceptions the microstructures of these two alloys are similar. Aging at 850°C results in a slight increase in hardness and a small drop in resistivity. Examination of the microstructure reveals a grain boundary reaction at very early times (10 minutes). The reaction appears as a classical Discontinuous

Precipitation reaction and is shown in Figure IV-37 and -44 for the two alloys aged for 192 hours at 850°C. Two types of precipitates are observed within the discontinuous reaction zones. The lamellar ones were identified by SEM as gamma, while the globular ones (especially at grain boundaries) were identified as delta phase; the surrounding matrix phase is alpha. Thus a discontinuous precipitation of delta and gamma phases can be said to occur. Besides this reaction, presence of Widmanstatten precipitates of gamma within grains can also be seen in Figure IV-37 and -44. With time, the discontinuous reaction regions gradually spread into the grains, the spreading being more in the higher chromium alloy. This is shown in Figures IV-38 and -45 for the two alloys aged at 850°C for 4500 hours. In the case of the 3.84 wt.% Cr alloy, it can be seen that the gamma and delta are present uniformly throughout the grains.

At 800°C, the reactions, confirmed by changes in the hardness and resistivity, are much slower than the lower chromium alloys. In both alloys, a discontinuous precipitation reaction commences at early times, but not to the extent to which it occurs at 850°C. Also the reaction appears to be strongly dependent on the relative orientation of adjacent grains. Shortly afterwards, small Widmanstatten plates appear usually within grains, indicating that a zone depleted in molybdenum adjacent to the grain boundary exists. Presumably most of the molybdenum around the grain boundaries diffuses to the boundary for the formation of richer molybdenum phases such as gamma and delta.

Typical Widmanstatten plate structure identified tentatively as the beta phase is shown for the 2.97 and 3.84 wt.% Cr alloys aged at

800°C for 16 hours in Figures IV-39 and -46 respectively. The Widmanstatten plates can be seen to possess 3-4 distinct orientations each parallel to a twin boundary, indicating formation on $\{111\}$ f.c.c. planes. Additionally a second type of short, lighter-etching Widmanstatten plates (not readily visible in the micrograph) are also seen. These plates also possess three orientations, two of which are different from the other type (not parallel to twin boundaries), while the third one is parallel to a twin boundary. This indicates that the plates form parallel to $\{001\}$ f.c.c. planes. The identity of these plates is not known at this point and requires more detailed analysis. The Widmanstatten beta plates increase slightly in number with time till about 192 hours, at which point thin, long Widmanstatten striations of the gamma phase in copious amounts begin appearing. This is shown in Figure IV-40 for the 2.97 wt.% Cr alloy aged for 2000 hours and in Figure IV-47 for the 3.84 wt.% Cr alloy aged for 4500 hours.

The thin Widmanstatten gamma possesses three orientations, each parallel to a $\{111\}$ f.c.c. trace. This observation can be understood by recalling from Figure II-4 (page 21) the crystal structure relationship between the gamma and alpha phase. The gamma can also be considered as a hexagonal close packed superlattice with the basal plane parallel to the $\{111\}$ of the alpha. This is supported by the fact that the atomic arrangement on these two planes is the same and minimum lattice strain results when $\{111\} // \{0001\}$. With time coarsening and break up of the striations into rectangular blocks as shown in Figures IV-40 and -47 occurs.

The gamma phase also appears as a secondary coarsening reaction at later times. These can be seen in Figures IV-40 and -47 as broad plates at the grain boundaries. The short beta plates persist in small amounts till the late stages of aging and are then replaced by similar looking but slightly broader Widmanstatten plates. These were identified by SEM as delta phase.

At 700°C, the reactions are somewhat slower in the 3.84 wt.% Cr alloy. After 16 hours, both alloys show segmented Widmanstatten beta plates. These possess the same orientation relationship as the ones at 800°C and display a propensity towards formation on twin boundaries. Since the hardness has not attained the values for LRO beta, this morphology is developing simultaneous with the LRO reaction. A grain boundary reaction also occurs but is much less~~er~~ than the one at the higher temperatures. These features are shown in Figures IV-41 and -48 respectively for the two alloys aged for 16 hours. Again in consistence with the resistivity and hardness results, the reactions are more rapid in the 2.97 wt.% Cr alloy than the 3.84 wt.% Cr alloy. Formation of the matrix beta phase was observed to occur with rapidity after 16 hours in the 2.97 wt.% Cr alloy, while in the 3.84 wt.% Cr alloy the Widmanstatten beta in an alpha matrix persists till longer times.

The rapid increase in hardness at later times in the 2.97 wt.% Cr alloy (Figure D-4, Appendix D), is marked microstructurally by the appearance initially of broader plates of gamma phase, followed by thin Widmanstatten gamma striations. In the 3.84 wt.% Cr alloy the sequences are reversed, the thin Widmanstatten gamma appearing first

and then the broader plates of gamma accompanied by rapid increase in hardness (Figure D-5, Appendix D). Thus it appears that the broad gamma plates are responsible for the high hardness at 700°C in these alloys. These features are shown in Figures IV-42 and -49 respectively for the two alloys aged at 700°C for 4500 hours. It can be seen that the 2.97 wt.% Cr alloy contains more matrix beta (darker regions in the micrograph) than the 3.84 wt.% Cr alloy. Moreover, the morphology and amounts of the gamma plates is different in the two alloys. While the plates are separated and aligned in one direction in the 2.97 wt.% Cr alloy, those in the 3.84 wt.% Cr alloy are more in quantity and grouped together in a lamellar morphology, emanating from the grain boundary and growing into the grain by consumption of the surrounding beta. It is clear that the structural features are rather complicated and requires detailed research.

At 600°C, the reactions are slower but occur at a slightly faster rate than the lower chromium containing alloys. Hardness and resistivity data indicate that the transformation is complete in 4500 hours, but the microstructures shown in Figures IV-43 and -50 show only segmented Widmanstätten beta plates in an alpha matrix. The matrix is presumably actually very fine beta and unresolvable under the optical microscope. In the 2.97 wt.% Cr alloy as seen in from Figure IV-44, the Widmanstätten beta plates possess three different orientations parallel to $\{111\}$ f.c.c. traces and row of these are aligned in a $\langle 111 \rangle$ direction. The same feature is observed in the 3.84 wt.% Cr alloy, but the plates are finer in appearance.

Discussions on the Effect of Time, Temperature and Composition on the Morphology and Stability of Phases

Since the main purpose of this research is to study the effect of 0-4 wt.% Cr on ordering transformations in Ni_4Mo alloys, this section is devoted to summarizing the effects of composition on the morphology and stability of phases observed based on hardness, resistivity and microstructural observations.

Morphology of phases. A very remarkable microstructural feature characterizing the ordered beta phase is the appearance on etching of distinct striations. This feature was reported by Guthrie and Stansbury (24) who suggested the striations were parallel to $\{100\}$ f.c.c. planes. Spruiell (93) using a two-surface trace analysis showed that at least one set was parallel to $\{111\}$ f.c.c. planes. Lei (10) confirmed this by observing as many as four orientations of striations, each one parallel to a twin boundary. These features have been observed in this research.

A classic example of the $\{111\}$ f.c.c. striations is illustrated in Figure IV-51. The center grain shows three twins forming a rough equilateral triangle. Since twins form on $\{111\}$ planes in f.c.c. materials, the fourth $\langle 111 \rangle$ direction must be nearly normal to the plane of the figure. Thus the orientation of the center grain is very close to a $\langle 111 \rangle$ direction. This can be analysed stereographically as shown in Figure IV-53. The $\langle 111 \rangle$ poles are plotted on a standard $[111]$ projection. The small-dashed lines T_1 , T_2 , T_3 represent traces of $\{111\}$ planes. The actual orientation of the twins in the center grain in Figure IV-53, shown schematically in Figure IV-52, are

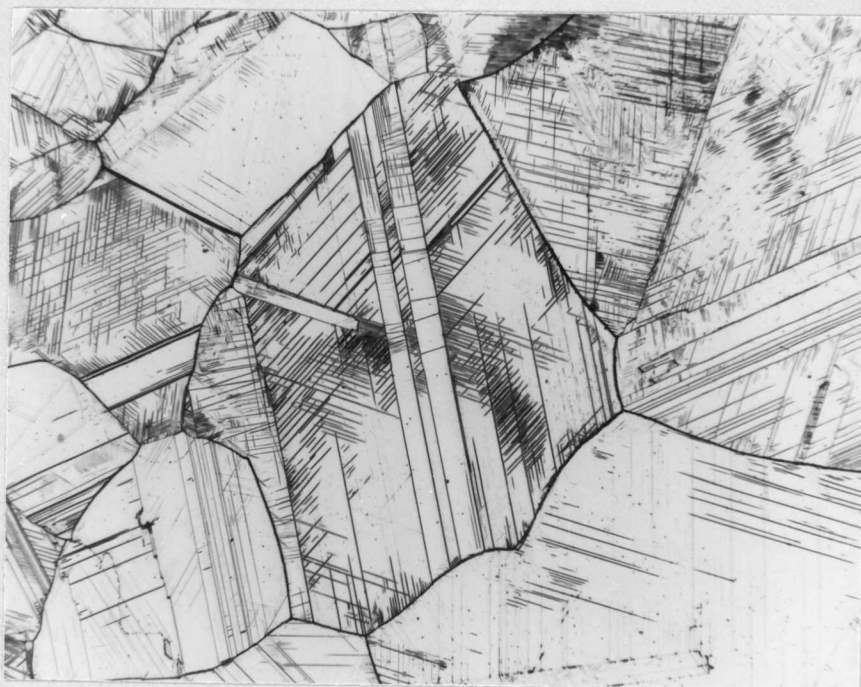


Figure IV-51. Micrograph showing the $\{111\}$ f.c.c. striations associated with the γ phase in Alloy NMCR6 ($\text{Ni}_4\text{Mo} + 0.41 \text{ wt.}\% \text{ Cr}$) aged at 800°C for 16 hours. 100X.

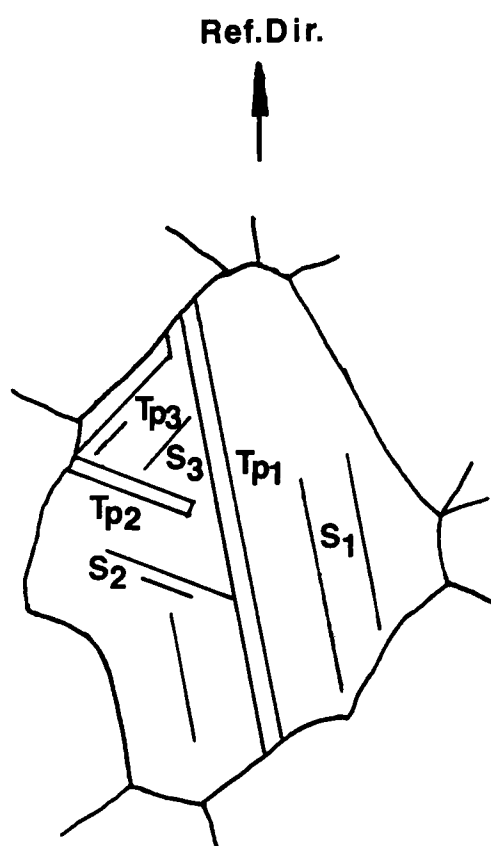


Figure IV-52. Schematic representation of the center grain in Figure IV-51.

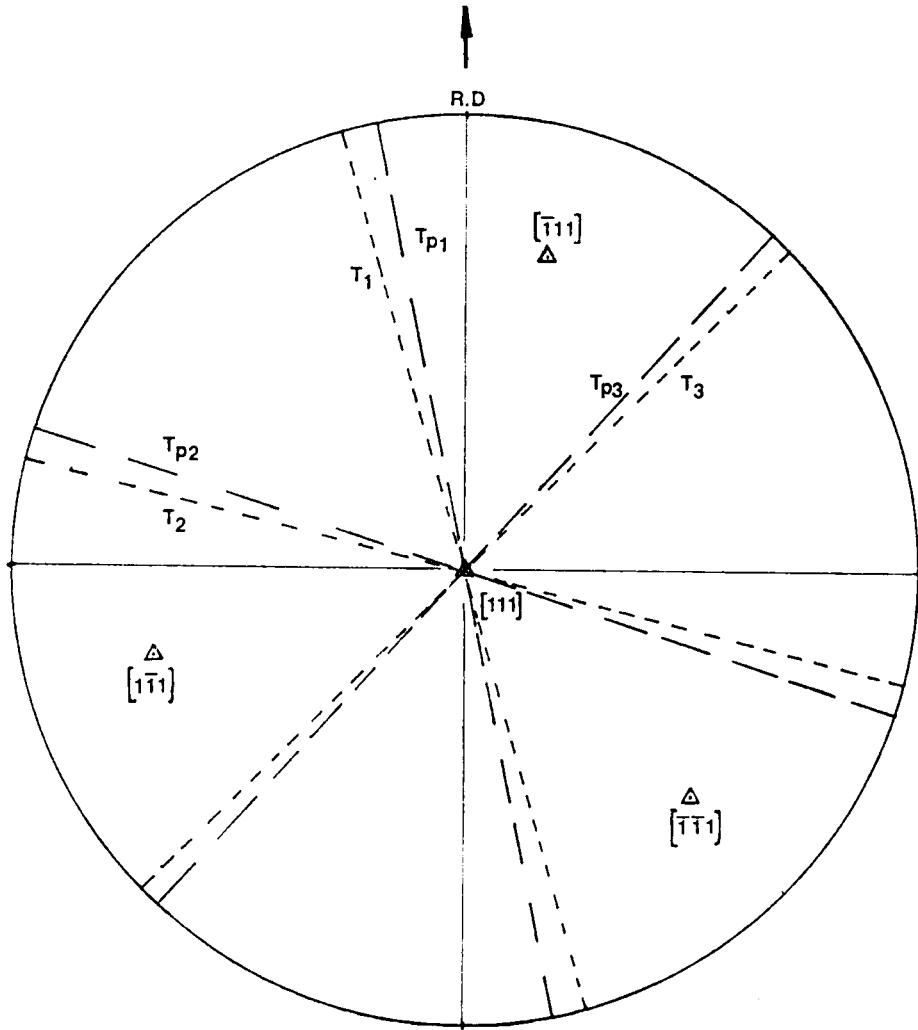


Figure IV-53. Stereographic trace analysis of Figure IV-52.

measured with respect to the left edge of the micrograph (reference edge). The traces of these three twins are superimposed on the stereographic projection in Figure IV-53 with the reference edge along the N-S axis of the projection. The traces of the twin planes are shown as long-dashed lines T_{p1} , T_{p2} and T_{p3} . With a small clockwise rotation about the center and a slight tilting of the projection these traces coincide with the traces of twinning planes T_1 , T_2 and T_3 respectively, proving that the orientation of the center grain in Figure IV-51 is indeed very close to a $\langle 111 \rangle$. Since the striations S_1 , S_2 and S_3 (Figure IV-52) are parallel to these twinning plane traces they must be parallel to $\{111\}$ f.c.c. planes.

In analysing the origin of the $\{111\}$ f.c.c. striations, the possibility that they result from stresses generated by water quenching was examined. In order to dispel this doubt, samples were aged for 16 hours at 800°C and cooled in air instead of water quenching. The striations were still observed but were slightly fewer in number, spaced closer to each other and their appearance was somewhat obfuscated by the presence of large numbers of tapered $\{110\}$ f.c.c. bands. Moreover, the striations did not seem to possess sharply defined boundaries unlike the water quenched samples and in places were segmented. In both cases though, at higher magnifications the boundaries appeared serrated, indicating that a strong etching effect perhaps prevails. In the higher chromium alloys on aging, instead of the continuous $\{111\}$ striations, segmented Widmanstätten plates aligned parallel to $\{111\}$ f.c.c. planes in both water-quenched and air-cooled samples were observed, suggesting that

the striations actually consist of strings of individual domains. Although it is rather difficult to visualize strings of domains stretching to such great lengths (as the striations do), this explanation is a possibility. In fact, Saburi et al (84) felt that the striations consisted of domains and appeared due to the preferential etching of perpendicular twin boundaries. Conversely, if the striations actually consisted of domains then they should coarsen on aging, which is not observed. Also, in agreement with the observations of Irani et al. (91), the striations formed before a maximum in hardness was attained. This implies that the striations are indeed mechanical/annealing twins in an ordered lattice, arising due to stresses generated by the tetragonality of the ordered phase. Though this is not a satisfactory explanation, within the limits of this present research it is possibly the best one.

Saburi et al. (84) and Irani et al. (91) observed striations in ordered Ni_4Mo and concluded they were parallel to $\{110\}$ f.c.c. planes. In this research a second type of striations usually making an angle of 45° with twin boundaries was observed at longer aging times. An example of these is shown in Figure IV-54 for a $\text{Ni}_4\text{Mo} + 0.41 \text{ wt.}\% \text{ Cr}$ alloy aged at 850°C for 2000 hours. In this figure the short Widmanstätten beta precipitates can be seen to possess six different orientations or variants, which is consistent with a $\{110\}$ f.c.c. habit plane. This has also been observed by Lei (10) and is in agreement with the observations of Saburi et al. (84) and Irani et al. (91). With an increase in chromium in Ni_4Mo these $\{110\}$ f.c.c. striations tend to become more curved, but still show six different orientations.

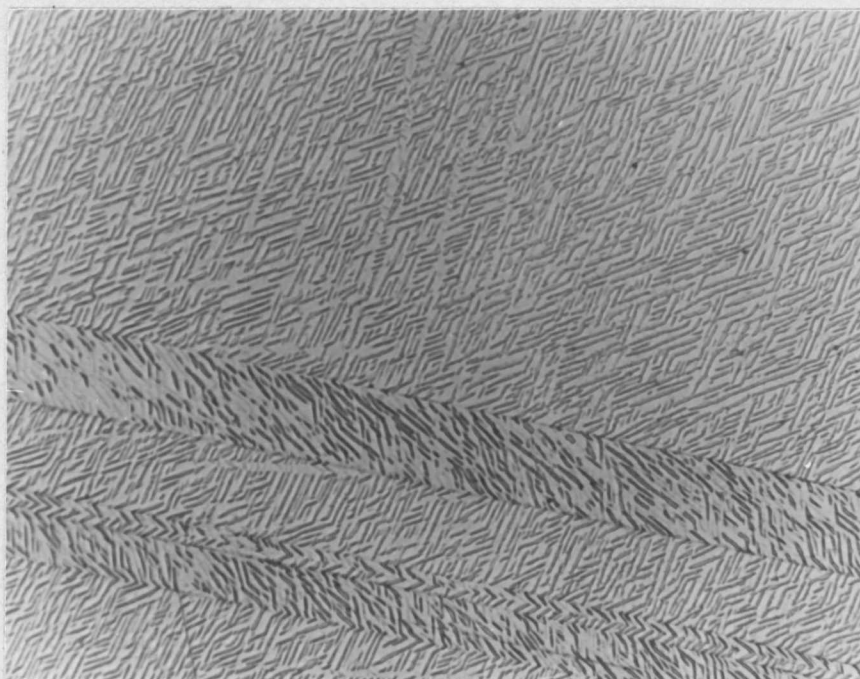


Figure IV-54. Micrograph showing the six different variants of the β domains in Alloy NMCR6 ($\text{Ni}_4\text{Mo} + 0.41 \text{ wt.}\% \text{ Cr}$) aged at 850°C for 2000 hours. 500X.

Results of resistivity measurements on continuous heating and cooling have shown that the temperature of ordering is depressed with the addition of chromium. For example, it is depressed to 825°C for the 2.08 wt.% Cr alloy. Aging at 600, 700, 800 and 850°C progressively changes the hardness and resistivity and the microstructure. Resistivity and hardness as a function of chromium on aging at 600, 700, 800 and 850°C for 4500 hours is shown in Figures IV-55 and -56 respectively.

Effect of chromium at 850°C. A series of SEM micrographs for alloys aged 4500 hours at 850°C is shown in Figure IV-57a-f. The phases present in each case are identified in each micrograph. With increasing chromium, the microstructure progressively changes from the β phase to $\alpha + \beta + \gamma$, $\alpha + \beta + \gamma + \delta$ and $\alpha + \gamma + \delta$ phases. Figure IV-55 shows that the initial resistivity at 850°C is low but increases rather dramatically beyond 0.74 wt.% Cr. The initial low resistivity corresponds to the beta phase. The slight increase in resistivity in the 0.41, 0.54 and 0.74 wt.% Cr alloys is associated with partial decomposition of the beta to the alpha and gamma phases and the high resistivity in the higher chromium alloys is due to the dominating influence of the short range ordered alpha phase. The insensitivity of the resistivity to changes in structure is presumably due to the relatively low volume fractions of the gamma and delta phases.

The hardness is more sensitive to structural changes and shows a slightly different trend. As shown in Figure IV-56, the average initial hardness at 850°C is high mainly due to the beta phase, after which there is a drastic decrease in the 2.08 wt.% Cr alloy due mainly

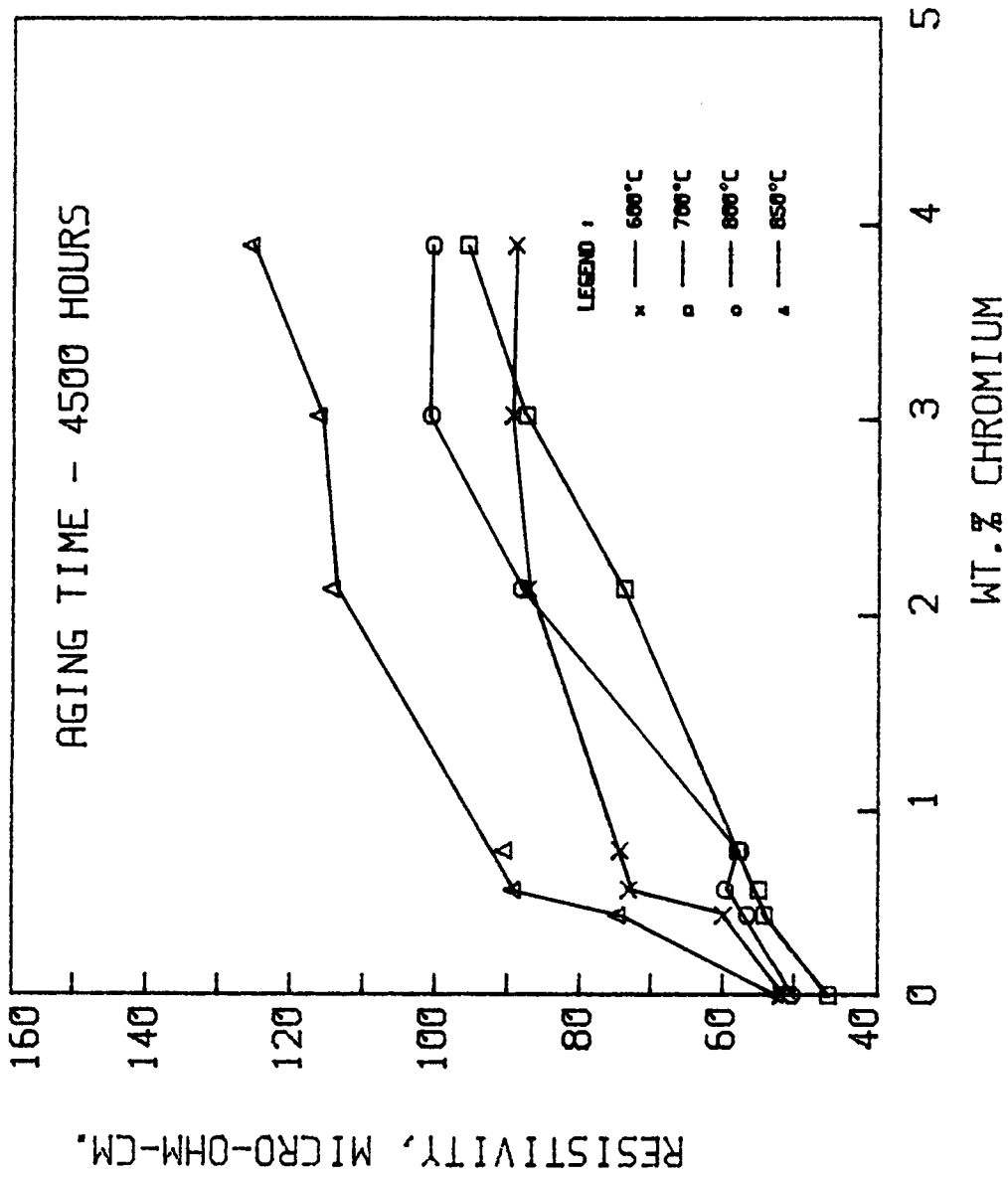


Figure IV-55. Resistivity as a function of chromium content on aging 4500 hours at 600, 700, 800 and 850°C.

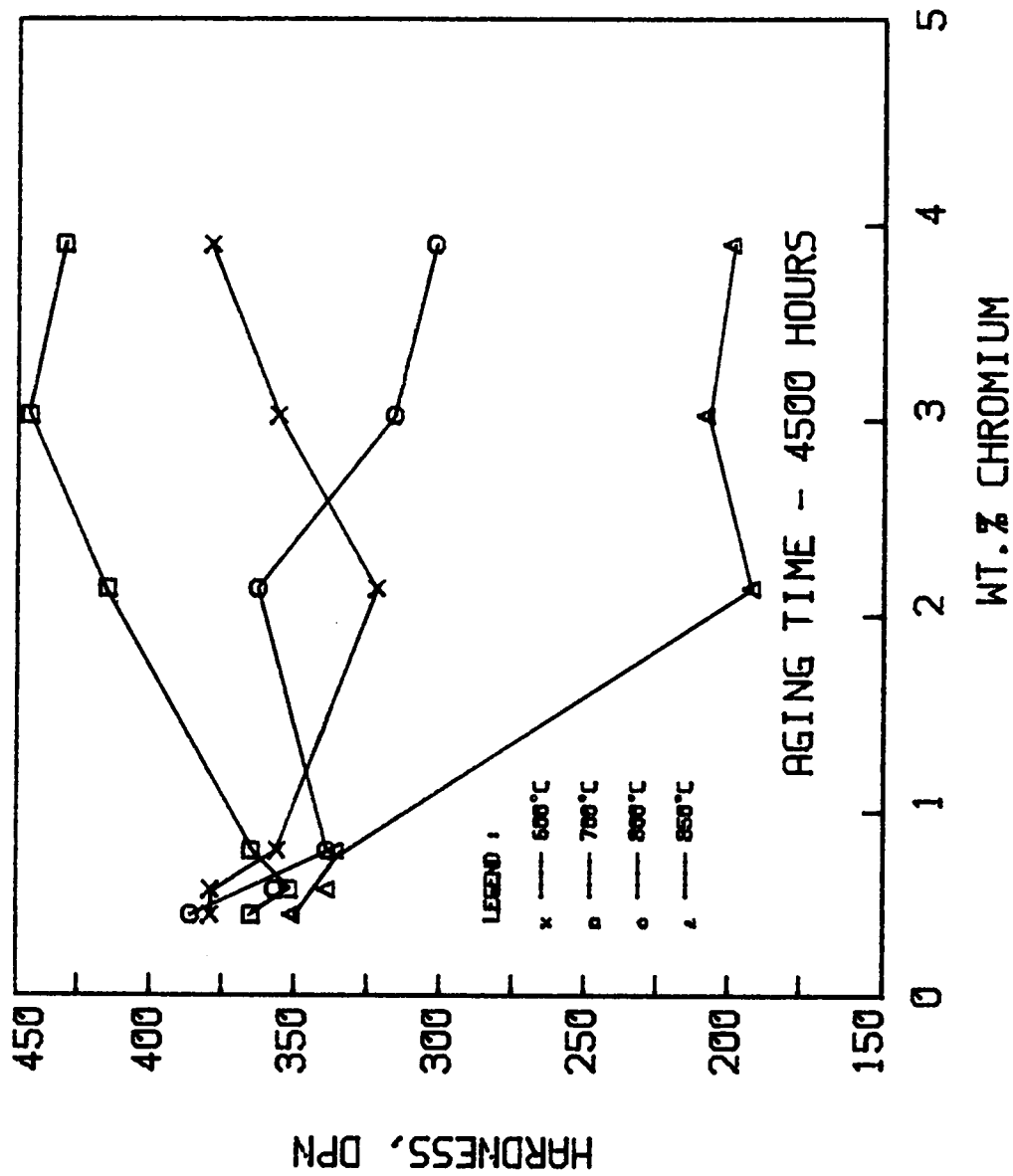


Figure IV-56. Hardness as a function of chromium content on aging 4500 hours at 600, 700, 800 and 850°C.

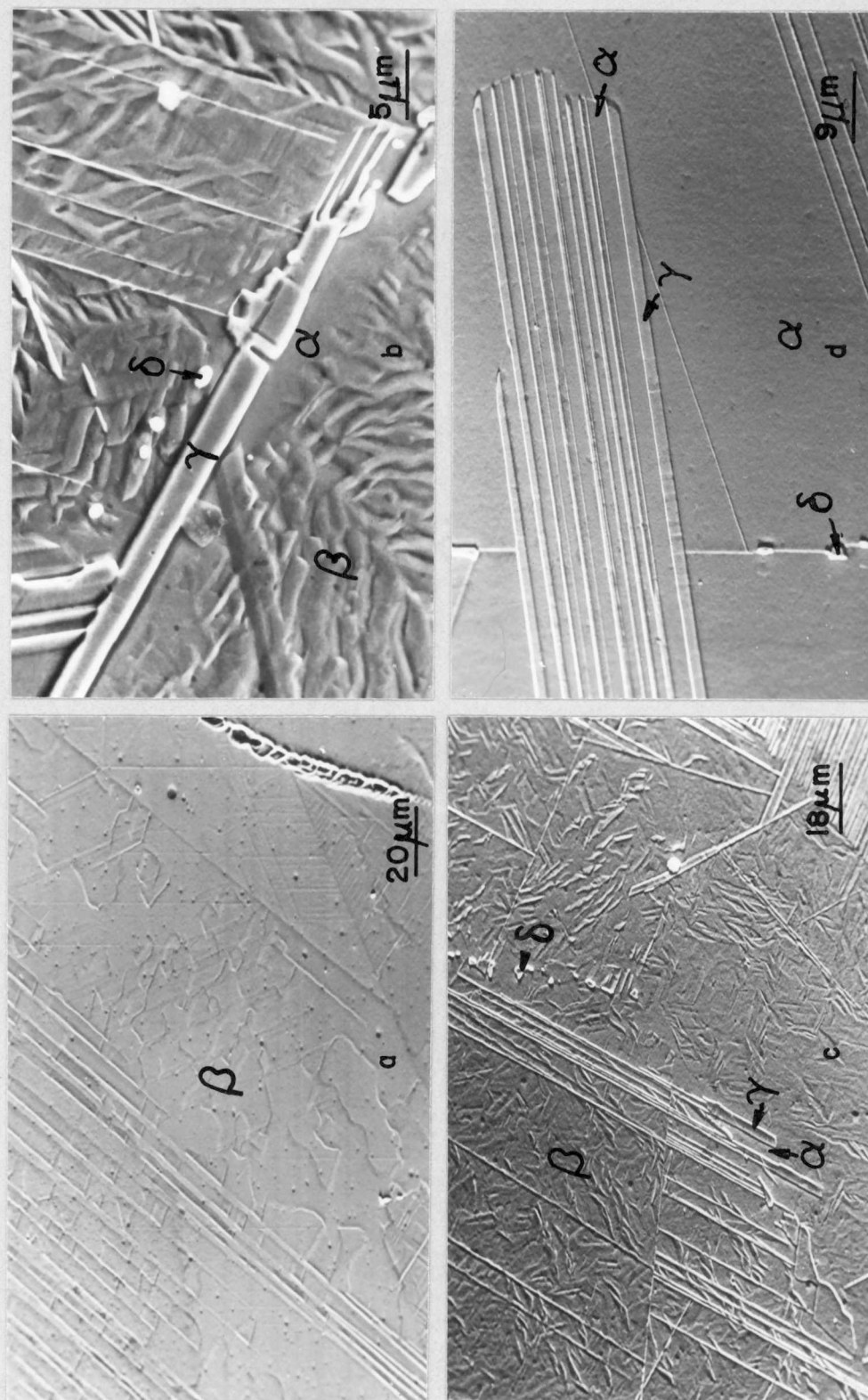


Figure IV-57. Scanning Electron micrographs of alloys aged at 850°C for 4500 hours.
 a) Ni_4Mo , b) 0.54 wt.% Cr, c) 0.74 wt.% Cr, d) 2.08 wt.% Cr, e) 2.97 wt.% Cr, f) 3.84 wt.% Cr.

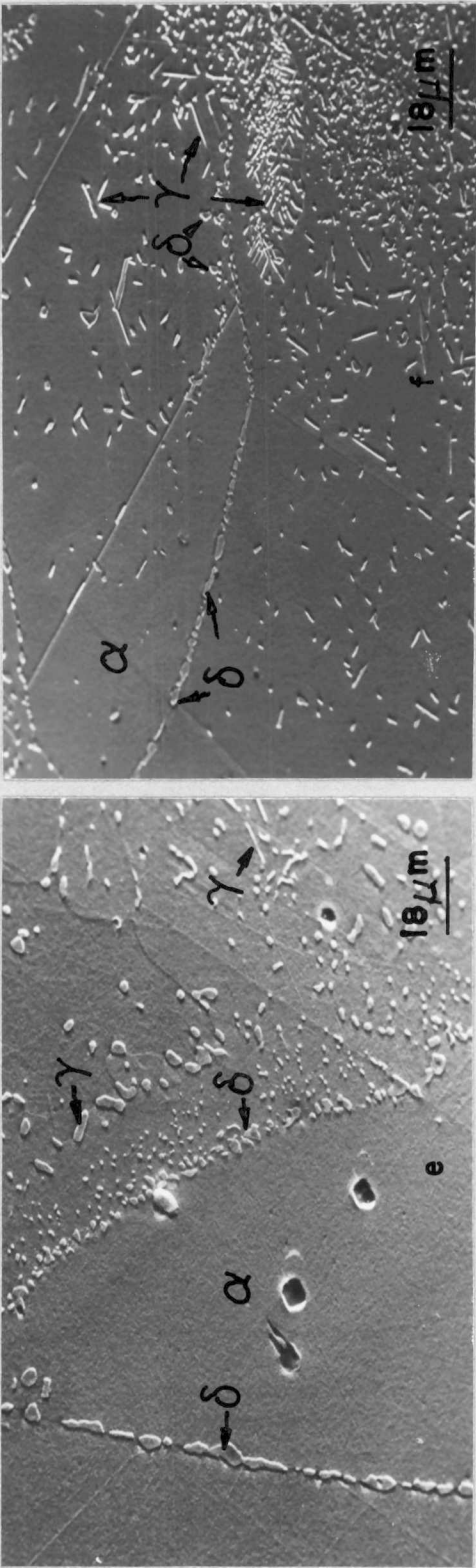


Figure IV-57. (Continued).

to the alpha phase with very small amounts of gamma and delta. Beyond 2.08 wt.% Cr the hardness increases slightly due to additional precipitation of gamma and delta phase.

Effect of chromium at 800°C. A series of SEM micrographs for alloys aged at 800°C for 4500 hours is presented in Figure IV-58a-f. With increasing chromium the microstructure changes from β phase to $\alpha + \beta + \gamma$, $\alpha + \beta + \gamma + \delta$ and $\alpha + \gamma + \delta$ phases. From Figure IV-55, the initial low resistivity is due to the beta phase. The slight increase in the low chromium range is due to partial decomposition of β to $\alpha + \gamma$ phases. This is accompanied by a hardness decrease from 390 to 343 DPN for the 0.74 wt.% Cr alloy. Further increase in resistivity is associated with larger amounts of alpha (adjacent to gamma) in a beta matrix. The large resistivity and lower hardness in the higher ranges of chromium is due to a predominantly alpha matrix containing gamma and delta phases. However, the hardness values are slightly more than 300 DPN, indicating a large amount of gamma and delta which is also supported microstructurally.

Effect of chromium at 700°C. A series of SEM micrographs for alloys aged at 700°C for 4500 hours is presented in Figures IV-59a-f. With increase in chromium, the microstructure changes from β phase to $\alpha + \beta + \gamma$ and $\alpha + \beta + \gamma + \delta$ phases. The initial low resistivity is due to the beta phase. The following increase in the the low chromium range is due to decomposition of beta into alpha and gamma phases at grain boundaries. From Figure IV-59e and -59f little or no alpha is observed. Values of resistivity in the higher chromium alloys appear to be equilibrium values. Hence the increase in resistivity in the

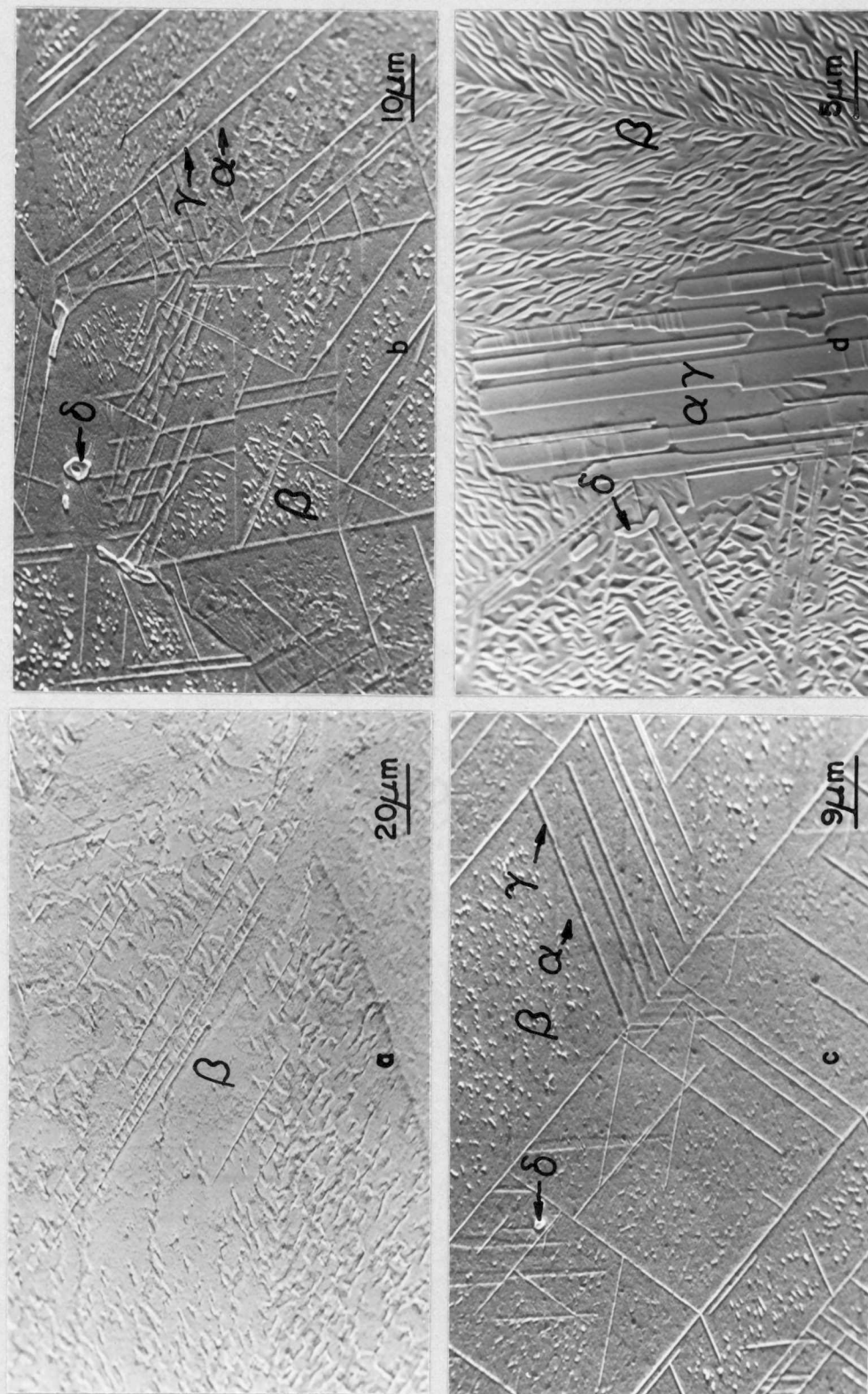


Figure IV-58. Scanning Electron micrographs of alloys aged at 800°C for 4500 hours.
 a) Ni_4Mo , b) 0.54 wt.% Cr, c) 0.74 wt.% Cr, d) 2.08 wt.% Cr, e) 2.97 wt.% Cr, f) 3.84 wt.% Cr.

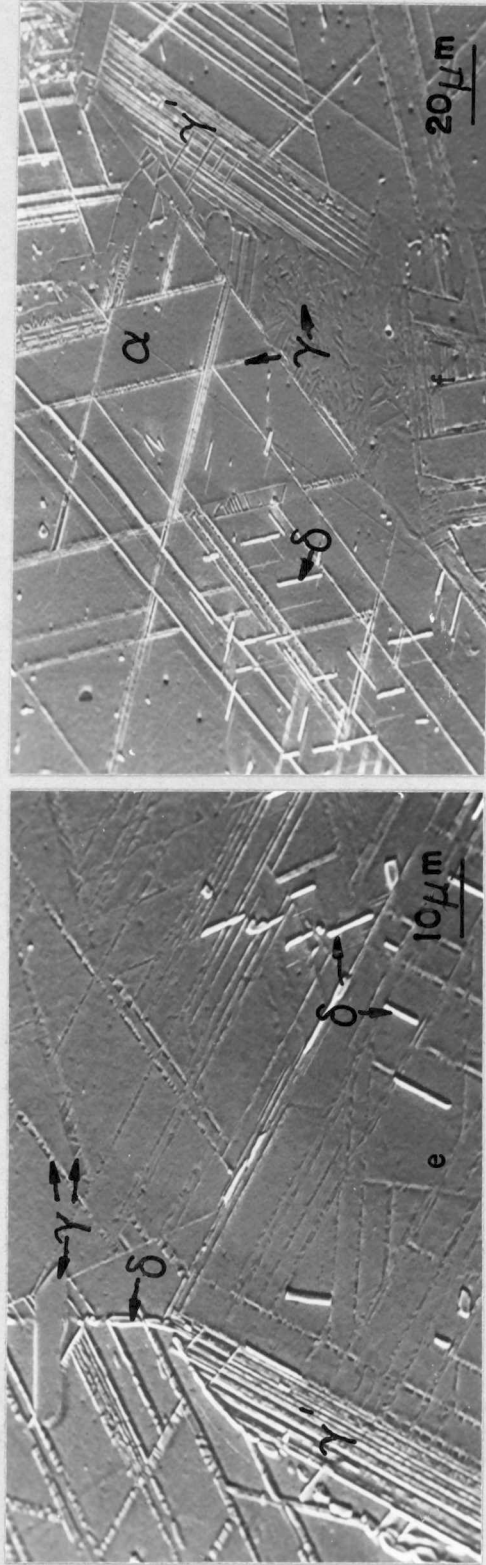


Figure IV-58. (Continued).

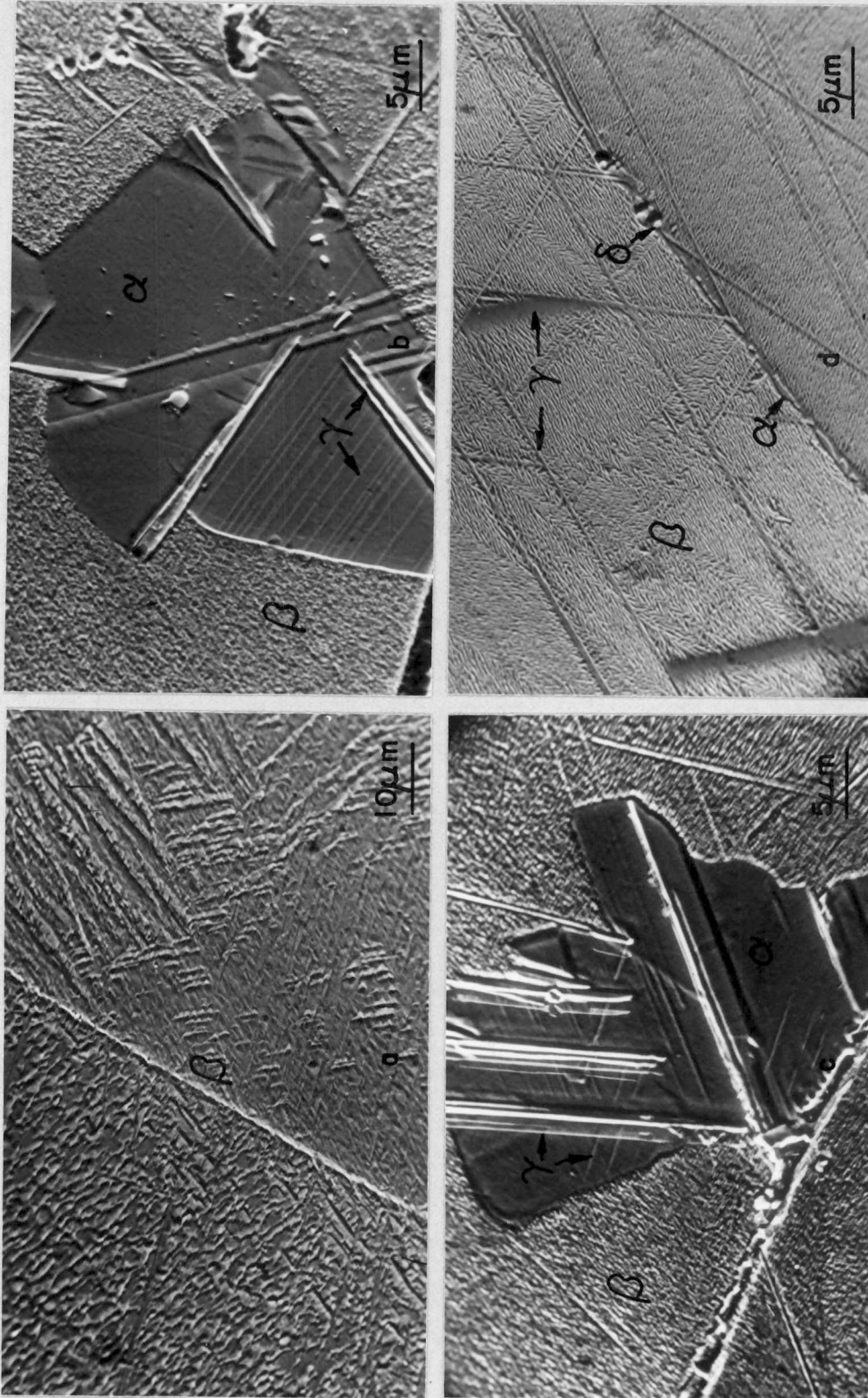


Figure IV-59. Scanning Electron micrographs of alloys aged at 700°C for 4500 hours.
a) Ni₄Mo, b) 0.54 wt.% Cr, c) 0.74 wt.% Cr, d) 2.08 wt.% Cr, e) 2.97 wt.% Cr, f) 3.84 wt.% Cr.

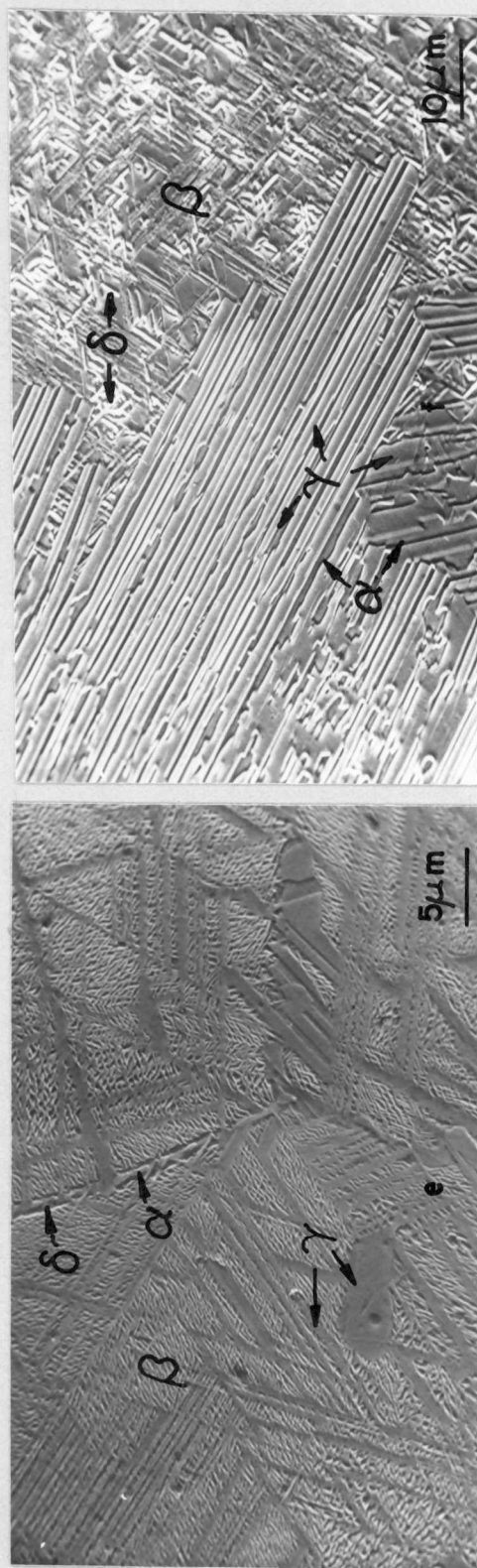


Figure IV-59. (Continued).

higher chromium alloys could be solely due to an increase in electron scattering.

The initial hardness value is high and relatively unchanged in the low chromium range. Further increase in chromium causes a rapid increase in hardness (average 425 DPN) due to increased gamma phase with a plate morphology. In the 3.84 wt.% Cr alloy, from Figure IV-59f besides alternate plates of beta and gamma, Widmanstatten delta precipitates are observed (determined by SEM).

At 600°C though microstructural details cannot be resolved owing to their fineness, similar consistent correlations between hardness, resistivity and microstructure can be deduced.

Phase relations. The task of deriving a partial Ni-Mo-Cr ternary phase diagram is rendered onerous by the inability with existing information, to state positively, whether equilibrium has been attained. Although the partitioning of chromium in each of the ordered phases was observed to be nearly the same, the exact solubility limits of chromium in the gamma and delta phases cannot be stated. Moreover, the amount of molybdenum in the grain boundary precipitates, interpreted as delta phase, varied from very high to moderately high in molybdenum, suggesting presence of a metastable phase such as Ni_2Mo . It is possible that addition of chromium makes this phase permanently stable. Nevertheless, in the light of the above observations and appearance of new phases at later stages of aging (4500 hours), it can be assumed that at least the equilibrium phases exist in the alloy. Both thermodynamic and kinetic factors would determine the presence of observed phases, though often, one of these

may gain precedence over the other. A four phase $\alpha + \beta + \gamma + \delta$ field exists at 850 and 800°C in all the chromium containing alloys and at 700°C in the higher chromium alloys. However, it is not thermodynamically possible for four phases to coexist in equilibrium in a three component system. Thus considerable difficulties are encountered in constructing a partial ternary Ni-Mo-Cr diagram. It would be possible to derive one by assuming that the sum total of all the other elements in the alloys constitute a fourth component. Since this introduces additional complications, the construction of a partial ternary Ni-Mo-Cr phase diagram is not attempted at this point. Instead, the final phases identified in this research after aging 4500 hours at 600, 700, 800 and 850°C are summarized in Figure IV-60.

The solubility of chromium in the beta phase is determined by the limiting line, as a function of chromium, below which the beta phase is present as the only phase within the range of temperatures and times of heat treatment. Based on Figure IV-60, the solubility of chromium in the beta phase is less than 0.41 wt.% at 700, 800 and 850°C and about 4 wt.% at 600°C.

Addition of chromium to Ni_4Mo is thus seen to cause rather complicated structural and morphological changes. It would be worthwhile to perform a more rigorous analysis using transmission electron microscopy and correlate these observations with hardness, resistivity and optical metallographic observations. This should yield fruitful results and enrich our present understanding of the ordering phenomenon in Nickel-Molybdenum ternary alloys.

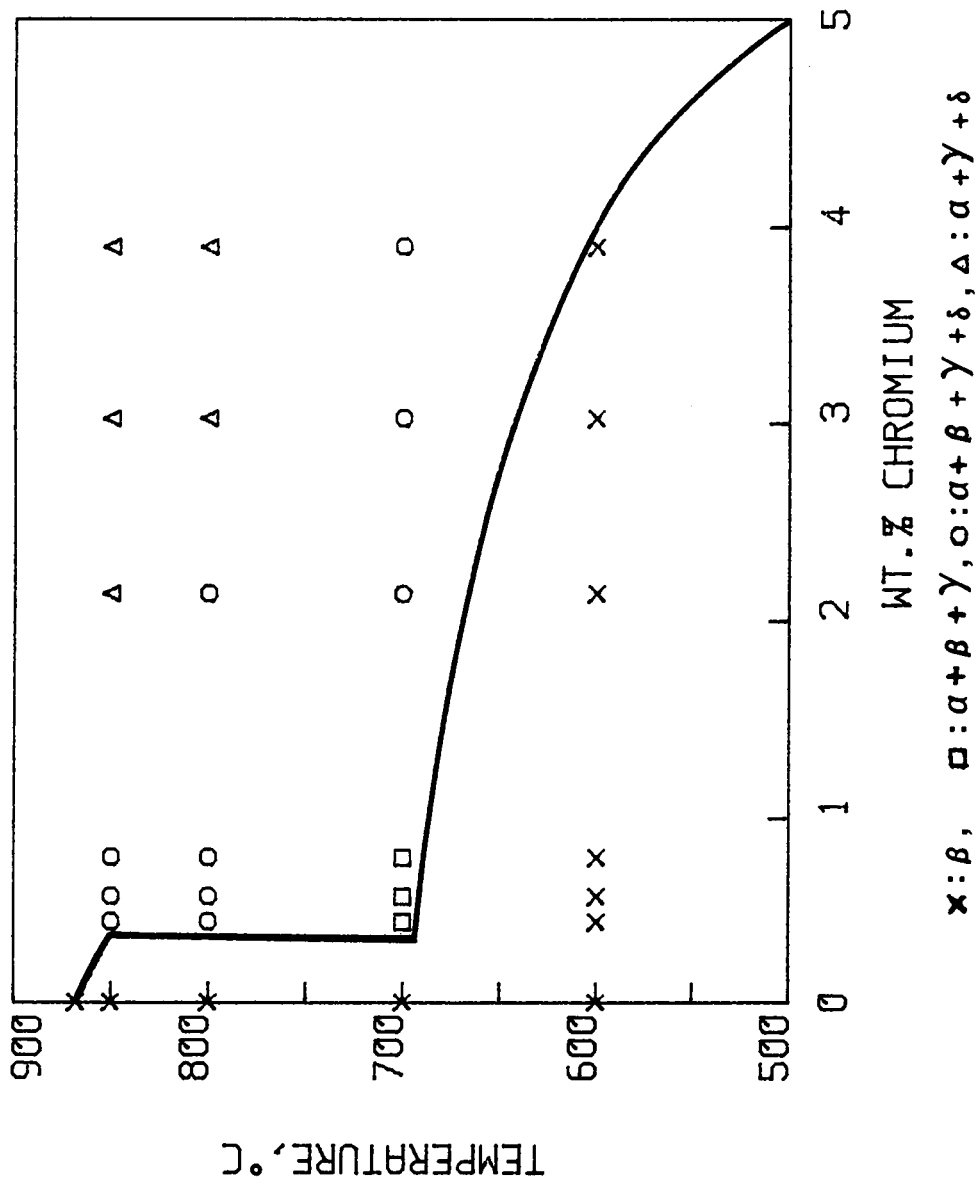


Figure IV-60. Phases corresponding to alloys aged 4500 hours at 600, 700, 800 and 850°C.

CHAPTER V

CONCLUSIONS

1. Short range order K-State effect exists in the retained alpha phase of all Ni_4Mo + 0-4 wt.% Cr alloys. About 68% reduction in area by cold work is sufficient to significantly reduce the resistivity and hence the short range order in the water-quenched phase. Cold working beyond this increases resistivity and is attributed to increased defect concentration becoming more effective in increasing the resistivity than the decrease in SRO is in decreasing it.

2. The short range order resistivity of chromium-containing Ni_4Mo alloys decreases with an increase in chromium.

3. The lattice parameter of the alpha phase Ni_4Mo increases with an increase in chromium content.

4. Short range order increases resistivity and long range order decreases resistivity. Large variations in resistivity can occur depending on relative amounts of each.

5. The critical temperature of ordering decreases with an increase in chromium, which is 868 ± 2 , 865, 850, 845 and 825°C for the Ni_4Mo , 0.41, 0.54, 0.74 and 2.08 wt.% Cr alloys respectively.

6. For a $1^\circ\text{C}/\text{min}$ cooling rate, the ordering temperature is depressed to 800, 795, 785, 770 and 725°C for the Ni_4Mo , 0.41, 0.54, 0.74 and 2.08 wt.% Cr alloys respectively.

7. Based on resistivity measurements, about 3 wt.% Cr in Ni_4Mo is sufficient to suppress long range ordering in alloys cooled at rates faster than $1^\circ\text{C}/\text{min.}$ from above the critical temperature.

8. Based on isothermal resistivity measurements at 700°C , time of initiation of ordering in Ni_4Mo is not influenced by prior cold work. However, at later stages of aging the ordering rate is higher the greater the degree of prior cold work. Alloys cold worked more than 68% RA had substantially higher ordering rates at all times beyond 20 minutes, than those cold worked less than this.

9. Based on the above conclusion, ordering in cold worked Ni_4Mo at 700°C , can be said to occur by a process of heterogeneous nucleation which appears optically as a homogeneous reaction.

10. Based on resistivity measurements, ordering in Ni_4Mo is complete in 24 hour at 850°C , 10 hours at 800°C , 96 hours at 700°C and 2000 hours at 600°C .

11. Based on hardness and resistivity measurements, kinetics of ordering of Ni_4Mo is not affected much by additions of chromium upto 0.74 wt.%. In alloys containing 2.08 wt.% Cr and above, the ordering rate however, decreased substantially at all temperatures except 700°C .

12. Distinct $\{111\}$ f.c.c. striations are observed in the beta phase on isothermal aging. Striations usually form before a maximum in hardness is attained and hence it is suggested that they are mechanical twins in an ordered lattice arising due to the stresses generated by the tetragonality of the ordered phase. Also, tapered $\{110\}$ f.c.c. striations are observed in the beta phase, often coexisting with the $\{111\}$ f.c.c. striations.

13. In the higher chromium-containing alloys, short Widmanstätten beta plates in a matrix of alpha, form parallel to $\{111\}$ f.c.c. planes.

14. Beta domains possess six distinct orientations in correspondence to a $\{110\}$ f.c.c. habit plane.

15. Beta domain growth is inhibited by the addition of chromium to Ni_4Mo .

16. The solubility of chromium in the beta phase is about 4 wt.% at 600°C and about 0.4 wt.% at 700, 800 and 850°C .

17. Widmanstätten gamma phase is observed in chromium-containing alloys. In the higher chromium alloys, the gamma phase is present in two morphologies, namely, thin Widmanstätten striations parallel to $\{111\}$ f.c.c. planes and massive Widmanstätten plates. The formation of the Widmanstätten gamma plates gives rise to a high hardness value.

18. In alloys located in the three phase $\alpha + \gamma + \delta$ region, a discontinuous precipitation of δ and γ phases is observed.

LIST OF REFERENCES

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1. Hastelloy - Developmental Alloy B-2, Stellite Division, Cabot Corp., Kokomo, Indiana.
2. F.G.Hodge and R.W.Kirchner, Materials Performance, P. 40, (1976).
3. T.V.Svistunova, Molybdenum in Nickel-Base Corrosion Resistant Alloys, paper presented at the Soviet-American Symposium on New Developments in the field of Molybdenum-Alloyed Cast Iron and Steel, Moscow, (1973).
4. G.N.Flint, J. Inst. Metals, Vol. 87, P. 303, (1958-59).
5. G.N.Flint, Metallurgia, Vol. 62, P. 105, (1960).
6. R.E.Clausing, P.Patriarca and W.D.Manly, Trans. ASM, Vol. 51, P. 123, (1959).
7. D.Y.Roan, Microstructure and Mechanical Properties of Hastelloy B-2 and its Wear Behavior Against Graphite in a Simulated Mechanical Face Seal, M.S. Thesis, The University of Tennessee, (1969).
8. W.B.Snyder and C.R.Brooks, in B.H.Kear et al. (eds.), Ordered Alloys, Proc. Third Bolton Landing Conf., Baton Rouge, LA, Claiter's, (1970).
9. W.E.Norem and E.E.Stansbury, An Investigation of Nickel-Rich Alloys Containing Molybdenum and Iron, Report to Union Carbide, Oak Ridge National Laboratory, Oak Ridge, Tennessee, (1963).
10. T.S.Lei, The Effect of 0-8 wt.% Iron on Transformations of Alpha Phase Ni-Mo-Fe Alloys with Ni:Mo Ratio Equal to 4:1, Ph.D. Dissertation, The University of Tennessee, (1979).
11. C.S.Barrett and T.B.Massalski, The Structure of Metals, Third Edition, McGraw Hill Inc., New York, (1966).
12. G.Tammann, A. Anorg. Chem., Vol. 107, P. 1, (1919).
13. E.C.Bain, Chem-Met-Eng., Vol. 28, P. 21, (1923); Trans. AIME, Vol. 68, P. 625, (1923).
14. C.H.Johannson and J.O.Linde, Amer. Physik, Vol. 78, P. 439, (1925).
15. W.L.Bragg and E.J.Williams, Proc. Roy. Soc. (London), Vol. A145, P. 699, (1934).

16. H.A.Bethe, Proc. Roy. Soc. (London), Vol. A150, P. 552, (1935).
17. J.M.Cowley, Phys. Rev., Vol. 77, P. 669, (1950); J. Appl. Phys., Vol. 21, P. 24, (1950); Phys. Rev., Vol. 120, P. 164, (1960).
18. J.E.Spruiell and E.E.Stansbury, J. Phys. Chem. Sol., Vol. 26, P. 811, (1965).
19. T.P.Chang, Investigation of Ordering in Nickel -10 and -20 Atomic Percent Molybdenum Alloys by Electrical Resistivity Measurements, M.S. Thesis, The University of Tennessee, (1965).
20. J.W.Christian, The Theory of Transformations in Metals and Alloys, Pergamon Press, Oxford, (1975).
21. J.W.Gibbs, Scientific Papers, Vol. 1, Dover, New York, (1961).
22. L.A.Nesbit and D.E.Laughlin, Acta Met., Vol. 26, P. 815, (1978).
23. B.Chakravarti, E.A.Starke Jr and B.G.Lefevre, J. Mats. Sc., Vol 5, P. 394, (1970).
24. P.V.Guthrie and E.E.Stansbury, X-Ray and Metallographic Study of the Nickel-Rich Alloys of The Nickel-Molybdenum System II, ORNL-3078, Oak Ridge National Laboratory, (1961).
25. D.Harker, J. Chem. Phys., Vol. 12, P. 315, (1944).
26. R.S.Irani, Contemp. Phys., Vol. 13, P. 559, (1972).
27. J.B.Newkirk, A.H.Geisler, D.L.Martin and R.Smoluchowski, Trans. AIME, Vol. 188, P. 1249, (1950).
28. P.S.Rudman, J.H.Westbrook (ed.), Intermetallic Compounds, Wiley, (1967).
29. G.Grube and H.Schlect, Z. Elektrochem., Vol. 44, P. 413, (1938).
30. N.Baar, Z. Anorg. Chem., Vol. 70, P. 353, (1911).
31. Dreibholz, Z. Physik Chem., Vol. 108, P. 8, (1924).
32. W.Koster and W.Schmidt, Arch. Eisenhüttenw, Vol. 8, P. 23, (1934-35).
33. F.H.Ellinger, Trans. ASM, Vol. 30, P. 607, (1942).

34. M.Hansen, Constitution of Binary Alloys, Second Ed., McGraw Hill, New York, (1958).
35. R.E.W.Casselton and W.Hume-Rothery, J. of the Less Common Metals, Vol. 7, P. 212, (1964).
36. H.Thomas, Z. Phys., Vol. 129, P. 219, (1951).
37. A.C.Damask, J. Appl. Phys., Vol. 27, P. 610, (1956).
38. A.C.Damask, J. Phys. Chem. Sol., Vol. 1, P. 23, (1956).
39. G.V.Starikova and A.A.Presnyakov, Phys. Met. Metallog., Vol. 10, P. 150, (1960).
40. V.S.Meskin, R.I.Sergienko and L.A.Potapov, Phys. Met. Metallog., Vol. 13, P. 113, (1962).
41. P.Chevenard, J. Inst. Metals, Vol. 36, P. 46, (1926).
42. E.E.Stansbury, C.R.Brooks and T.L.Arledge, J. Inst. Metals, Vol. 94, P. 136, (1966).
43. H.G.Baer, Z. Metallk., Vol. 56, P. 79, (1965).
44. B.T.Lampe, An Investigation of the Order-Disorder Transformation in the Nickel - 29.9% Molybdenum Alloy by Electrical Resistivity Measurements, M.S. Thesis, The University of Tennessee, (1965).
45. B.G.Lefevre, A.G.Guy and R.W.Gould, Met. Trans., Vol. 242, P. 788, (1968).
46. H.J.Logie, J.Jackson, J.C.Anderson and F.R.N.Nabarro, Acta Met., Vol. 9, P. 707, (1961).
47. W.H.Aarts and A.S.Houston-Macmillan, Acta Met., Vol. 13, P. 957, (1965).
48. H.G.Muller and P.Muth, Z. Metallk., Vol. 50, P.217, (1959).
49. W.Chen and M.E.Nicholson, Acta Met., Vol. 12, P. 687, (1964).
50. B.G.Livshits and G.A.Rymashevski, Phys. Met. Metallog., Vol. 13, P. 41, (1962).
51. B.Chakravarti, E.A.Starke Jr, C.J.Sparks and R.O.Williams, J. Phys. Chem. Sol., Vol. 35, P. 1317, (1974).
52. E.Ruedl, P.Delvaigette and S.Amelinckx, Mat. Res. Bull., Vol. 2, P. 1045, (1967).

53. T.Saburi, K.Komatsu, M.Yamamoto, S.Nenno and Y.Mizutani, Trans. AIME, Vol. 245, P. 2348, (1969); Trans. Jap. Inst. Metals, Vol. 11, P. 120, (1970).
54. G.Van Tendeloo, R. De Ridder and S.Amelinckx, Phys. Stat. Sol., Vol. 27, P. 457, (1975).
55. P.R.Okamoto and G.Thomas, Acta Met., Vol. 19, P. 825, (1971).
56. S.K.Das, P.R.Okamoto, P.M.J.Fischer and G.Thomas, Acta Met., Vol. 21, P. 913, (1973).
57. S.K.Das and G.Thomas, in H.Warlimont (ed.), Order-Disorder Transformation in Alloys, Springer-Verlag, New York, (1974).
58. J.P.A.A.Chevalier and W.M.Stobbs, Acta Met., Vol. 24, P. 535, (1976).
59. G.Thomas and R.Sinclair, Acta Met., Vol. 25, P. 231, (1977).
60. W.M.Stobbs and J.P.A.A.Chevalier, Acta Met., Vol. 26, P. 233, (1978).
61. B.G.Lefevre, M.Grenga and B.Ralph, Phil. Mag., Vol. 18, P. 1127, (1968).
62. P.C.Clapp and S.C.Moss, Phys. Rev., Vol. 142, P. 418, (1966); Vol. 171, P. 764, (1968).
63. S.Saito and P.Beck, Trans. AIME, Vol. 215, P. 938, (1959).
64. E.Ruedl and S.Amelinckx, Mat. Res. Bull., Vol. 4, P. 361, (1969).
65. S.K.Das and G.Thomas, Phys. Stat. Sol. (a), Vol. 21, P. 177, (1974).
66. G.Van Tendeloo, Mat. Sci. Eng., Vol. 26, P. 209, (1976).
67. L.E.Tanner, Acta Met., Vol. 20, P. 1197, (1972).
68. G.Van Tendeloo, R. De Ridder and S.Amelinckx, Phys. Stat. Sol. (a), Vol. 27, P. 457, (1975).
69. C.B.Shoemaker and D.P.Shoemaker, Acta Cryst., Vol. 16, P. 997, (1963).
70. G.Van Tendeloo and S.Amelinckx, Mat. Res. Bull., Vol. 8, P. 721, (1973).
71. E.E.Stansbury, Unpublished Research, The University of Tennessee, (1966).

72. H.Yamuchi and D. de Fontaine, in H.Warlimont (ed.), Order-Disorder Transformation in Alloys, Springer-Verlag, New York, (1974).
73. C.Sykes and H.Evans, J. Inst. Metals, Vol. 58, P. 235, (1936).
74. J.Rothstein, Phys. Rev., Vol. 94, P. 1429A, (1954).
75. G.J.Dienes, Acta Met., Vol. 3, P. 549, (1955).
76. A.S.Nowick and L.R.Weisberg, Acta Met. Vol. 6, P. 258, (1958).
77. R.Feder, M.Mooney and A.S.Nowick, Acta Met., Vol. 6, P. 266, (1958).
78. H.Sato and R.Kikuchi, Acta Met., Vol. 24, P. 797, (1976).
79. J.W.Cahn, Acta Met., Vol. 9, P. 795, (1961).
80. Fu-Wen Ling and E.A.Starke Jr, Scripta Met., Vol. 5, P. 741, (1971).
81. R.Muto, Inst. Phys. Chem., Research Sci. Papers (Tokyo), Vol. 30, P. 99, (1936).
82. G.J.Dienes, J. Appl. Phys., Vol. 22, P. 1020, (1951).
83. T.Saburi, K.Komatsu and S.Nenno, Phil. Mag., Vol. 20, P. 109, (1969).
84. T.Saburi, E.Kanai and S.Nenno, J. of Less Common Metals, Vol. 37, P. 59, (1974).
85. Fu-Wen Ling and E.A.Starke Jr, Acta Met., Vol. 19, P. 759, (1971).
86. K.C.Chen, Fu-Wen Ling and E.A.Starke Jr, Mat. Sci. Eng., Vol. 13, P. 255, (1974).
87. J.E.Spruiell, Lee M. Ruch and C.R.Brooks, Met. Trans., Vol. 6A, P. 1301, (1975).
88. J.W.Goodrum and B.G.Lefevre, Met. Trans., Vol. 8A, P. 939, (1977).
89. I.Kiriyenko, E.E.Poplavskaya and L.P.Potapov, Phys. Met. Metallog., Vol. 33, P. 132, (1972).
90. N.Vlasova, Y.D.Tyapkin and V.D.Plakhiti, Sovt. Phys. Dokl., Vol. 19, P. 32, (1974).

91. R.S.Irani, Fu-Wen Ling and R.W.Cahn, Metallography, Vol. 6, P. 141, (1973).
92. H.M.Tawancy, J. Mat. Sc., Vol. 15, P. 2597, (1980).
93. J.E.Spruiell, X-Ray Study of Short Range Order in Nickel Alloys Containing 10.7 and 20.0 Atomic Percent Molybdenum, Ph.D. Dissertation, The University of Tennessee, (1963).
94. L.N.Larikov, V.V.Geichenko and V.M.Fal'chenko, Diffusion Processes in Ordered Alloys, Published for Amerind Pub. Co., New Delhi, India, (1981).
95. R.G.Davies and A.J.Funes, Acta Met., Vol. 9, P. 979, (1961).

APPENDICES

APPENDIX A

NAMES OF TASKS AND THEIR FUNCTIONS

- CALCU: Calculates and converts primary data to final form, such as emfs to temperatures, voltage drops, current and sample dimensions to resistivity.
- CLEAR: Clears all interface devices at termination of run; called as last step in master program ERM.
- DATA1: Selects through system common, parameters entered through RUNDA and PIDSET and required by current run.
- DATA2: Selects through system common, parameters entered through RATES and required by current run.
- ERM: The master program designed to call and communicate with sub-programs through system common. Directs all actions required to conduct run, such as:
- 1) Open a new FILE NAME on DEC TAPE.
 - 2) Output a higher rate of power to increase the heating rate.
 - 3) Select output from thermocouple emf amplifier or IR drop amplifier for transmission to A/D converter of the computer.
 - 4) Sampling and controlling the specimen temperature.
- GRAPH: Open and read specific file stored on DEC TAPE and output data to X-Y plotter or strip chart recorder.
- NEXT: Terminates current run and advances to next run.
- PARAM: Sets primary parameters which characterize the specimen identification and dimensions.

PIDER: Performs PID control algorithm and returns through common values required to reset power to specimen.

PIDSET: Sets PID parameters for the control algorithm.

RATES: Sets up specific heating or cooling rates and temperature range for a specific run.

RUNDA: Identifies data set. Sets temperature limits for heating, cooling and/or isothermal runs and initial holding time.

STOP: Terminates ERM or current series of runs under ERM.

STPRC: Converts resistivity data to proportional voltage output to strip chart recorder to obtain resistivity-time curves.

SUPAR: Sets supplemental parameters defining successive heating, cooling or isothermal runs.

TTOUT: Output of experiment data on TTY during run.

XYPLT: Converts resistivity and temperature data to proportional voltage outputs to X-Y plotter to obtain resistivity-temperature curves.

XYSET: Sets upper and lower limits of coordinates on the X-Y plotter.

XYWRT: Open and read specific file stored on DEC TAPE and output to TTY.

APPENDIX B

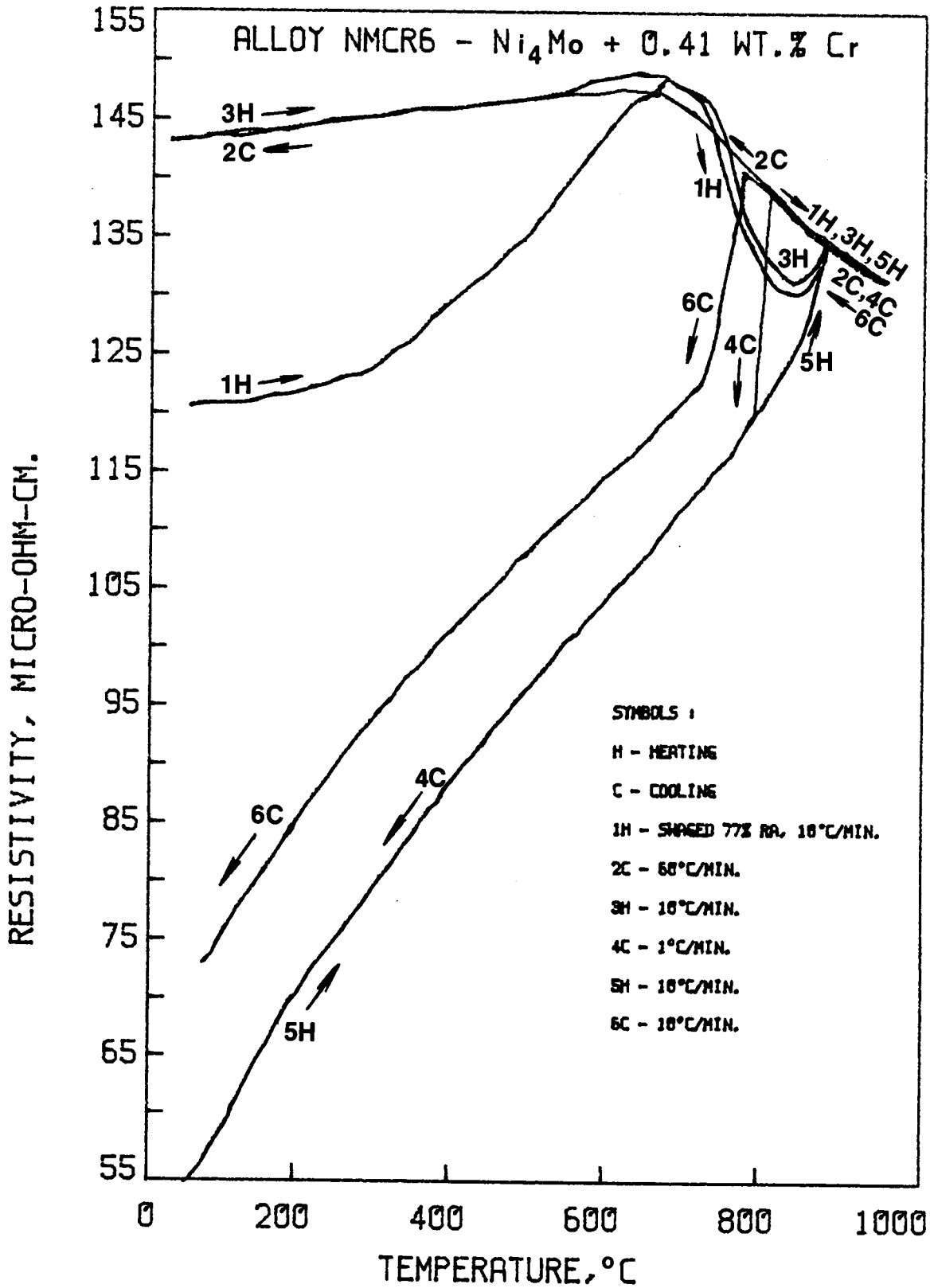


Figure B-1. Resistivity as a function of temperature for Alloy NMCR6 on continuous heating and cooling.

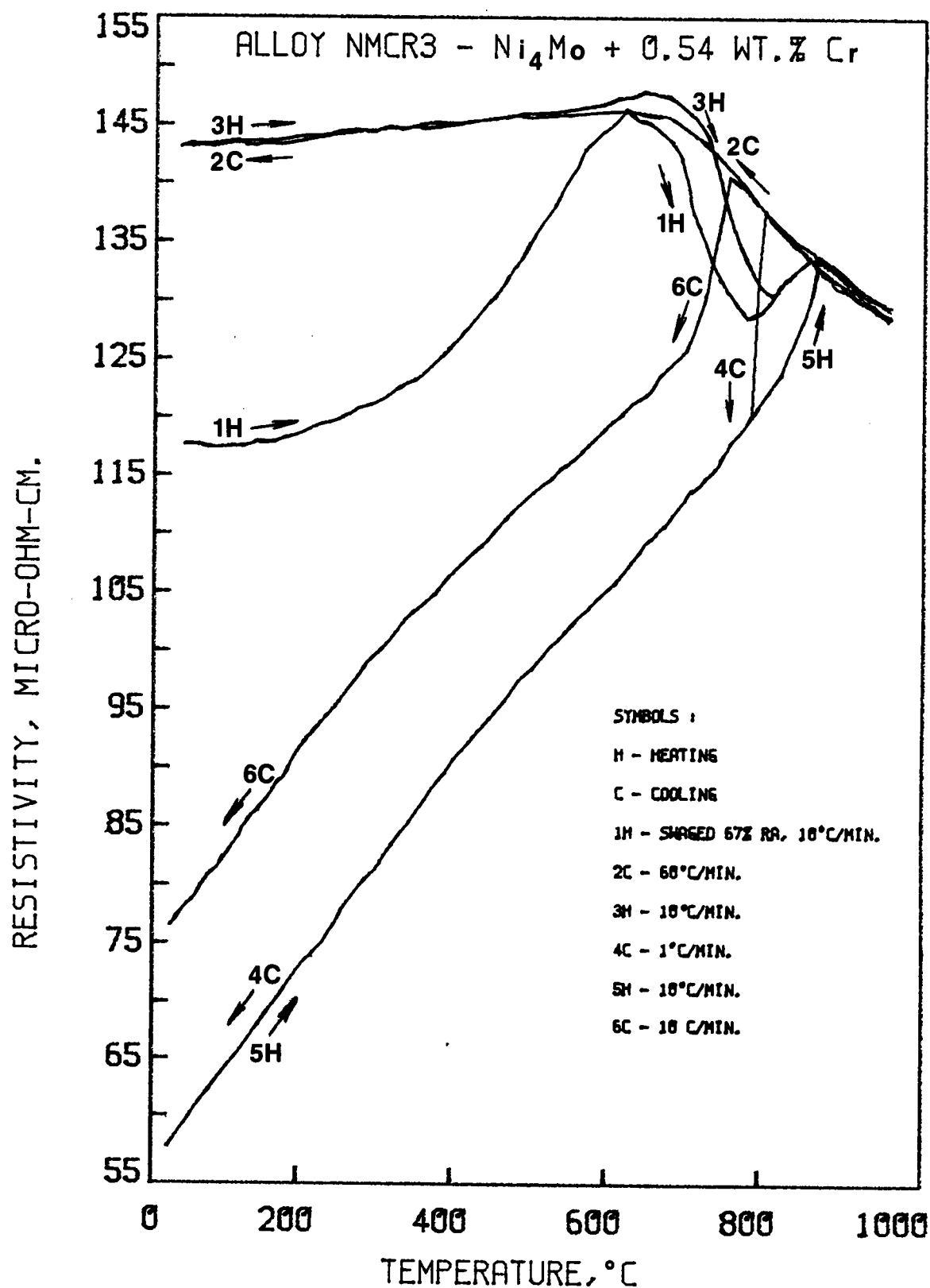


Figure B-2. Resistivity as a function of temperature for Alloy NMCR3 on continuous heating and cooling.

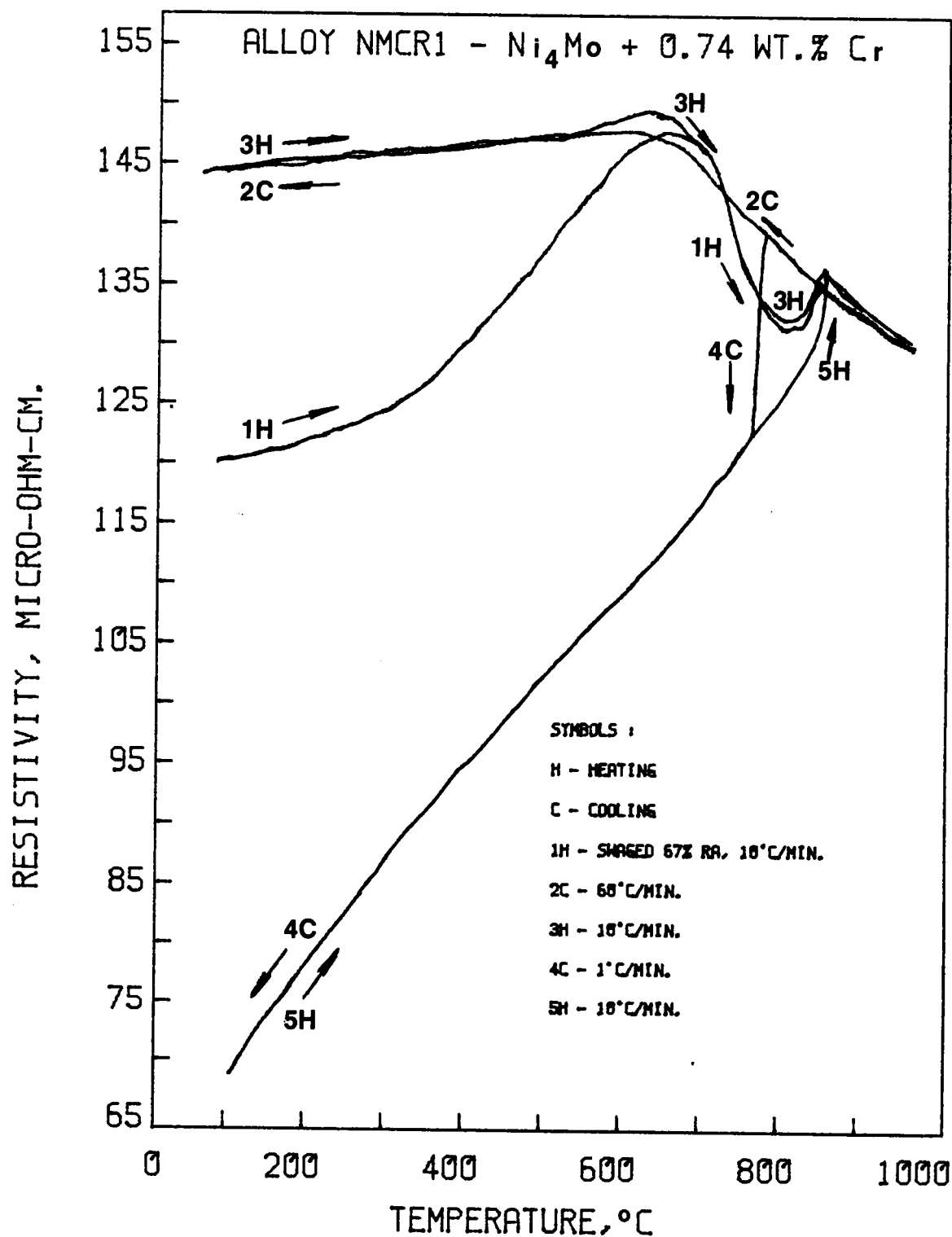


Figure B-3. Resistivity as a function of temperature for Alloy NMCR1 on continuous heating and cooling.

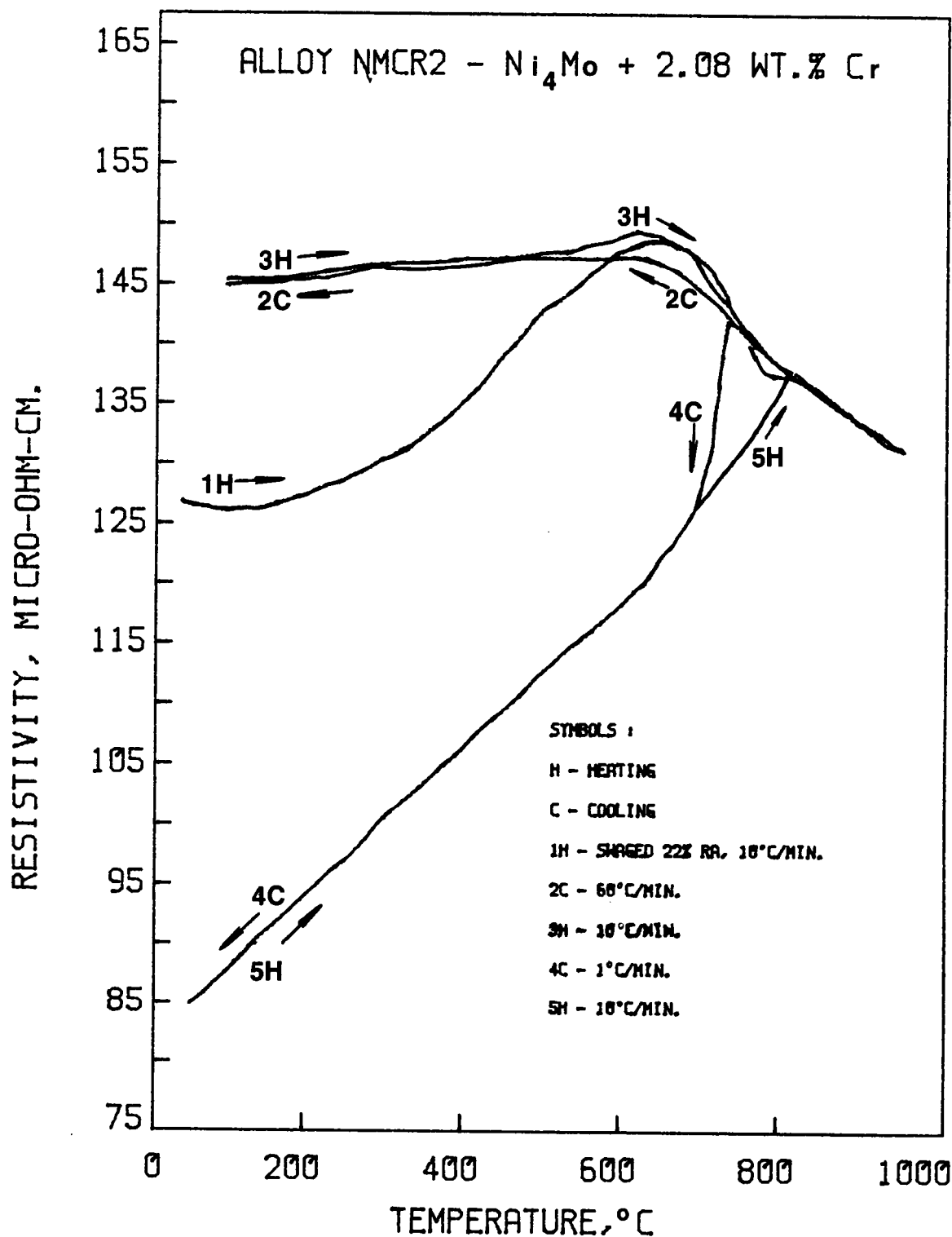


Figure B-4. Resistivity as a function of temperature for Alloy NMCR2 on continuous heating and cooling.

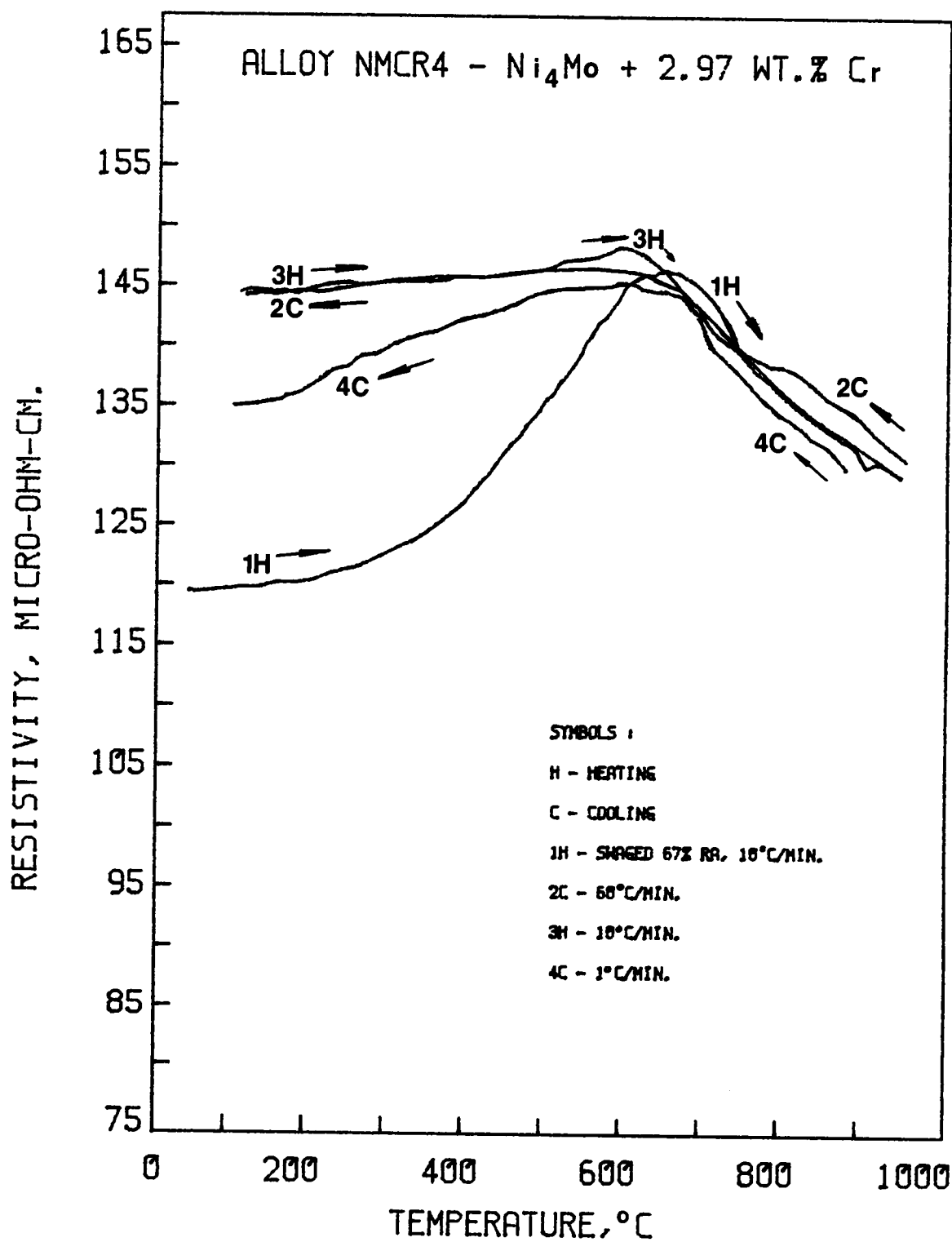


Figure B-5. Resistivity as a function of temperature for Alloy NMCR4 on continuous heating and cooling.

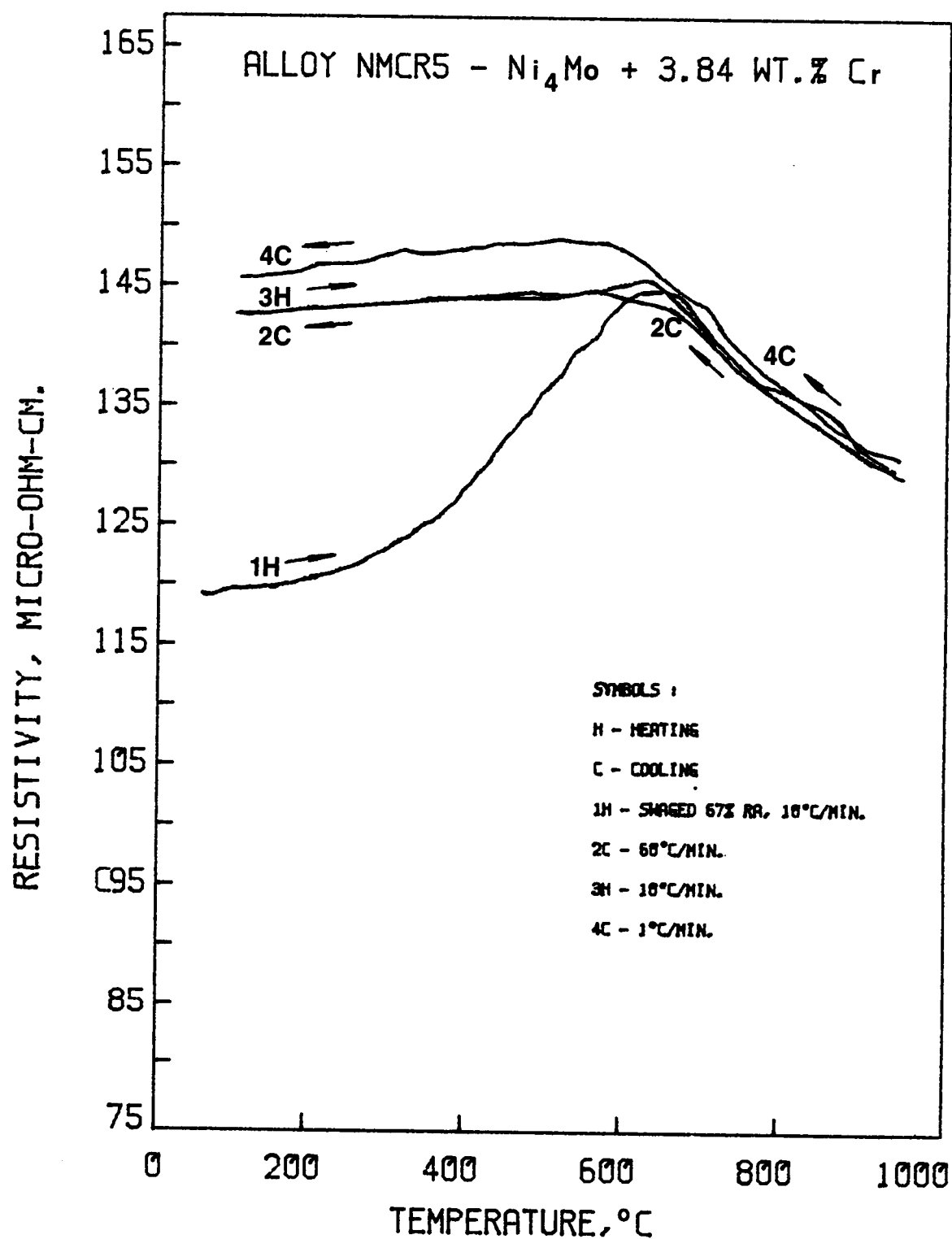


Figure B-6. Resistivity as a function of temperature for Alloy NMCR5 on continuous heating and cooling.

APPENDIX C

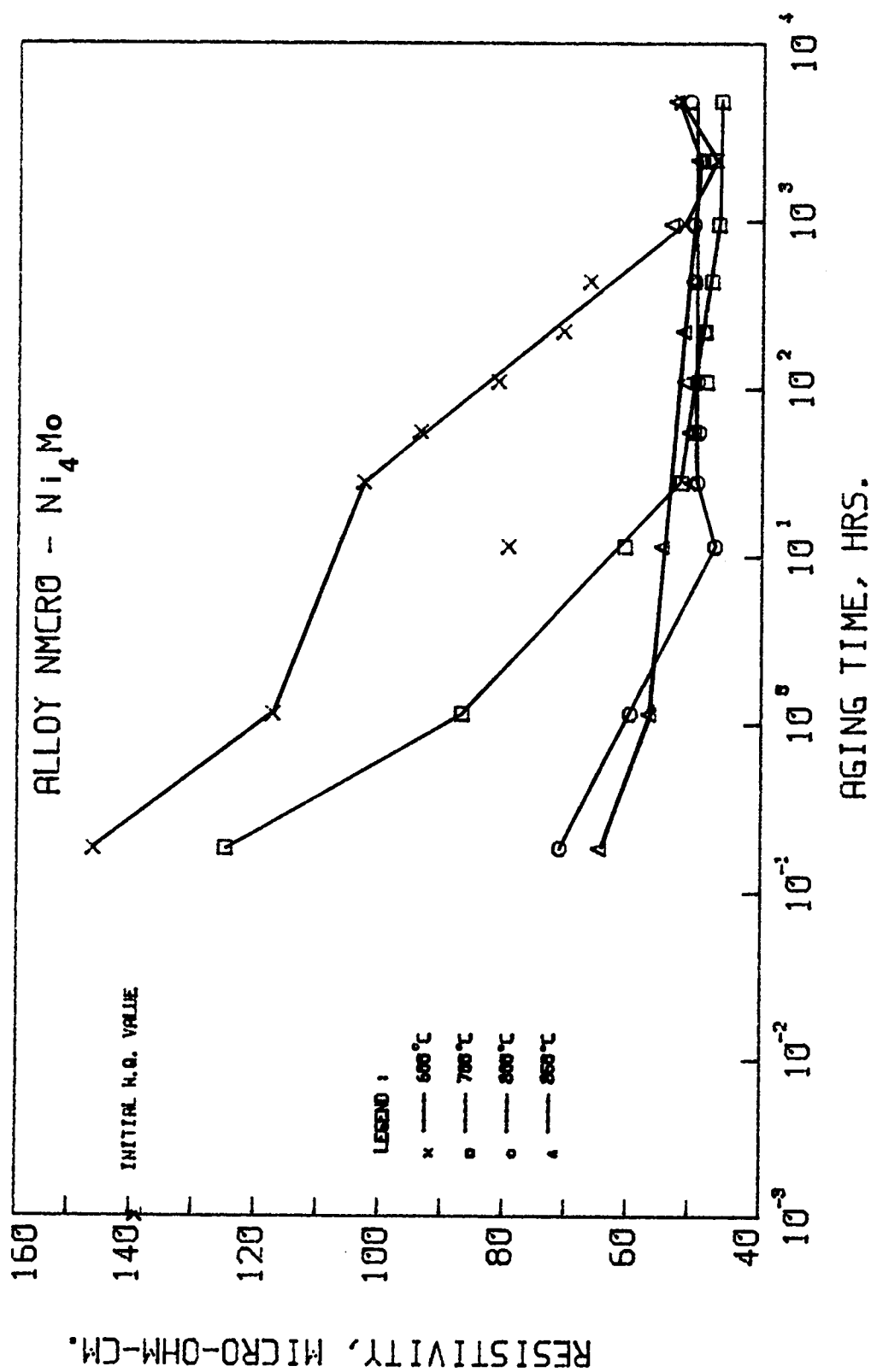


Figure C-1. Resistivity as a function of aging time for Alloy NMCRO at 600, 700, 800 and 850°C.

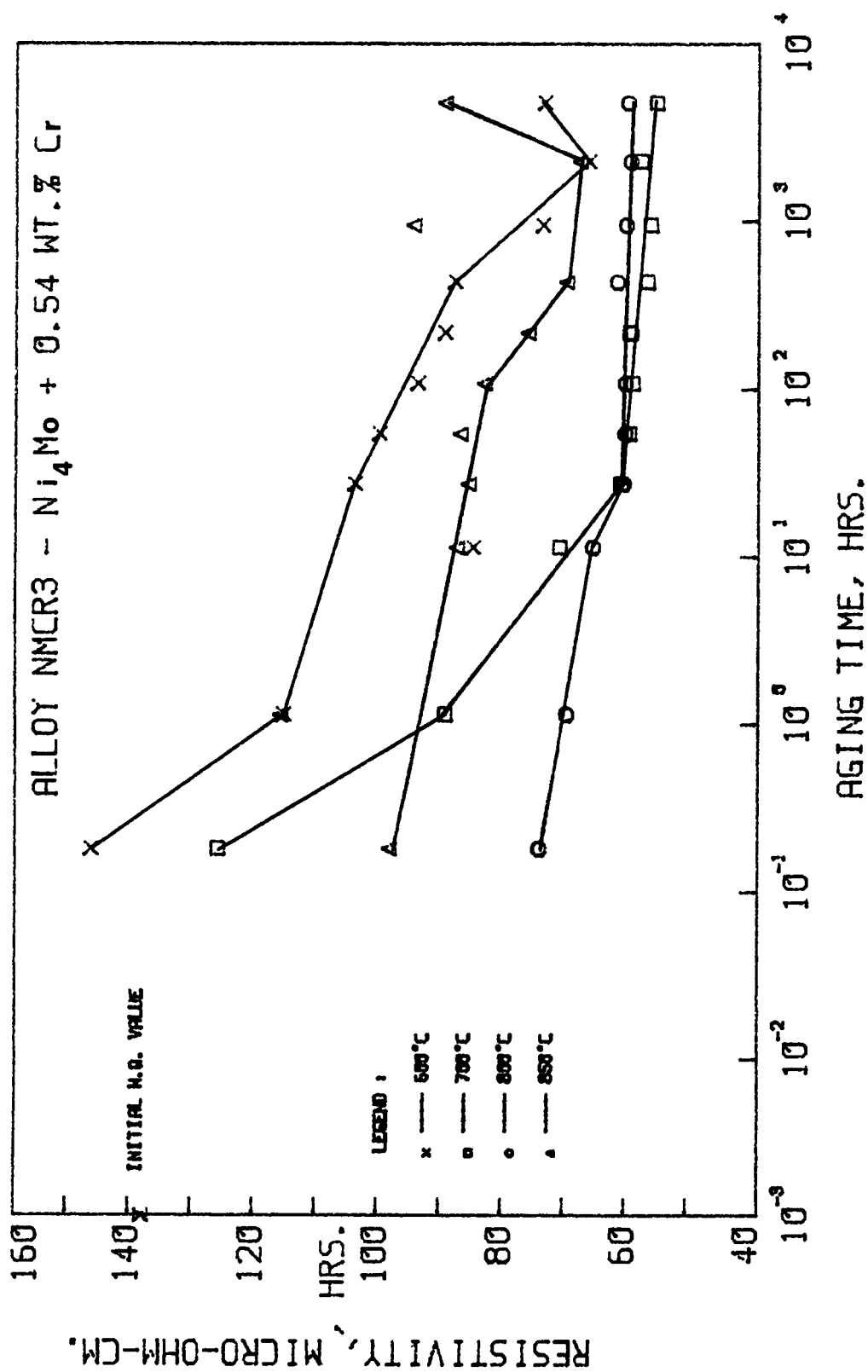


Figure C-2. Resistivity as a function of aging time for Alloy NMCR3 at 600, 700, 800 and 850°C.

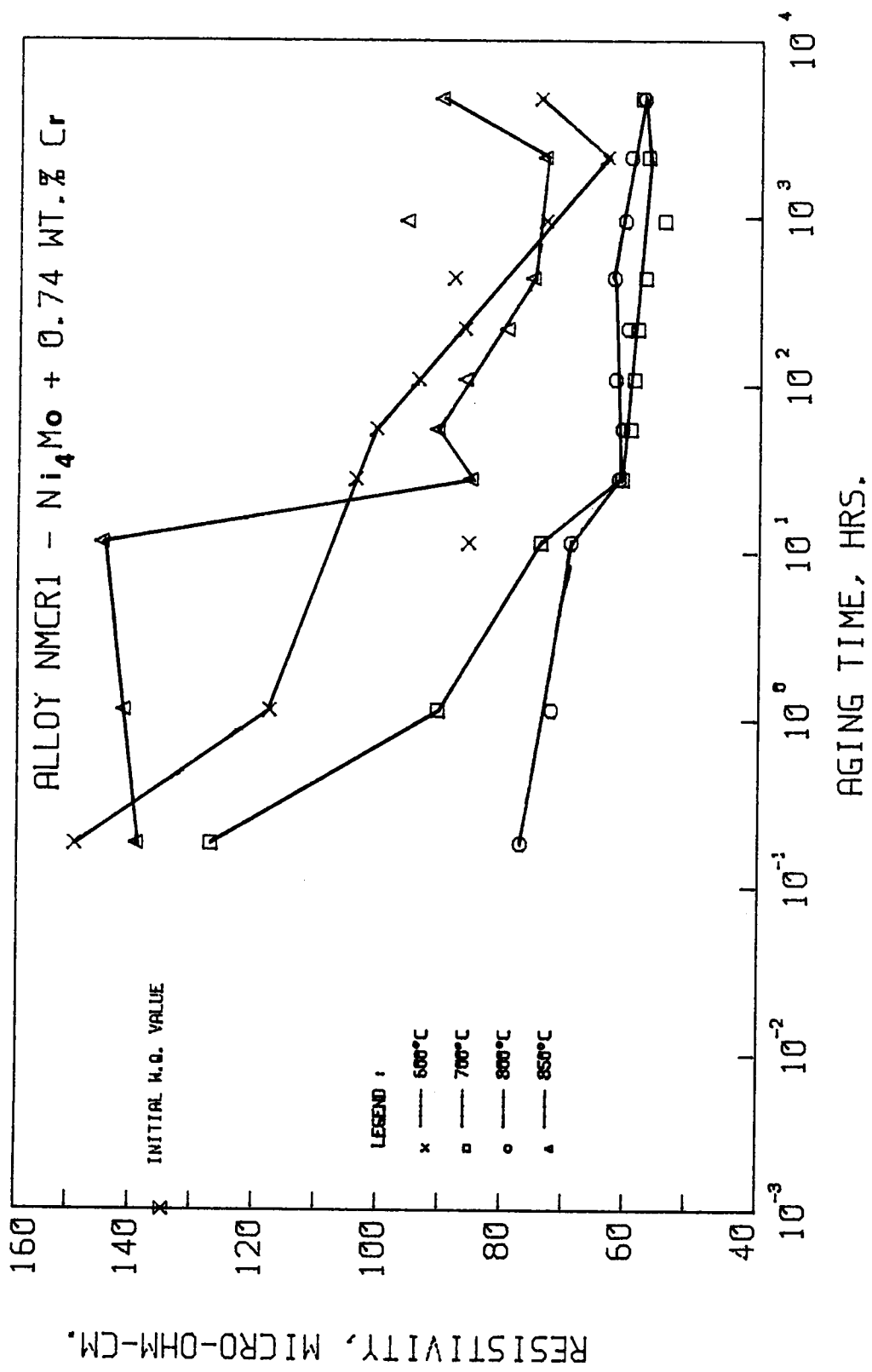


Figure C-3. Resistivity as a function of aging time for Alloy NMCR1 at 600, 700, 800 and 850°C.

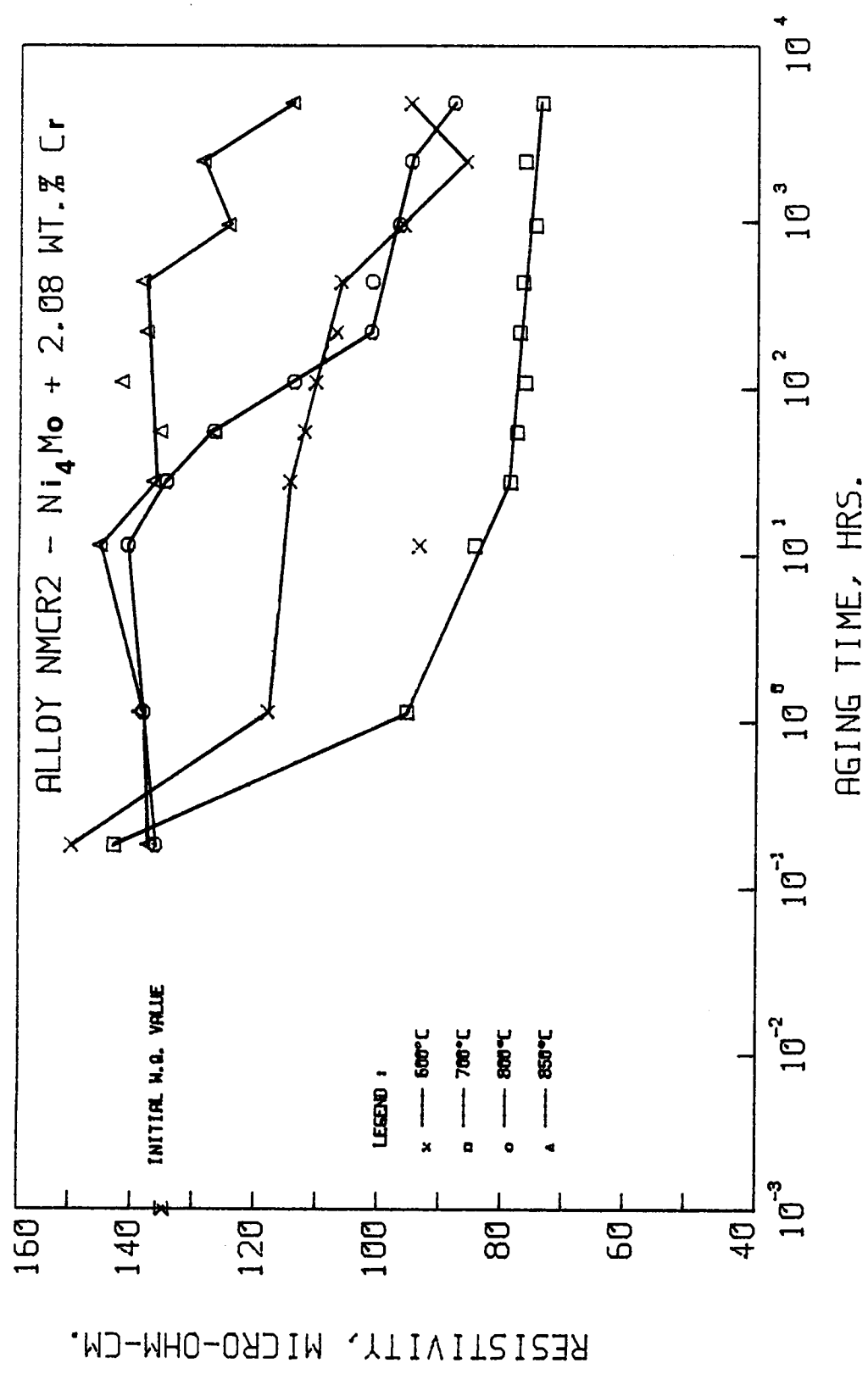


Figure C-4. Resistivity as a function of aging time for Alloy NMCR2 at 600, 700, 800 and 850°C.

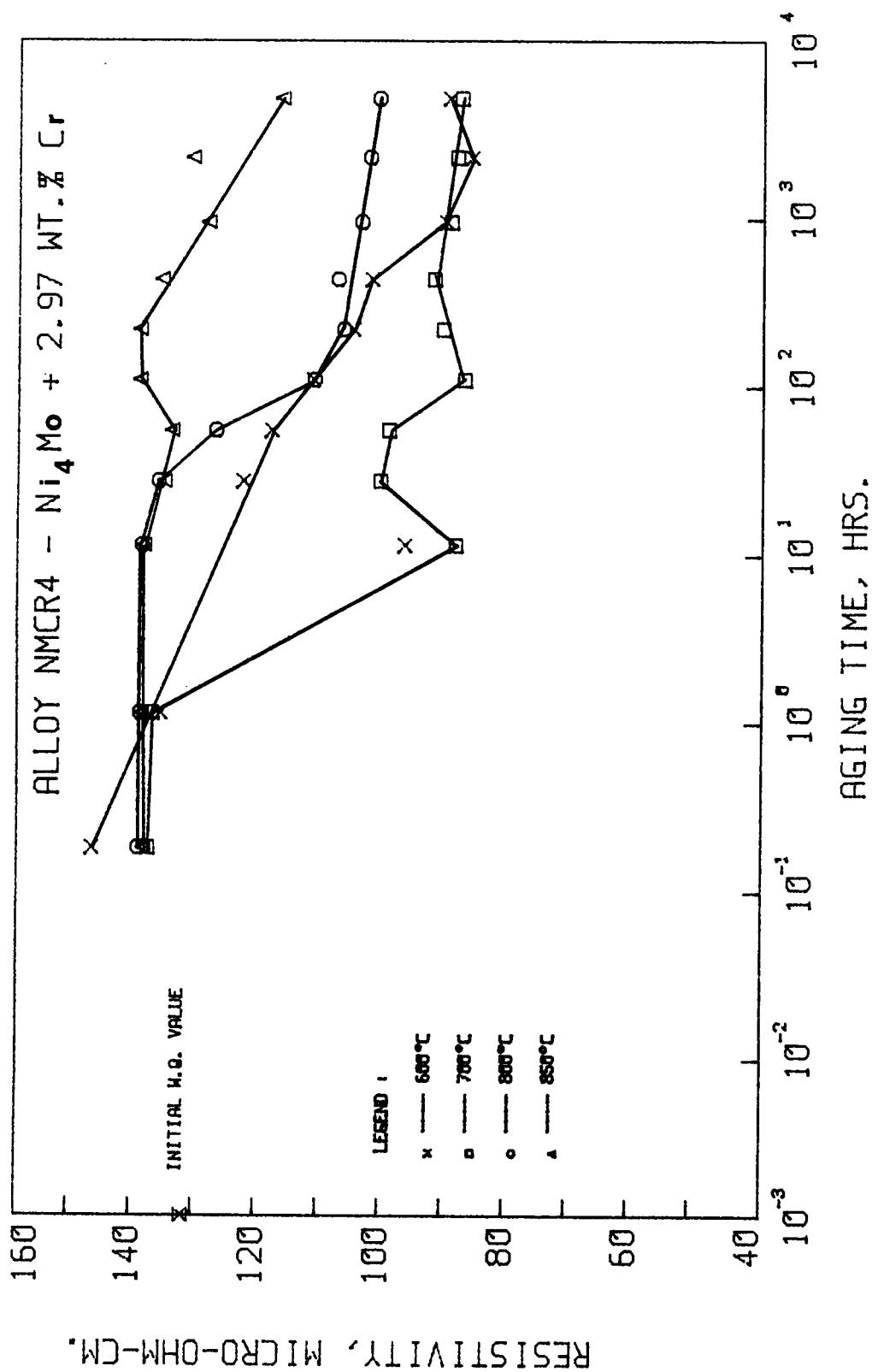


Figure C-5. Resistivity as a function of aging time for Alloy NMCr4 at 600, 700, 800 and 850°C.

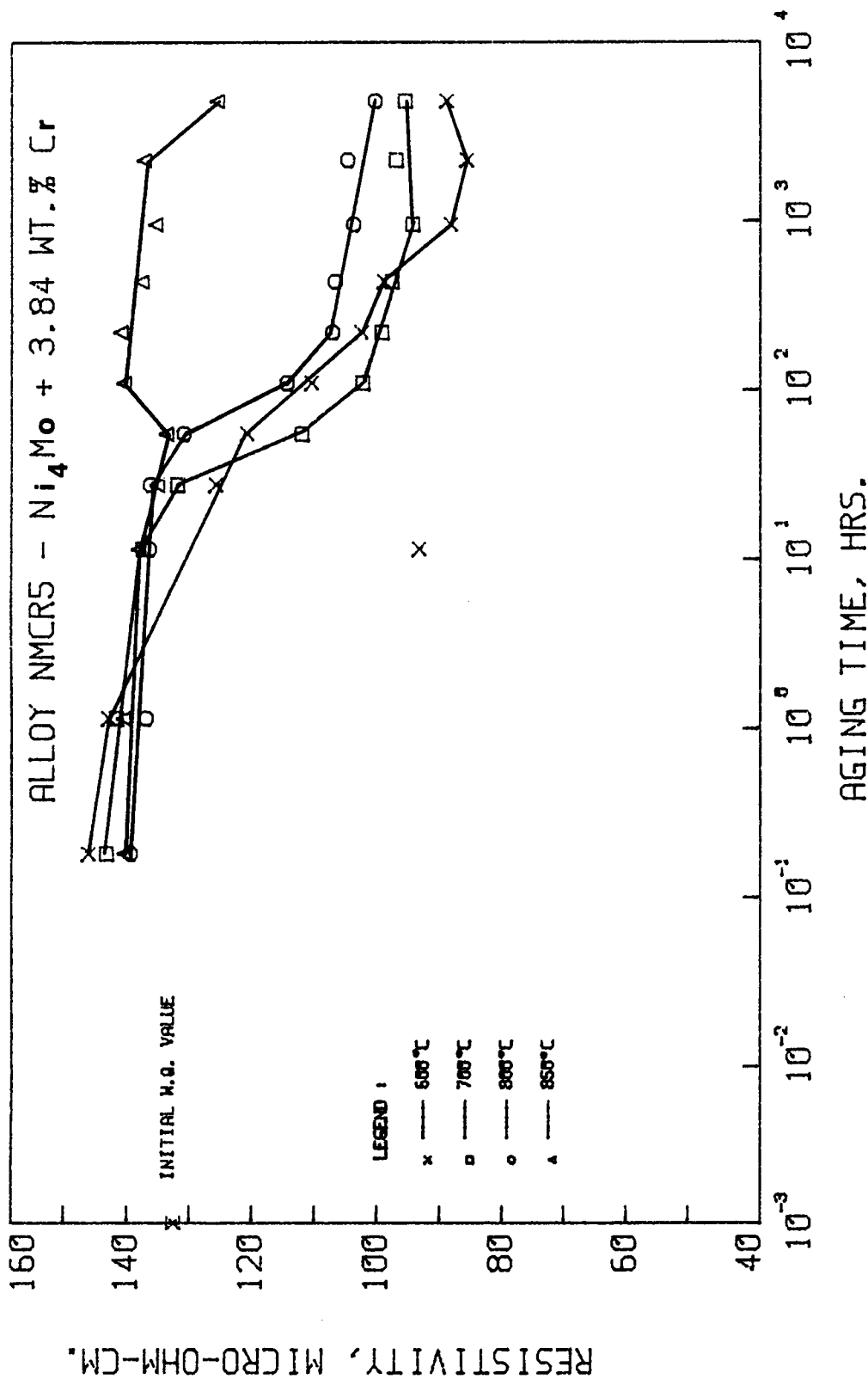


Figure C-6. Resistivity as function of aging time for Alloy NMCR5 at 600, 700, 800 and 850°C.

APPENDIX D

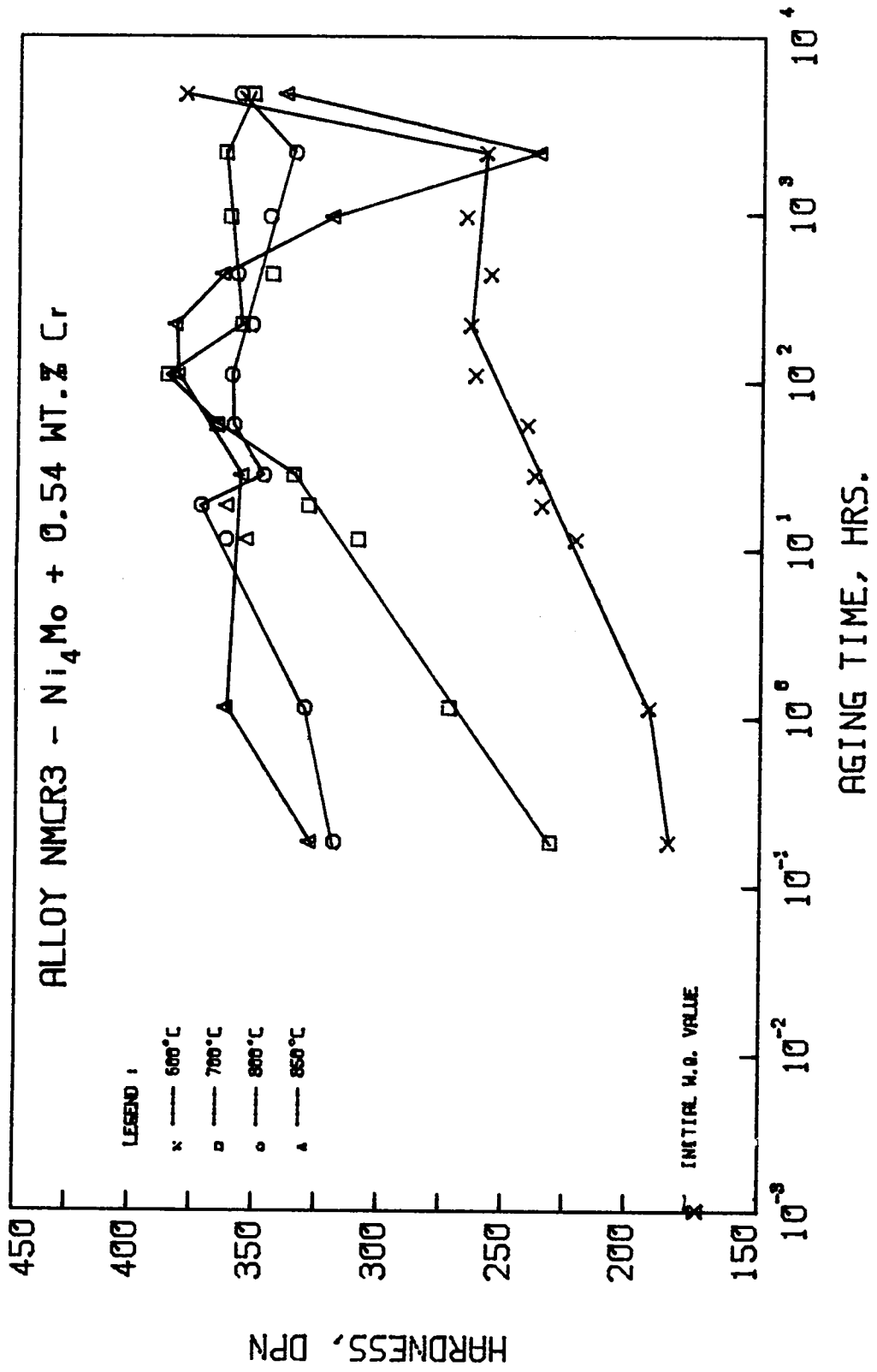


Figure D-1. Hardness as a function of aging time for Alloy NMCR3 at 600, 700, 800 and 850°C.

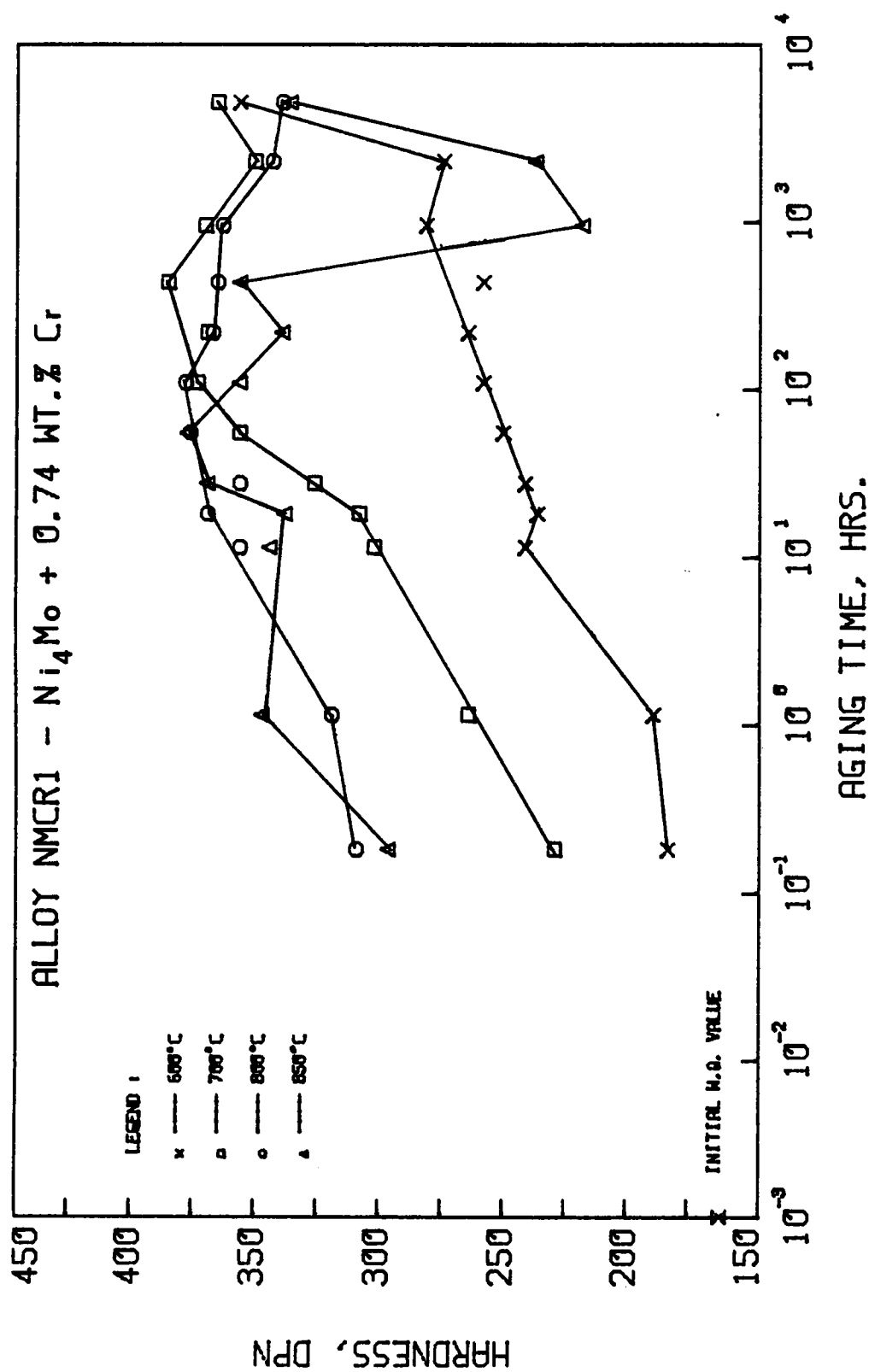


Figure D-2. Hardness as a function of aging time for Alloy NMCR1 at 600, 700, 800 and 850°C.

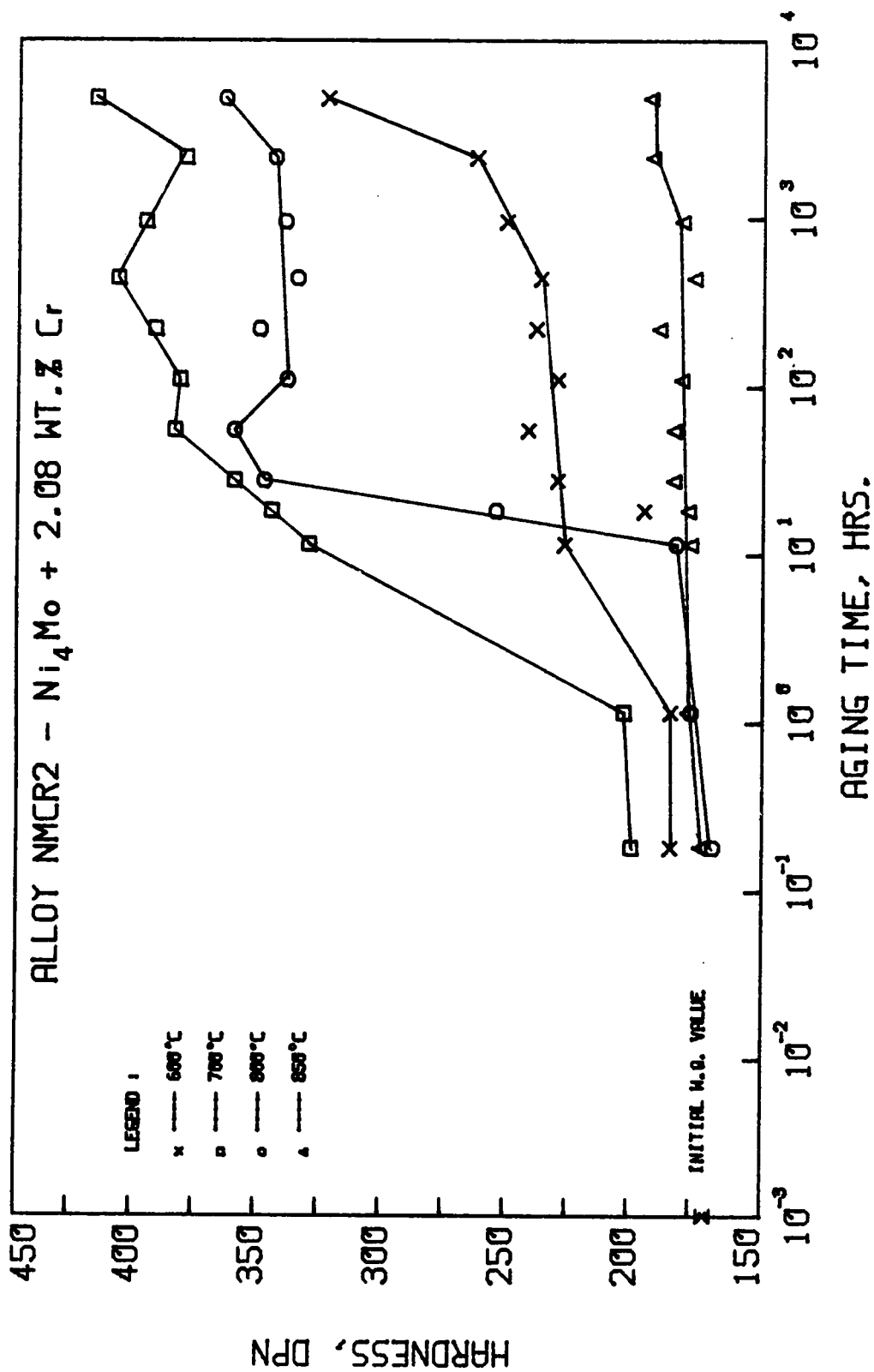


Figure D-3. Hardness as a function of aging time for Alloy NMCR2 at 600, 700, 800 and 850°C.

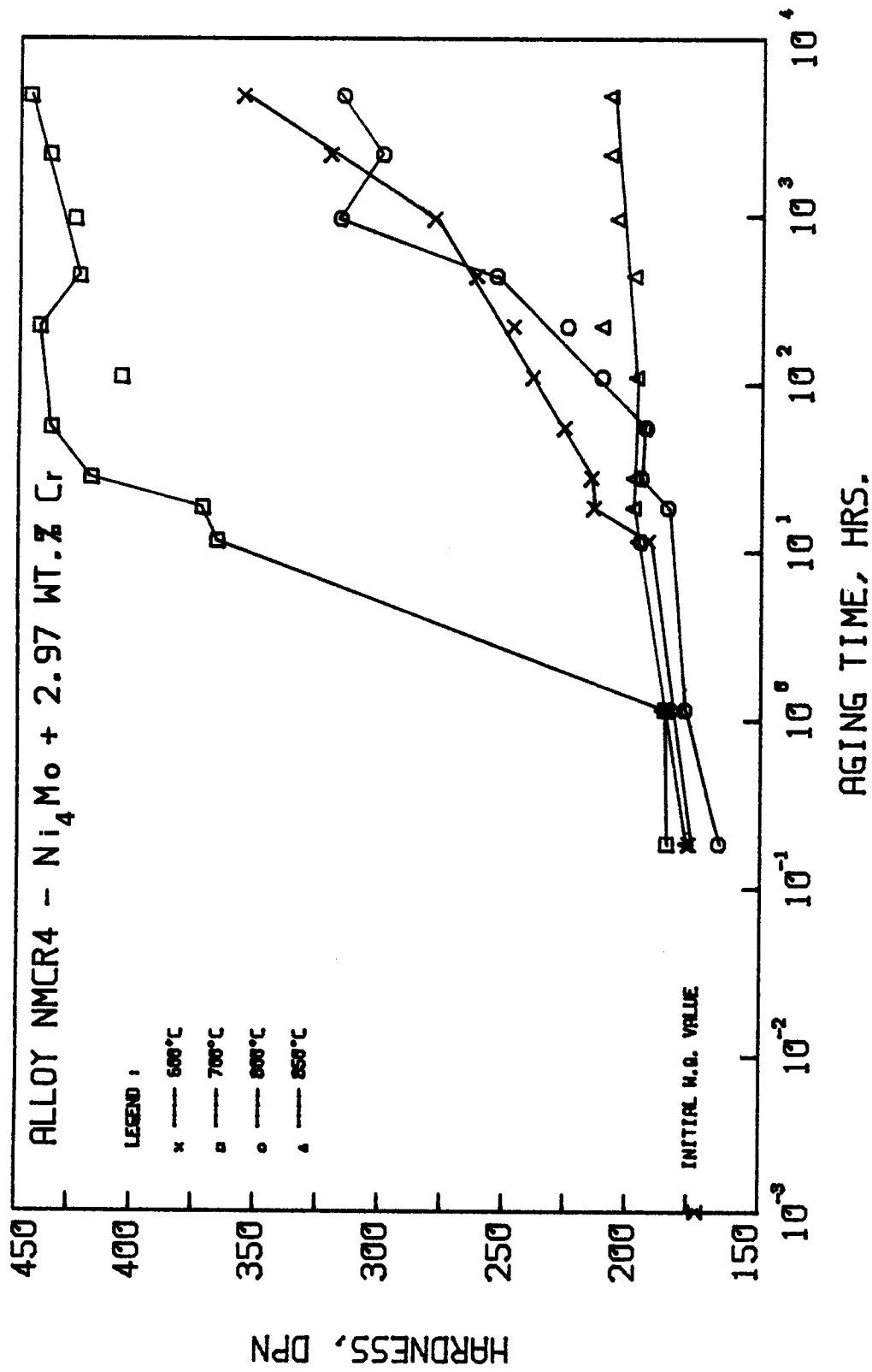


Figure D-4. Hardness as a function of aging time for Alloy NMCr4 at 600, 700, 800 and 850°C.

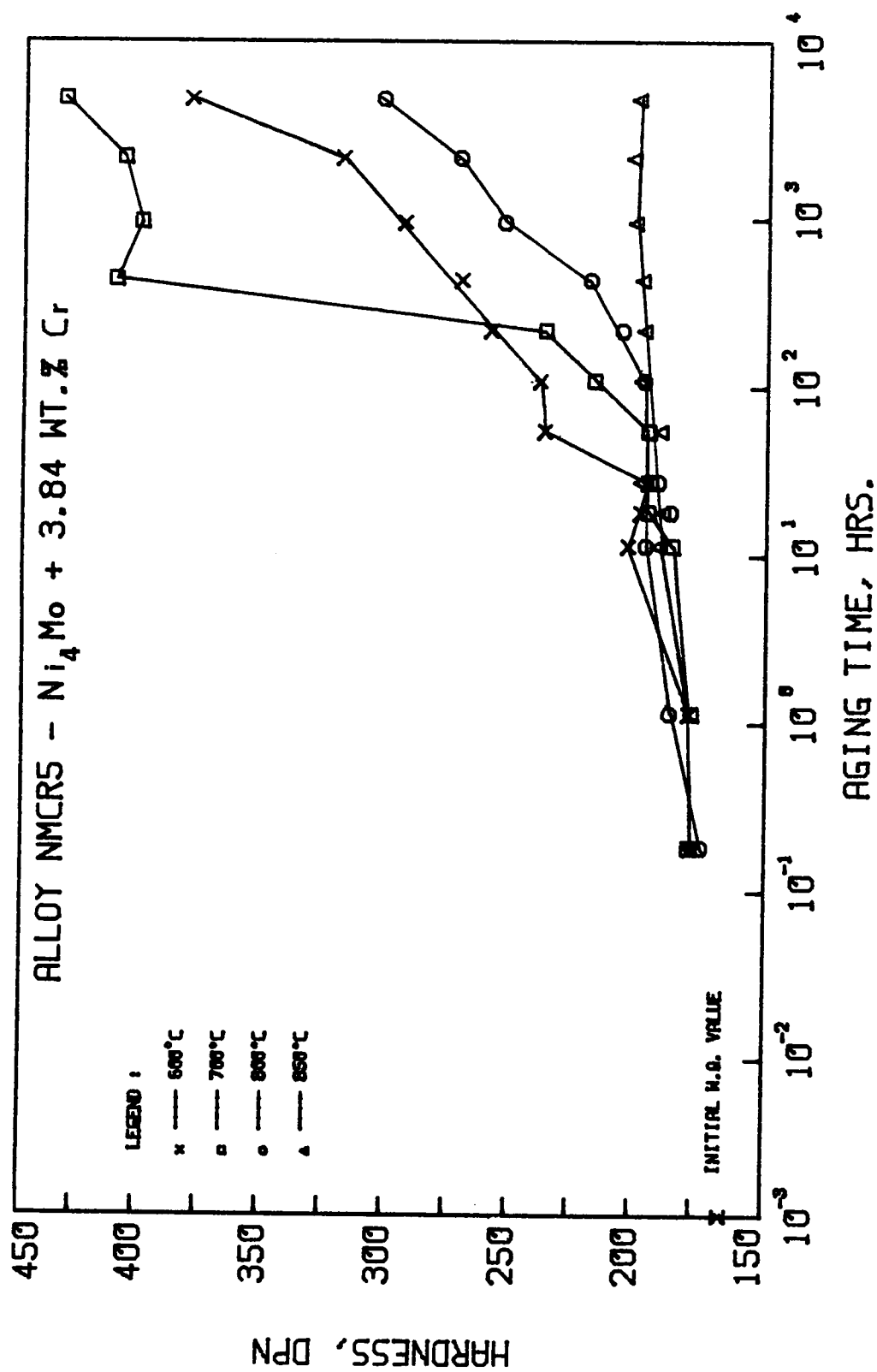


Figure D-5. Hardness as a function of aging time for Alloy NMCR5 at 600, 700, 800 and 850°C.

VITA

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