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THE EFFECT OF NICKEL ON THE BEGINNING OF TRANSFORMATION
OF AUSTENITE IN A 0.55 CARBON, 0.35 MOLYBDENUM STEEL

by

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ABSTRACT

This study is carried out to find the effect of nickel on the beginning of isothermal transformation of austenite in an iron-carbon-molybdenum alloy containing 0.55 carbon and 0.35 molybdenum. An introduction describes the iron-carbon equilibrium system, the products of slow cooling of austenite, the relation between slow cooling and isothermal transformation at temperatures below equilibrium, and a full discussion of terminology used. A literature review discusses theories of transformation and previous work on the effect of nickel on austenite transformation. Development of experimental technique in isothermal transformation and melting of pure alloys is discussed.

The isothermal transformation diagrams are shown for beginning of transformation of austenite of base composition 0.55 carbon and 0.35 molybdenum, relatively free from impurities (silicon, manganese, etc.), showing the effect of nickel on the beginning of transformation. Nickel additions used are 0, 2.13, 3.69, and 5.31 percent. Isothermal transformation is shown by photomicrographs which are discussed fully.

The effect of increasing nickel on the isothermal

transformation of an alloy containing 0.55 carbon and 0.35 molybdenum is as follows: (1) the pearlite reaction is delayed appreciably: (2) ferrite formed at intermediate temperatures (880 to 1000 deg. F.) becomes more prominently acicular, the acicular ferrite reaction taking the place of the upper bainite reaction of low nickel alloys: (3) the acicular ferrite reaction is followed first by rejection of carbide particles, and later by agglomeration and growth of the carbide phase: (4) the acicular ferrite and feathery bainite reactions as represented on the isothermal transformation diagram become separated by the appearance of a bay in the isothermal transformation curve.

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OBJECT

The phenomena accompanying the decomposition of austenite have not yet been fully or satisfactorily explained despite the fact that they have been examined by many observers and that they play an extremely important part in the heat treatment of steel. Especially lacking is the effect of single elements added to alloys of iron and carbon in which no other residual elements are present to complicate the experimental results. Once this effect of individual elements has been established it should be possible to find the effect of one alloy on that of another either directly or indirectly, and, by so doing, some of the phenomena accompanying austenite decomposition may be explained more satisfactorily than they are at present. Studies of this type should provide quantitative data for relating the isothermal transformation curve and hardenability, and from which the form of this curve and the hardenability curve could be predicted.

Establishing data fully for the above involves a long range study, and this thesis describes only one step toward the ultimate objective.

The object of this phase of the work is to establish the quantitative effect of nickel on the beginning of

isothermal transformation of austenite in a pure iron-carbon-molybdenum alloy containing 0.55 carbon, 0.35 molybdenum, and substantially no silicon, manganese, or other alloying element.

SUMMARY

A method of melting has been established for producing pure alloy samples having a predetermined carbon and alloy content, substantially free from silicon and manganese. Base materials are Norway iron, pure graphite powder, pure ferro-alloys, and pure nickel shot.

The method of melting involves using approximately 100 grams of material in a 35 cc alundum crucible, protected against thermal shock and oxidation in a globar furnace by a shaped graphite block container and lid. The melts are poured as quarter-inch-diameter ingots in a graphite mold. The ingots are annealed 30 minutes at 1500 deg.F. and cut into one-twelfth inch discs before isothermal heat treatment.

The beginning of isothermal transformation of austenite has been determined for alloys containing 0.55 carbon, 0.35 molybdenum, and 0, 2.13, 3.69, and 5.31 percent nickel at temperatures 650, 700, 750, 800, 880, 930, 1000, 1100, and 1200 deg. F. for times up to 20,000 seconds ($5\frac{1}{2}$ hours). A photomicrographic record was made of beginning of

transformation, and of progress of transformation at all temperatures where two products form.

Adding increasing amounts of nickel to an alloy containing 0.55 carbon and 0.35 molybdenum gives the following effects on the isothermal transformation of austenite: (1) the isothermal transformation curve is pushed generally to the right, (2) the pearlite reaction is delayed much more than any other reaction, (3) the tendency towards formation of acicular ferrite at intermediate temperatures is more noticeable, and on growth of acicular ferrite a carbide precipitates from ferrite, agglomerates, and grows as a separate phase formed directly from austenite, (4) the upper bainite reaction is displaced by the acicular ferrite reaction, (5) the lower bainite reaction as represented on the curve becomes separated from the rest of the curve by the appearance of a bay between the acicular ferrite and lower bainite reactions, and (6) the upper temperature of formation of lower bainite is not lowered as rapidly as the eutectoid temperature.

INTRODUCTION

To understand thoroughly precipitation of the various products from austenite during cooling or at constant temperature it is necessary to have a clear understanding of the basic metallurgy of pure alloys, or the iron-rich portion of the system iron-carbon. The portion of the iron-carbon constitution or equilibrium diagram¹ relating to plain carbon alloys and their heat treatment is shown in Figure 1.

For any steel of the carbon range covered in Figure 1, heating for several minutes to the area marked austenite at a temperature above the lines A_3 and A_{cm} transforms the steel entirely to austenite, a solid solution of carbon in face-centered (gamma) iron. By slowly cooling any steel of carbon content less than 0.8 percent (eutectoid or pearlite composition) a solid solution of carbon in body-centered (alpha) iron of extremely low carbon content, called ferrite, begins to precipitate at approximately the temperature indicated by the line A_3 . Further slow cooling to the temperature marked A_1 precipitates all the excess or proeutectoid ferrite, and, as the ferrite precipitates, the composition of the remaining austenite progresses with decreasing temperature down line A_3 to the eutectoid composition (0.8 percent carbon). The proportion of ferrite to austenite is shown in Figure 1 for a 0.4 carbon steel at 1400 deg. F. as the ratio of Y₂ to 1 - Subscripts refer to the bibliography at the end.

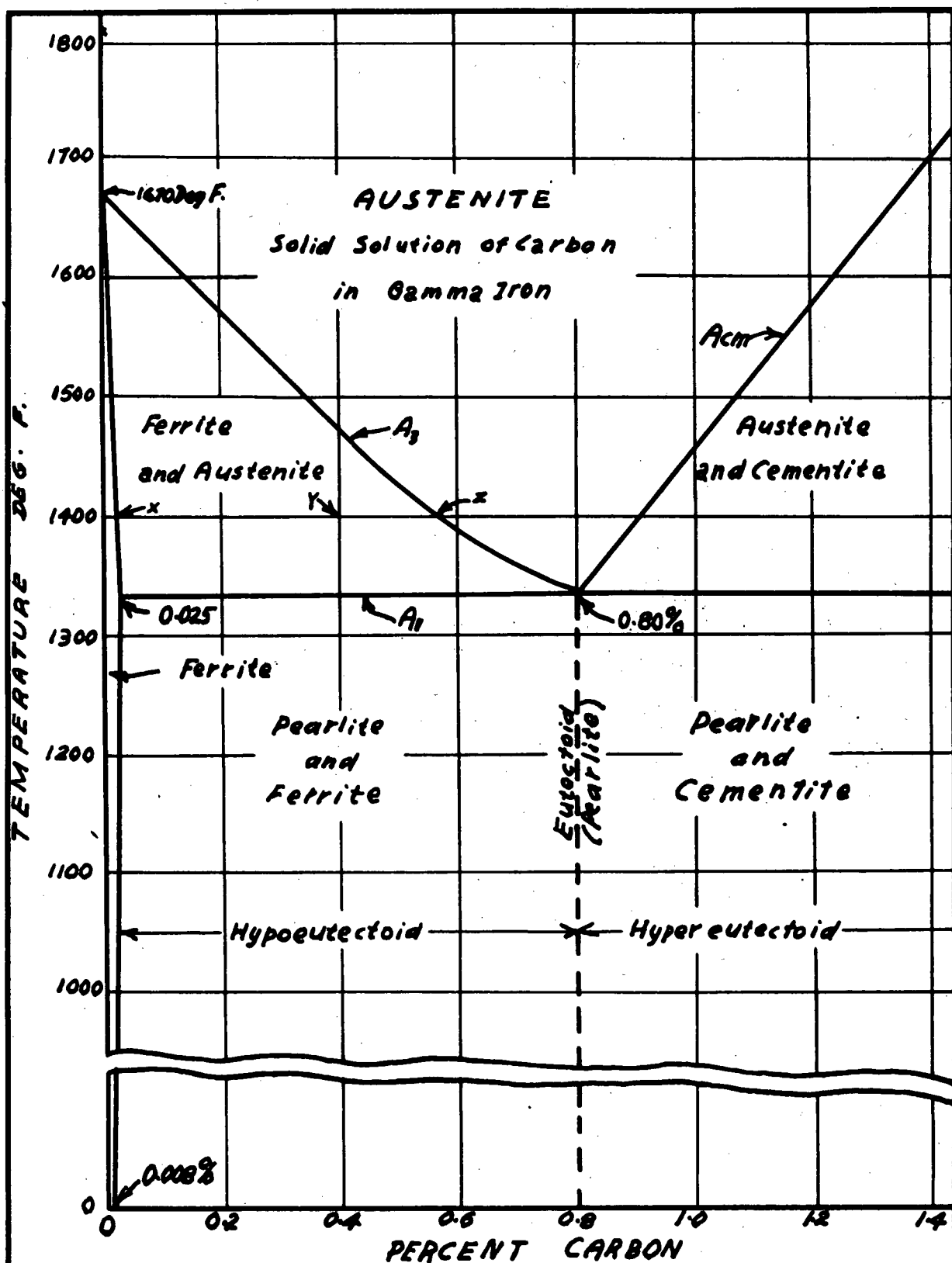


Fig 1 - Iron-Carbon Equilibrium Diagram Showing Steel Heat Treatment Portion.

x y. As the temperature is slowly lowered below the A_1 line the remaining austenite transforms to eutectoid (pearlite), which has a microstructure of alternate parallel cementite (Fe_3C) plates and ferrite. No appreciable change in structure occurs between A_1 and room temperature.

Cooling any steel above eutectoid composition is similar to the above except that the proeutectoid constituent appearing at the line A_{cm} is cementite, a compound of iron and carbon with preferred orientation of interstitial solid solution carbon atoms in a body-centered iron lattice.

The transformation process for heating a steel is the reverse to that described for cooling.

Figure 1 is reproduced in practice only with steels of low residual alloy content, and then only with extremely slow cooling, which may be expected from the fact that the lines on the diagram represent equilibrium between two phases which requires that the free energy is the same for each phase. Precipitation of any phase from austenite can occur only when the free energy of the phase is lower than that of the austenite, the excess free energy of the austenite that transforms being used up in surface energy of the precipitating phase. The adjustment in composition of the remaining austenite changes the equilibrium conditions to give the austenite a free energy equal to that of the precipitating phase. Precipitation stops when the free energies are equal.

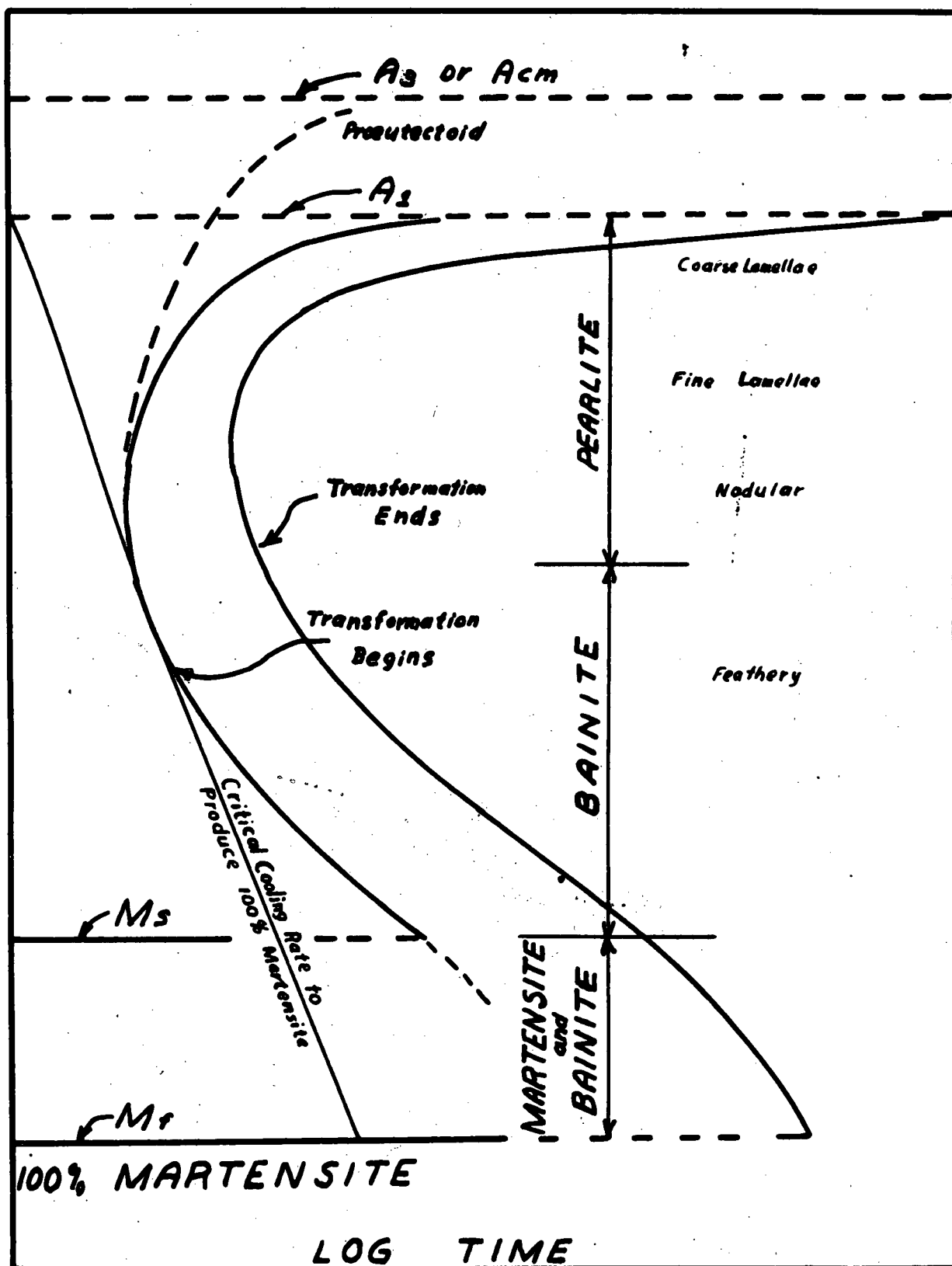


Fig2- Schematic Representation of Isothermal Transformation

Cooling at any rate faster than that required for conditions given in fig. 1 changes equilibrium relationships and produces a difference in the microstructure of the transformed product, and if cooling is fast enough metastable phases other than ferrite and pearlite are produced. These different conditions are best related in fig. 2 which is a schematic representation of the isothermal transformation diagram. Temperature is represented vertically, time on a logarithmic horizontal scale. The two solid curved lines represent beginning and end of isothermal transformation of austenite after quenching rapidly from austenitizing temperature to isothermal temperature. The dotted line represents a proeutectoid constituent, ferrite for hypoeutectoid steels, cementite for hypereutectoid steels, which is non-existent for a eutectoid steel. The area between the proeutectoid line and the beginning curve is greater the farther the carbon content of the steel is from the eutectoid composition. The two horizontal lines M_s and M_f represent 0 percent and 100 percent martensite which forms during cooling if the cooling is fast enough to avoid the curved portion, and also during cooling if transformation is arrested at any time after beginning at a temperature higher than M_s by quenching the specimen to room temperature; the martensite reaction is not isothermal. Martensite has a highly strained, distorted body-centered lattice structure which approaches a tetragonal lattice. The

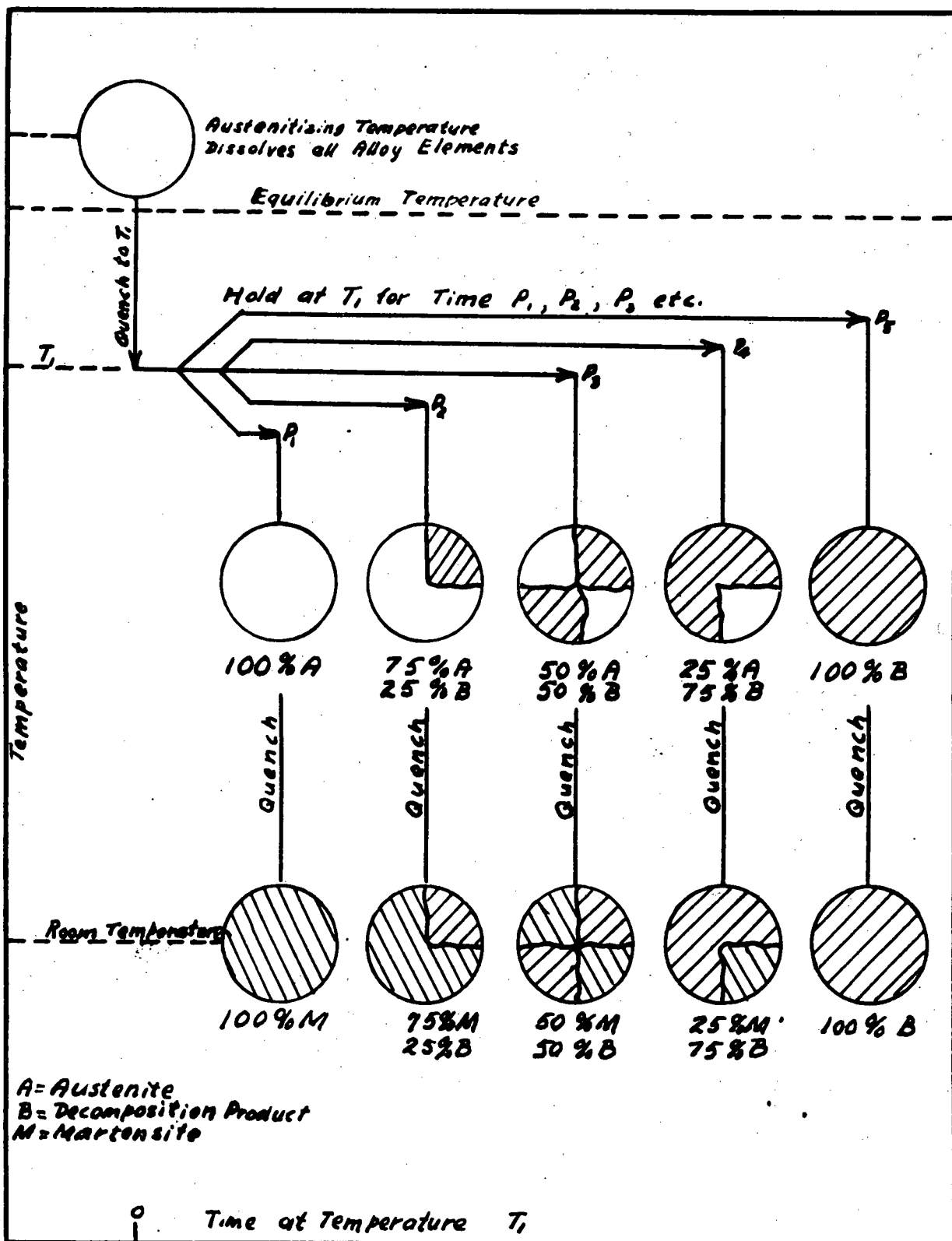


Fig 3- Method of Studying Isothermal Transformation
Metallographically Represented Schematically

body-centered lattice is attained after reheating martensite for tempering.

A schematic method of producing the isothermal transformation diagram is shown in fig. 3.

The products of transformation of steel vary with temperature of formation. Just below the A_1 temperature pearlite which forms is coarse lamellar, almost spheroidal. As the temperature of formation is lowered the resulting pearlite lamellae are finer and the start of the reaction is increasingly faster down to the "nose" which represents the maximum rate of reaction. At this maximum another very finely lamellar product is formed, commonly called upper bainite. Below the "nose" the product is bainite, an acicular aggregate of extremely fine feathery lamellae, now more commonly referred to as lower bainite. The austenite which does not transform to martensite on quenching and holding isothermally at a temperature between M_s and M_f eventually transforms to lower bainite.

Partially transforming to any product and quenching to room temperature immediately stops the reaction and as the specimen is cooled through the range M_s to M_f the untransformed austenite transforms to martensite. This has made possible isothermal studies of the beginning and progress of transformation by metallographic methods.

THEORIES OF TRANSFORMATION

During the past few years several theories have been advanced to explain the mechanism of nucleation and growth of precipitating phases during austenite decomposition in steels. The first work reported on isothermal transformation is that of Bain and Davenport², and from their work has been developed what is now known as the isothermal transformation diagram.

Later investigators^{3,4} have shown that the bottom portion of "S-curve" should be a series of horizontal lines, indicating that martensite does not form isothermally, but only by lowering the temperature. Recent investigators^{5,6} have realized the importance of interpreting the curved portion of the "S-curve" as two "C-curves", namely, pearlite and bainite, although previous workers recognized a difference in the type of transformation to pearlite and bainite. A theoretical basis for the isothermal transformation diagram was presented by Zener⁵ which explains some of the lesser understood facts, but this has been open to question^{7,8, 29} because of too many assumptions which may not be valid. Hultgren⁹ recently proposed six distinct reactions in his description of decomposition of austenite in alloy steels.

An experimental fact that transformation to pearlite and bainite normally begins at grain boundaries has been shown to be theoretically true by Zener⁵. With this assumed and

observed fact in mind earlier workers_{10,11,12} presented analytical theories of nucleation and growth of pearlite, all based on certain assumptions. It must be noted that any theory for solid-solid reactions cannot be accepted as fact because many of the variable factors cannot be measured or, rather, have not yet been measured. Yet many facts can be observed empirically even if they cannot be directly measured, and analytical theories may be produced by analogy with those experimentally measurable for gas-liquid-solid reactions.

Mehl and Jetter₁₃, Mehl₁₀ and Bowman₁₄ have advanced the nucleation theory that, during the random migration of the solute atoms in austenite, volumes of the correct composition and size are established by chance, depending upon energy relationships, for the formation of a nucleus, and this nucleus can remain or grow only if the free energy of the precipitating phase is lower than that of austenite.

Wells and Mehl₁₅, Pellissier, Hawkes, Johnson and Mehl₁₆ have shown that local diffusion currents of solute atoms are very necessary for the formation and growth of pearlite, keeping in mind that for plain carbon steels only carbon and iron atoms have to diffuse, whereas in alloy steels each alloy atom, as well as carbon and iron, has to diffuse either to or away from a potential nucleation site. Mehl₁₀ and Ham₁₇ advanced the theory that diffusion away from

an area of a potential carbide nucleus of an alloy element not appearing in the carbide phase and diffusion towards that area of elements appearing in the carbide phase must take place simultaneously before the potential nucleus can form.

Mehl₁₀ related his diffusion nucleation theory to interlammellar spacing decreases to describe the gradual change from pearlite to bainite nucleation at the pearlite maximum or "nose" of the "S-curve".

The greatest number of lattice discontinuities or imperfections exist where there is a break in curvature of the lattice which is the case for grain boundaries, the greater the curvature or smaller the radius the greater the discontinuity of the lattice. For impure steels inclusions also cause sharp discontinuities. Zener₄ postulated that alloying elements tended to congregate at lattice imperfections (although why they should is questionable) and the carbide or ferrite which forms usually has definite high or low alloy content compared with normal plain carbon steel ferrite and carbide.

Because alloying elements change the carbon diffusion rate very little_{14,16,18,19} and alloy elements diffuse at much lower rates than does carbon₁₇, nucleation and growth is delayed by the slower diffusion of the alloying element. This same type of reasoning can be applied to the delay in formation of proeutectoid phases and bainite.

Some general and specific alloy effects upon the "S-curve" of austenite decomposition have been presented by Davenport₂₀ and Bain₂₁, but it is assumed because it is not stated otherwise and because manganese is included in the analysis of steels used, that alloy additions have been made to commercial steels. Much work has been coordinated by the United States Steel Corporation and published in their "Atlas of Isothermal Transformation"₂₂ giving the isothermal transformation diagrams of many commercial steels. An extensive compilation of "S-curves" published up to 1945 has been presented by Morral₂₃, nearly all of which are for impure or commercial alloys.

Some workers have noted_{14,18,21,24} the partition of alloying elements between the ferrite and carbide phases, and have advanced some theories on the partition effect to explain the effect of alloying elements upon the "S-curve". The main outline of this theory is that some alloys appear only in ferrite, others only in carbide, and some with varying degrees of partition between the two phases. The low diffusion rate of alloy elements slows down formation of nuclei of sufficient size to grow, and also slows down growth by the slow movement of the various partitioning elements to the respective phases.

Investigators have indicated_{4,10,25,26,27} by X-ray studies and other means the theory that pearlite is nucleated by cementite or carbide, and bainite is nucleated by ferrite.

Bainite has the same orientation relation as ferrite in respect to the austenite from which it is formed. Bainite differs from proeutectoid ferrite only in microstructure and composition, the difference in composition being that bainite has a higher Carbon content on formation and retains increasingly more carbon to completion of transformation as the formation temperature is lowered. One possible further proof that proeutectoid ferrite and bainite are similarly formed from the same nucleus is offered by Hollomon, Jaffe, and Norton²⁸, in showing that holding a hypoeutectoid steel isothermally in the proeutectoid range without transforming visibly to ferrite, markedly reduces the time to form bainite by a subsequent quench to the bainite temperature. This is even more revealing when it is shown that the fractional times (to form visible amounts) held in each range add up to unity. This would substantiate the theory that nucleation begins the instant the steel is reduced below the critical temperature range. The apparent additiveness of the ferrite and bainite reactions is possibly not general since energy relationships and diffusion rates are different at different temperatures, and the nucleation and growth rates would depend on energy and diffusion rates.

The theory that nucleation begins instantly on an atomic scale is contrary to the theory that nucleation starts on a microscopic scale about visual beginning, as is usually

assumed in theoretical discussions^{4,10,11,12,29}. The same variance of opinion was voiced in trying to explain precipitation hardening where hardening is obtained before particles could be detected by X-ray, which leads to an assumption that "quasi-nuclei" can possibly exist.

Some of the above theories can be combined or expanded to give the theories presented by Blanchard, Parke and Herzig³⁰, and Bowman¹⁴ that decomposition of austenite can be explained on a basis of rates of nucleation and growth of both cementite and ferrite, each of the four rates being some function of temperature.

The reaction to martensite is a different type, in which a new set of energy relationships supplant the normal nucleation and growth reactions, and some form of strain mechanism^{2,3,4,10} operates so that instantaneous reaction occurs as the temperature is lowered, and the strain thus set up by partial transformation changes the required energy conditions so that a lowering of temperature is necessary to cause further transformation.

THE EFFECT OF NICKEL

Some previous investigators^{17,19,21,22,32,33} have noted the effect of nickel on the isothermal transformation of various types of steels, most of which were of commercial grade with varying amounts of impurities such as manganese

and silicon. This did not permit a strictly comparative, quantitative estimate of the effect of nickel. It has been reported by Davenport²⁰ that, in general, nickel moves the "S-curve" to the right with little change in shape except that caused by lowering the Ae temperatures.

Both nickel and manganese produce a sluggish transformation reaction in carbon free iron alloys and lower considerably the Ae Temperatures in carbon alloys^{31,34}. This sluggishness was reported³⁴ to be so great that two years were required to measure equilibrium in a 4.8 percent nickel alloy. As a result of these observations Ham¹⁷ assumes that carbon does not necessarily have to be present in manganese and nickel alloys of iron to retard the decomposition of the gamma phase (austenite in carbon alloys). Hence Ham concludes that manganese and nickel retard austenite transformation because of their presence in the original austenite and in the subsequently-formed ferrite which must contain both elements. This is apart from any effect they may have on the rate of formation and growth of any precipitating phase other than ferrite. Expanding the reasoning further, the effect of manganese and nickel in shifting the pearlite reaction to longer times may be caused by the fact that they must appear in ferrite rather than in the carbide phase, and that their inherent sluggishness on the austenite to ferrite reaction delays the austenite to carbide reaction proportionally.

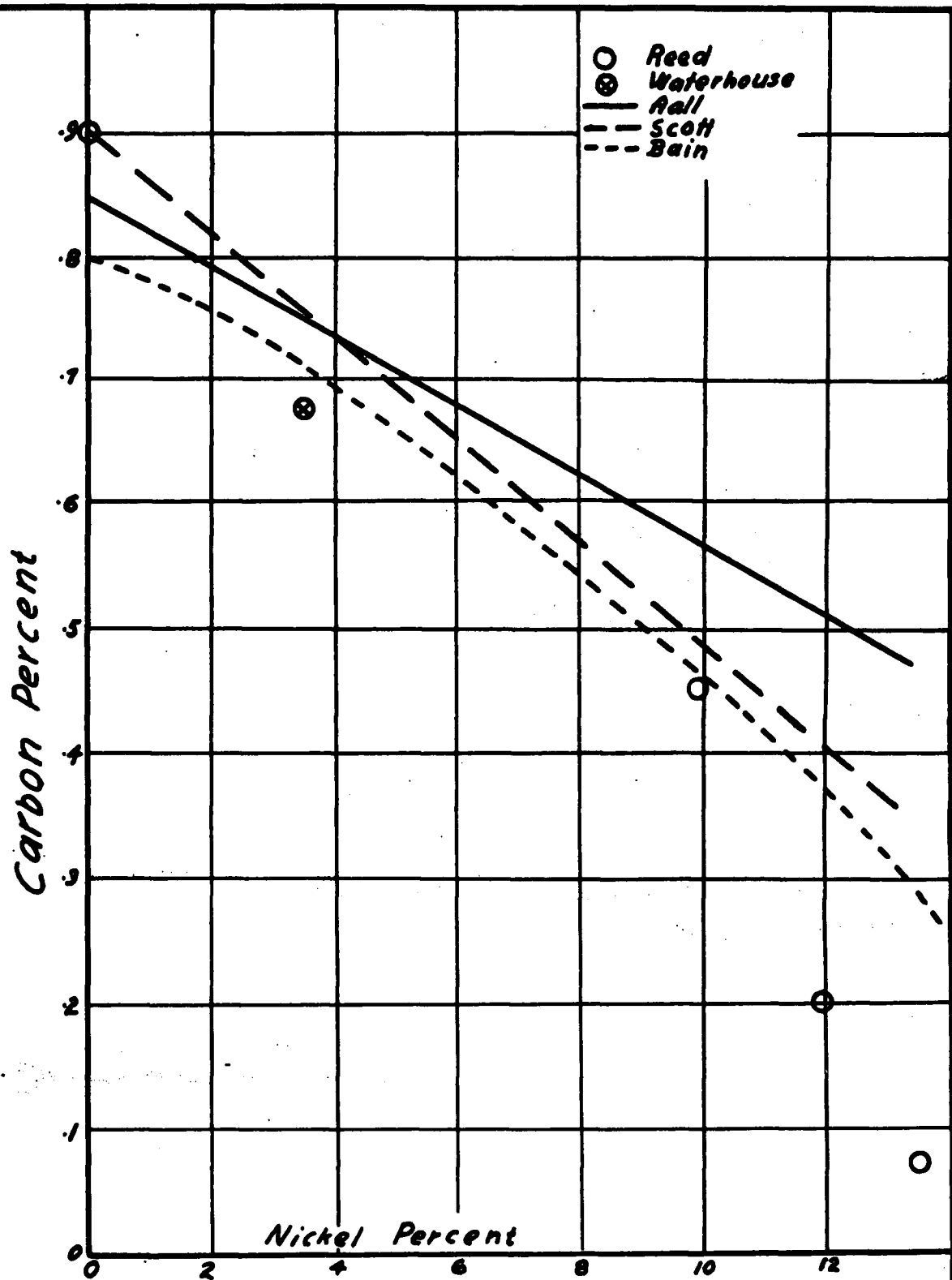


Fig 4 - Effect of Nickel on Eutectoid Carbon Content in Steel

Ham₁₇ has recognized that diffusion must be accounted for in any theory explaining the decomposition of austenite by nucleation and growth. Much useful data has been presented on diffusion coefficients for nickel_{14,35}, manganese₃₅, carbon_{14,37}, and molybdenum_{17,38}.

Ham's explanation of the effect of nickel and manganese on the "S-curve" does seem to hold true in the bainite region where it has been shown_{25,26,27} that bainite is formed from ferrite nuclei. Because both nickel and manganese produce an equilibrium sluggishness in the gamma to alpha transformation the delay in proeutectoid ferrite and bainite reactions should be proportional to the degree of sluggishness in the gamma to alpha transformation.

This reasoning may not hold true for the effect in delaying the pearlite reaction since it is generally conceded that pearlite is nucleated by carbide_{4,10,23,26,27} and not by ferrite. The common conception is that the addition of carbide-forming elements (Cr, Mo, W, V, Ti) delays nucleation and growth of carbides simply because of diffusion requirements of the carbide-forming elements, and that nickel additions with carbide forming elements delay the reaction still more because of sluggishness. However, this may not be the case as it is conceivable that the stronger carbide-forming elements may hasten nucleation so that extremely small "quasi-nuclei" form, much smaller than the stable size for

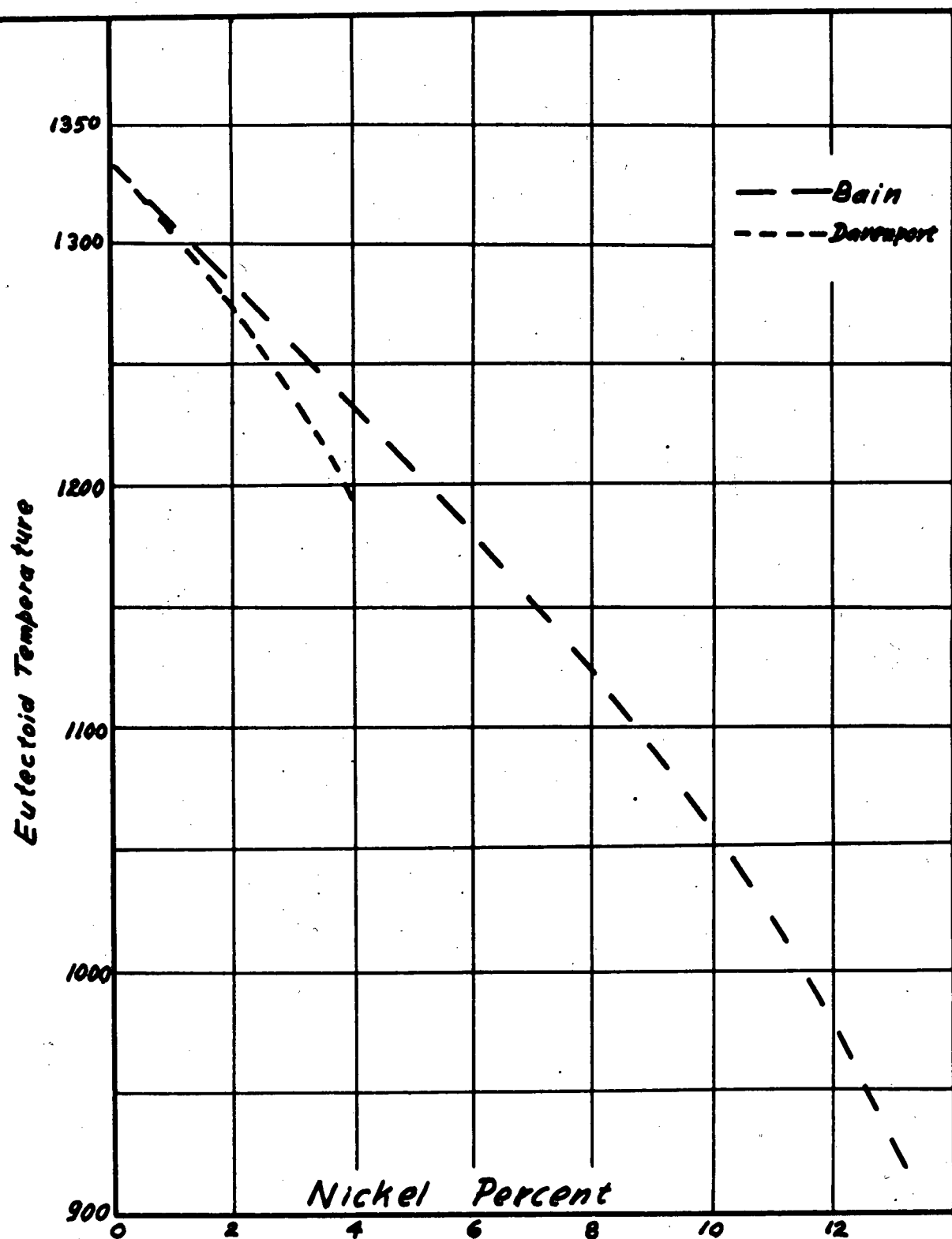


Fig 5 - Effect of Nickel on Eutectoid Temperature in Steel.

growth requirements, yet potentially stable. The delay in transformation may be caused by the slow diffusion of the "quasi-nuclei" to form nuclei of a size required by energy relationships for growth to occur and large enough to see. It is also conceivable that ferrite-forming elements contribute to the delay in the pearlite reaction because of intensifying effects on the carbide-formers.

Graphical representation of the effects of alloying elements on the A_e temperature and the eutectoid carbon composition is given by Bain₂₁. Reasonable agreement up to 6 percent nickel has been shown by Marsh₃₁ for the effect of nickel on the eutectoid carbon content, which is reproduced in fig. 4 with the addition of Bain's data. The effect of nickel on the eutectoid temperature is shown in fig. 5.

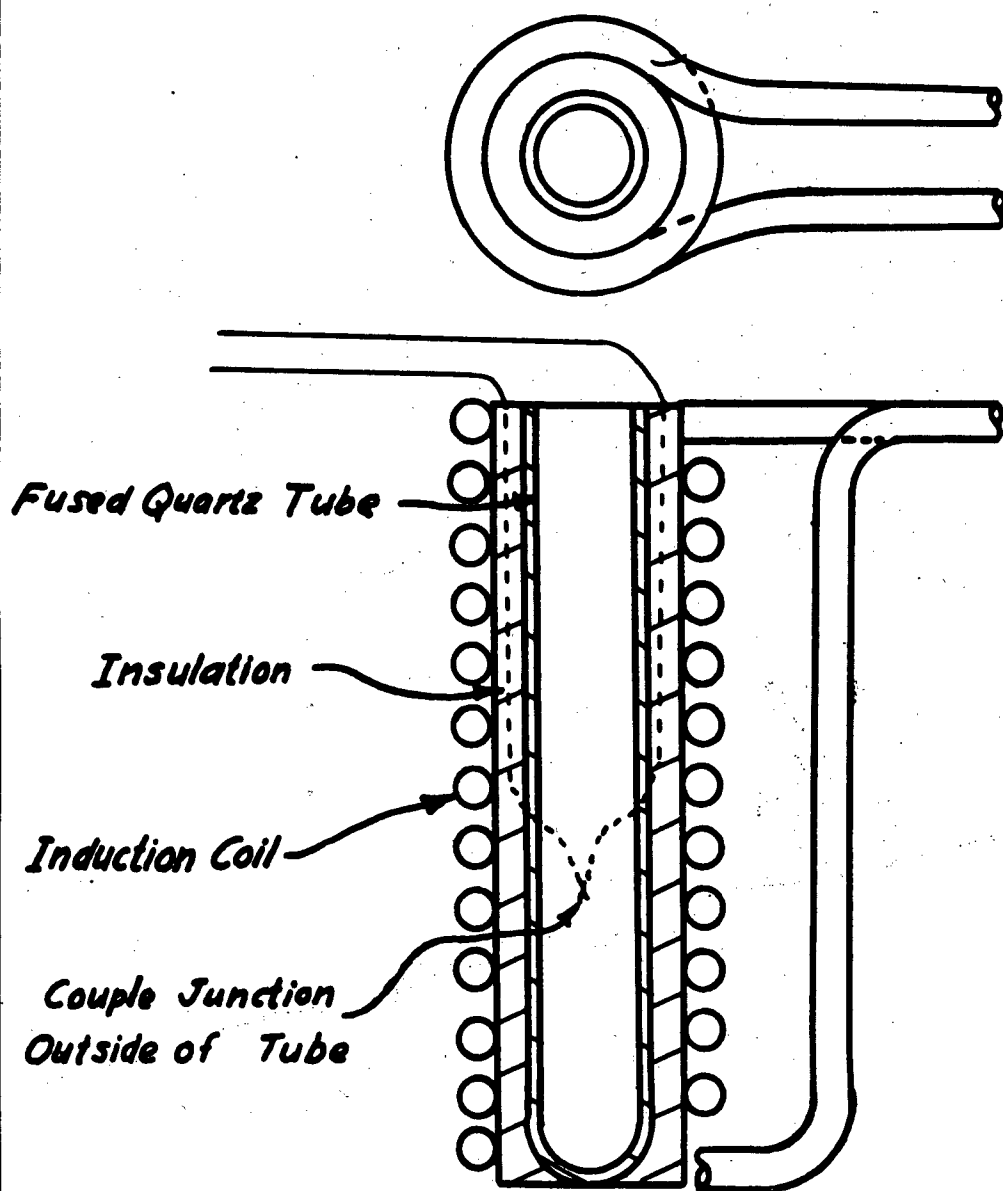


Fig 6 - Crucible For Induction Melting.

EXPERIMENTAL TECHNIQUE IN MELTING

After preliminary experimental work melting steel samples in a high frequency induction furnace using various types of crucibles and in a glo-bar type furnace, it was decided that the most satisfactory melts can be obtained in the glo-bar furnace.

One of the difficulties encountered in producing steel samples from pure materials is obtaining uniform carbon and alloy contents from accurately weighed materials. Carbon unites with the oxygen which is always present in varying quantities in the melt, depending upon the purity of the materials used, the method of melting, time of melting, and degree of atmosphere protection given the melts. Hence complete carbon pickup in the steel from weighed amounts of pure graphite is difficult unless complete atmosphere protection and similar melting conditions for each melt are maintained.

Induction Furnace

Reasonably uniform carbon analyses were obtained by melting in the induction furnace, but several difficulties were experienced. The temperature of the melt was hard to control because the crucible did not heat uniformly nor to as high a temperature as the melt itself, and accurate measurement of the temperature of the steel itself was not possible. The temperature of the melt was measured empirically by strap-

ping a platinum, platinum-rhodium thermocouple to the outside of the silica tube inside layers of asbestos insulation (fig. 6), assuming 50 to 75 deg. F. lag between the melt and the thermocouple itself. Melting proceeded until a Potentiometer indicated the outside of the tube was 2900 deg. F. Time of melting for approximately 75 gram samples was one and one half to two minutes.

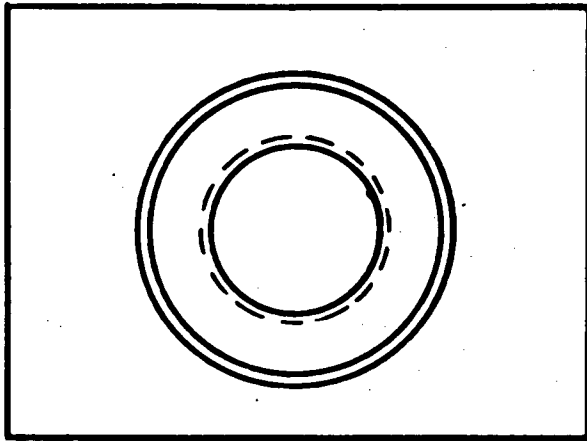
Because the top of the crucible was much colder than the melt itself considerable steel froze during pouring. Hence the melts used for analyses were frozen in the tube, which had to be broken to remove the ingot.

A protective atmosphere could not be supplied without affecting the temperature of the melt. Five ingots gave carbon analyses within a range of 0.05 percent carbon, but a 50 percent carbon loss was obtained when attempting to make a 0.50 carbon steel. Complete recovery of molybdenum from ferromolybdenum and nickel from nickel shot was obtained.

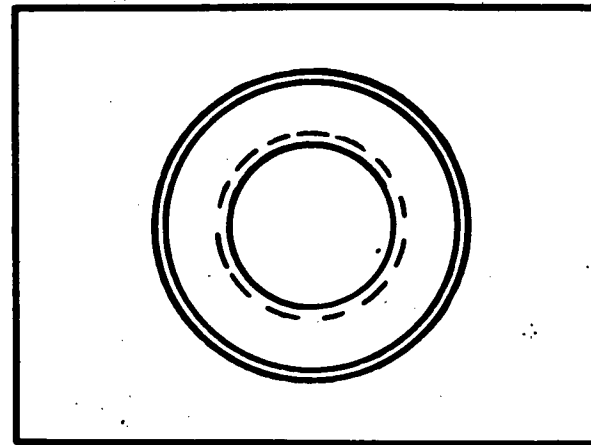
Possible methods for producing uniform temperatures throughout the crucible and melt in the induction furnace are: (1) fit a ready made crucible into a shaped graphite block, and (2) make a paste crucible of magnesia or zirconia inside a graphite mold and dry very slowly.

Glo-bar Furnace

The melt and crucible can be heated to a uniform controllable temperature in the glo-bar furnace. Thus small



*Old Method, Crucible Removed From
Block for Pouring*



*New Method, Crucible Not
Removed For Pouring*

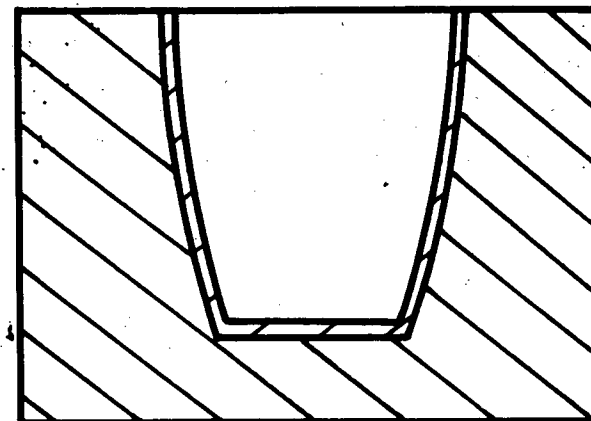
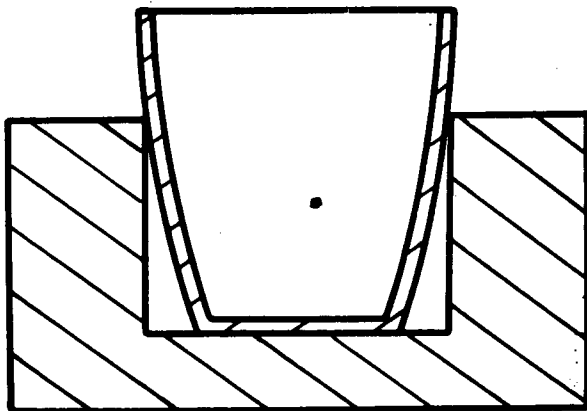


Fig 7 Melting Crucible and Carbon Block Support.

melts can be poured readily without much cooling of the charge. As the temperature required to melt the steels is in the range 2950 to 2975 deg. F. it is necessary to have a crucible which has high thermal shock resistance and reasonably high strength at the high temperature. Very few materials are satisfactory or obtainable for use directly in a basic-lined furnace. High grade alundum crucibles have proved satisfactory.

To prevent oxidation and subsequent attack on the crucible lining, and also to reduce thermal and mechanical shock, the alundum crucibles are placed in a graphite block and covered with a graphite lid. In this way reasonably small carbon losses occur; sometimes, indeed, there is a small carbon pickup from graphite powder falling from the lid.

The method finally adopted for making 100-gram steel melts is as follows:-

(1) Using Norway iron as the base material, holes are drilled in one end of small rods, into which are packed pure graphite powder and the required ferroalloy (ferromolybdenum, ferrochromium, etc.) in weighed amounts.

(2) The Norway iron bars are placed, packed-end down, in 35 ml porous alundum crucibles, and any required amounts of nickel added in the form of shot.

(3) The crucible is placed in a shaped graphite block (fig.7) in the furnace, covered with a graphite lid,

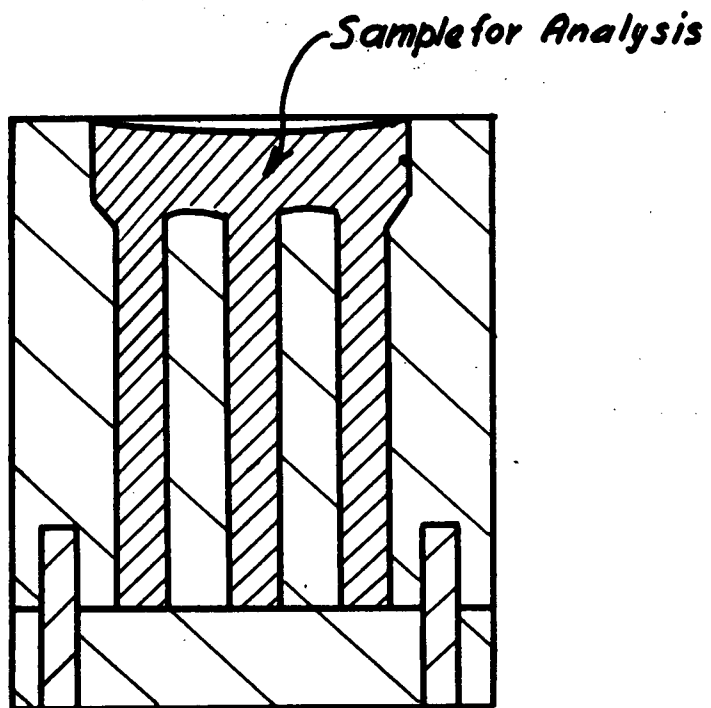
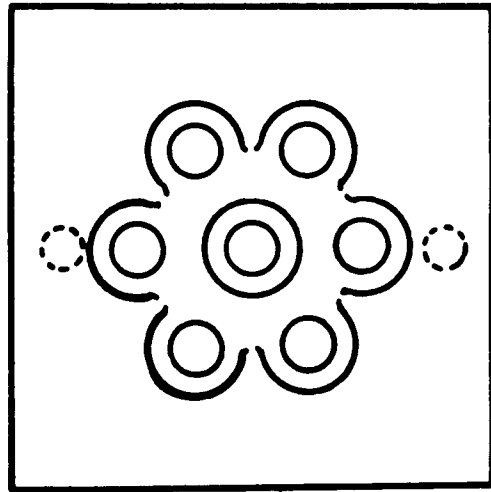


Fig. 8 Carbon Mold For Casting Steel Melts.

and the furnace brought up to 2975 deg. F.

(4) A small amount of calcium-silicon is added as a deoxidizer and the furnace temperature which drops to 2925 is brought up to 2950 deg. F.

(5) The steel is poured into a heated graphite mold (fig. 8) to make quarter-inch bars from which small specimens are cut after fully annealing in a salt bath furnace.

Preliminary melts showed that, for Norway iron accurately packed with sufficient pure graphite to make a 0.60 percent carbon steel, the resultant product for three melts contained 0.57, 0.56, and 0.61 percent carbon respectively, which indicates that reasonably close carbon content can be obtained by this technique.

Melts made without an addition of deoxidizer before pouring produced some hollow and some honeycombed bars. Examination of every small specimen cut from eight deoxidized melts showed macro-cavities to be practically non-existent.

Samples for analysis were machined from the top of the casting (see fig. 6) which had been thoroughly cleaned and given the same softening treatment as the bars.

The alundum crucibles used in the glo-bar furnace withstand the high temperature reasonably well after a thorough drying. Although the crucibles are not attacked chemically, it was found that they are very susceptible to

thermal shock after one melt.

Another type of crucible which may be used in the glo-bar furnace to withstand the high temperatures and give atmosphere protection is a paste of zirconia or magnesia inside a graphite block. This type has not been tried.

Total recovery of added alloying elements was obtained in all melts when nickel shot, ferromolybdenum, and ferrochromium were used. Very little silicon was added to the melts from the deoxidizer calcium-silicon.

EXPERIMENTAL TECHNIQUE IN ISOTHERMAL TRANSFORMATION

Experimental technique in producing isothermal transformation diagrams was developed using a commercial alloy steel NE8740. The technique followed is similar to the methods developed and described in detail^{1,37} wherein both metallographic and dilatometric methods are used.

Dilatometric specimens were cut $1\frac{5}{8}$ inch longitudinally from a $1\frac{1}{2}$ inch diameter bar of hot-rolled, air cooled NE8740 steel. Metallographic specimens $\frac{1}{4}$ inch square were cut from 1/16 inch transverse discs from the same bar. Specimens for microscopic work were wet-ground to a point approximately 1/32 inch below the surface, near the center of a 1/16 by $\frac{1}{4}$ face, so that any decarburization was absent from the section examined, and so that the longitudinal banding was visible.

Since this steel showed marked banding, the criterion of beginning of transformation was the first precipitating particles which could be detected visually at 1300 magnifications. Because of the marked banding and the high magnifications required to detect each constituent, estimates of percentage transformation are difficult if less than 10 percent is transformed.

All specimens were austenitized 15 minutes at 1550 deg. F. in a neutral salt bath, producing average ASTM grain sizes 7 and 8. The metallographic specimens were suspended by 22 gauge chromel wire threaded through a small hole drilled in the centre of a $\frac{1}{4}$ -inch square face. The dilatometer specimens were handled with preheated chromel tongs. All transformations were carried out in salt baths controlled pyrometrically within plus or minus 5 deg. F. Times were measured from the instant the specimens entered the baths: less than two seconds was required to transfer the dilatometer specimen from the austenitizing bath to the quench bath; less than one-fifth of a second was required to transfer a metallographic specimen from one bath to the next.

Metallographic methods were found the more accurate. The dilatometer can only be used below 800 deg. F. and then only when the time to begin transformation is long. The M_s line was found by the method of Greninger and Troiano³, in which, briefly, specimens are quenched to form some martensite

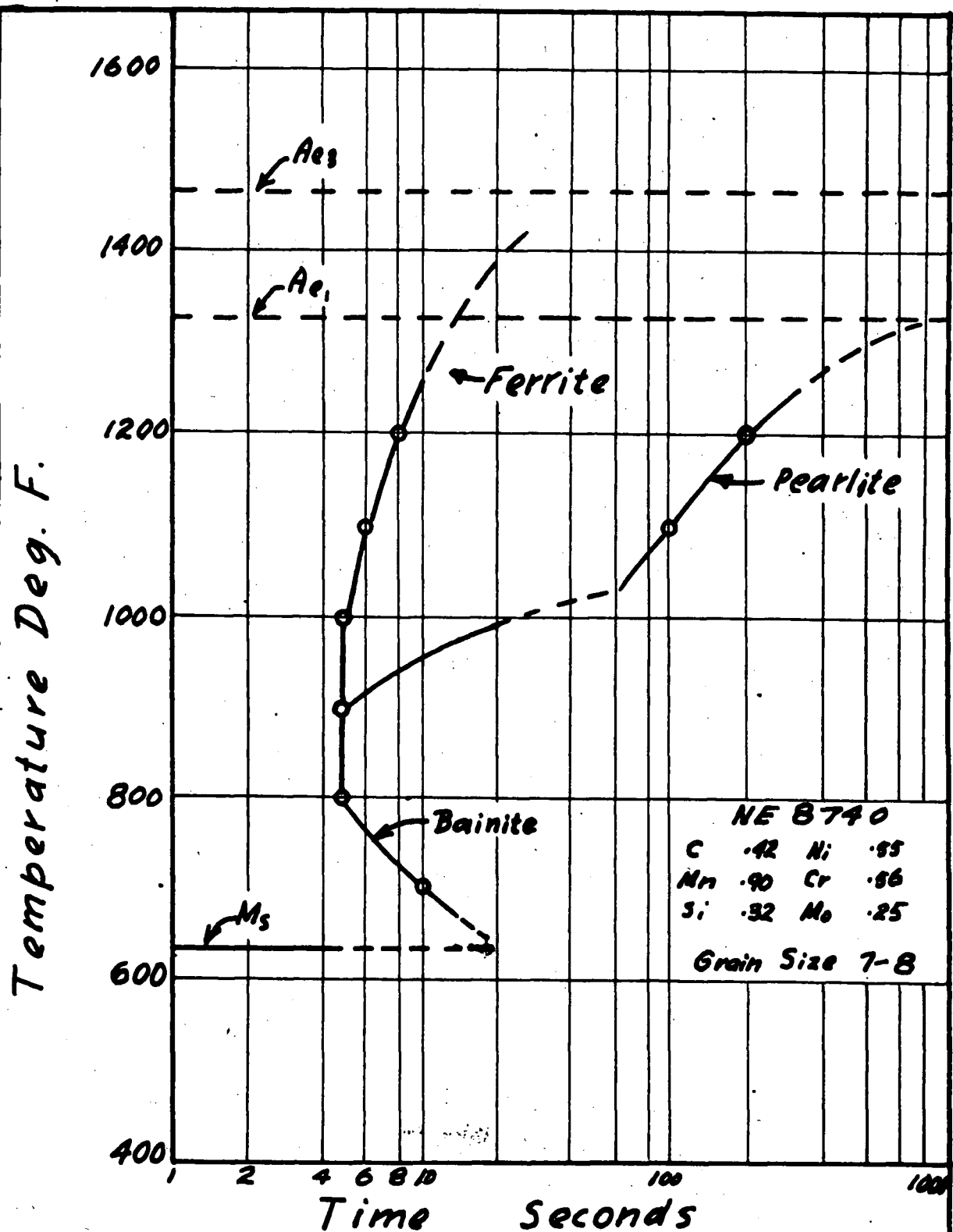


Fig 9 - Beginning of Isothermal Transformation
of Steel NE 8740 Austenitized 1550 F.

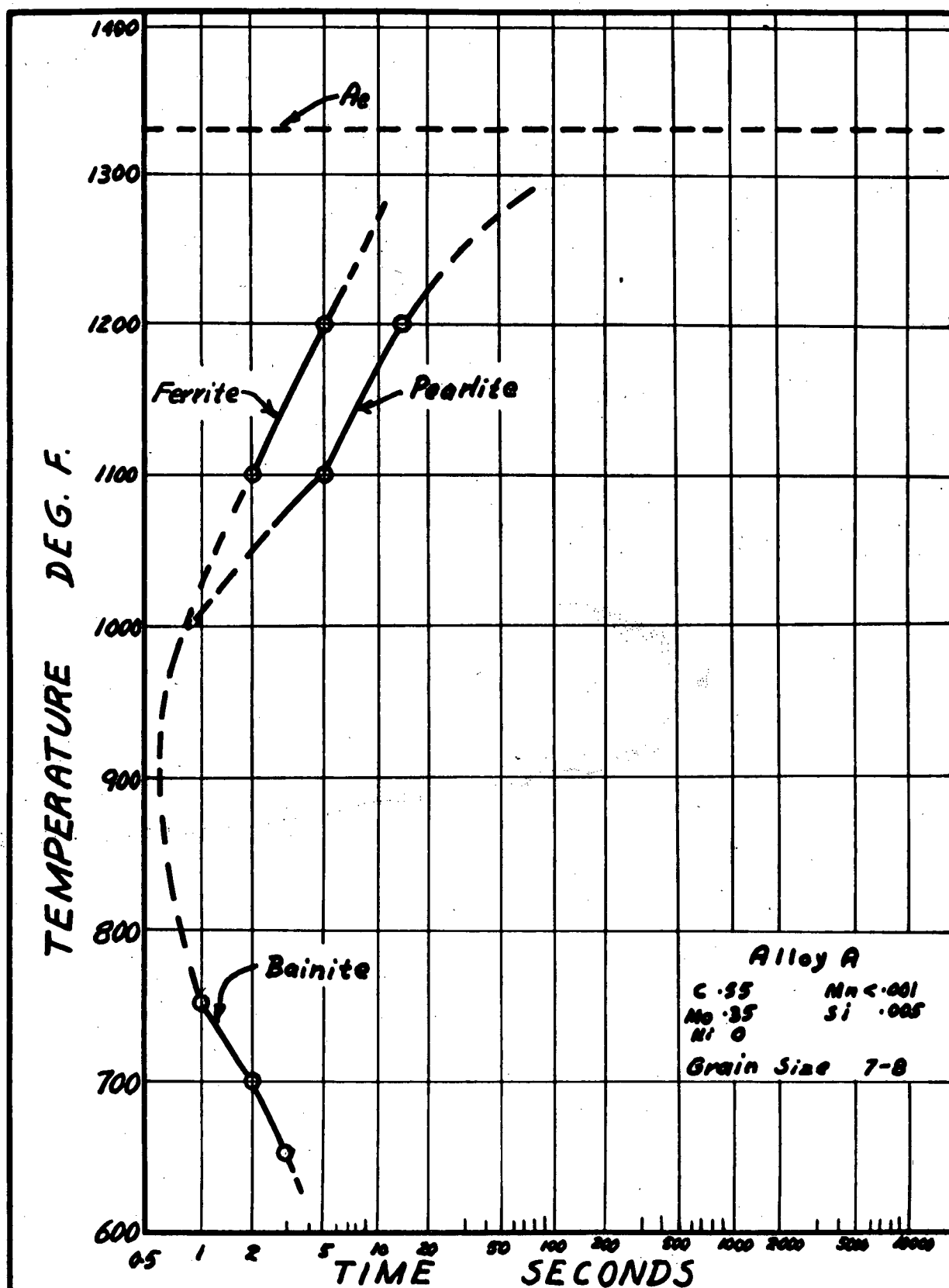
at a particular temperature and held 10 seconds, raised above the Ms Temperature to 700 deg. F. for 3 seconds to temper the martensite, and then quenched to room temperature. The tempered martensite etches dark whereas the untempered martensite does not.

The beginning of transformation is shown in the form of an "S-curve" (fig. 9) and data is given in Table 1.

TABLE 1

Time to Begin Transformation for NE 8740 Steel

Temperature deg. F.	Time to Begin Transformation seconds
1250	10
1200	8
1100	6
1000	5
900	5
800	5
700	10



**Fig10 Beginning of Transformation of Alloy Containing 0% Ni.
 Isothermally Held After Quenching From 1550 F.**

EXPERIMENTAL WORK

The composition of Norway iron used as a base material of the alloys is given in Table 2 along with the analysis of the nickel-molybdenum series used for isothermal transformation diagrams.

TABLE 2

Analysis of Alloys Investigated and Norway Iron

Alloy No.	Chemical composition percent					Ae ₁ Temperature deg. F.	Grain Size ASTM
	C	Mn	Si	Ni	Mo		
Norway iron	0.02	<0.001	0.004	---	---		
A	0.55	<0.	0.005	---	0.35	1333	7-8
AA1	0.55	0.	0.02	2.13	0.34	1275	8
AA2	0.50	0.	0.01	3.61	0.35	1210	9
AA3	0.59	0.	0.02	5.39	0.35	1160	7-9

The method used for isothermal transformation of the alloy steels was the metallographic technique developed by Bain₁. To conserve specimens in finding the beginning of transformation times used for preliminary surveys were five or ten second intervals. The exact time of beginning of transformation was found by a final survey at times between the last one showing no transformation and the first one showing transformation has begun.

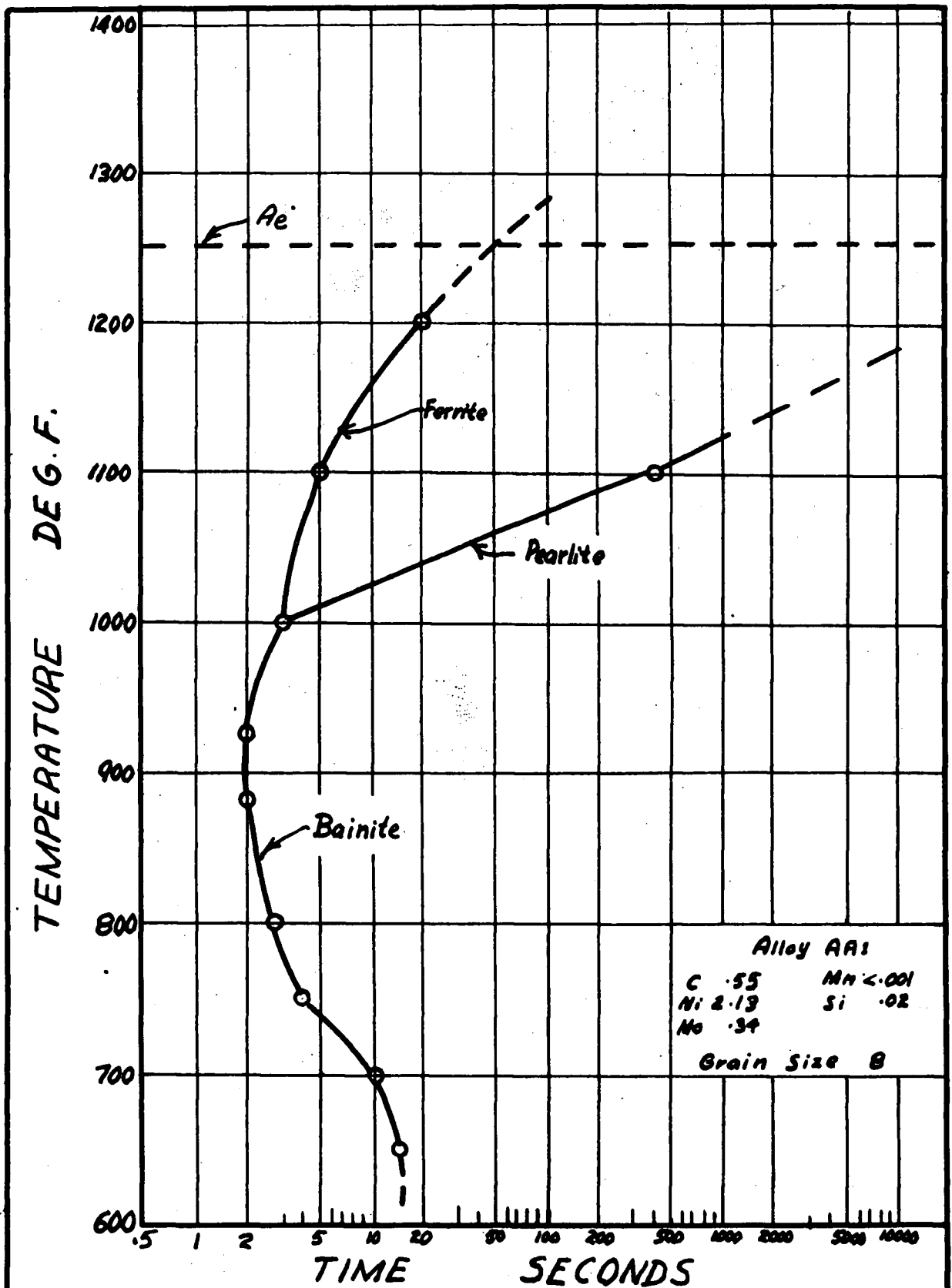


Fig. Beginning of Transformation of Alloy Containing 2.13% Ni
Isothermally Held After Quenching From 1550 F.

Specimens for isothermal transformation were cut approximately one-twelfth of an inch thick from the cast bars which had been annealed. Small holes were drilled in the center of each specimen through which 22 gauge chromel wire was threaded to serve as a handle for transferring the specimen from one bath to the next. Three minutes at austenitizing temperature of 1550 deg. F. were required to completely austenitize the specimen, and hence all specimens isothermally treated were heated six minutes at 1550 deg. F. in a neutral salt bath. Transformation temperatures used were 1200, 1100, 1000, 930, 880, 800, 750, 700, and 650, all in deg. F. Specimens were quenched for a measured time at one of the above temperatures in a salt bath, followed by an immediate quench to room temperature in an 8 percent brine solution.

The flat faces of the transformed specimens were smoothed on No. 2 emery paper, the specimens mounted in transoptic, polished, etched, examined at 1800 magnifications, and a suitable series of specimens photographed to illustrate beginning of decomposition where one product is formed, and to illustrate progress in transformation where more than one product is formed.

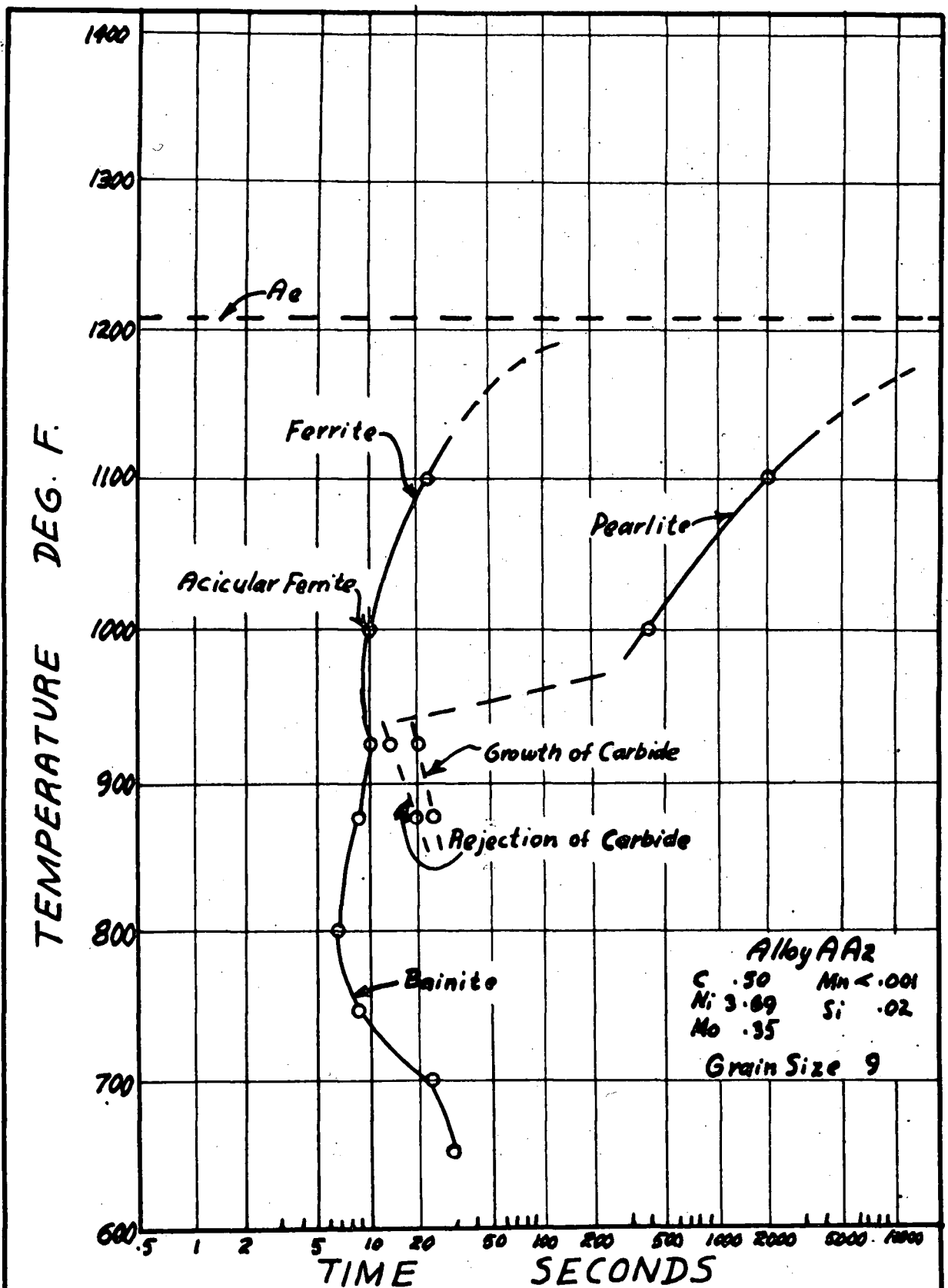


Fig12 Beginning of Transformation of Alloy Containing 3.69%Ni:
 Isothermally Held After Quenching From 1550 F.

EXPERIMENTAL RESULTS

The beginning of isothermal transformation of austenite for the series of 0.55 carbon, 0.35 molybdenum, 0, 2.13, 3.69, and 5.31 percent nickel austenitized six minutes at 1550 deg. F. is shown in fig. 10 to 13. The pearlite reaction is delayed much more than can be explained by the lowering of the equilibrium temperature. Increasing nickel produces a bay in the curve at 880 deg. F. Ferrite formation in the intermediate temperature range 880 to 1000 deg. F. becomes increasingly more acicular, and during growth of the acicular ferrite carbides are rejected either from the ferrite or at the ferrite-austenite interface, followed at later times by growth of the carbide phase, at first between groups of acicular ferrite and eventually into the untransformed austenite surrounding the ferrite.

The results showing the effect of nickel on the isothermal transformation products of austenite are shown as photomicrographs in fig. 14 to 101.

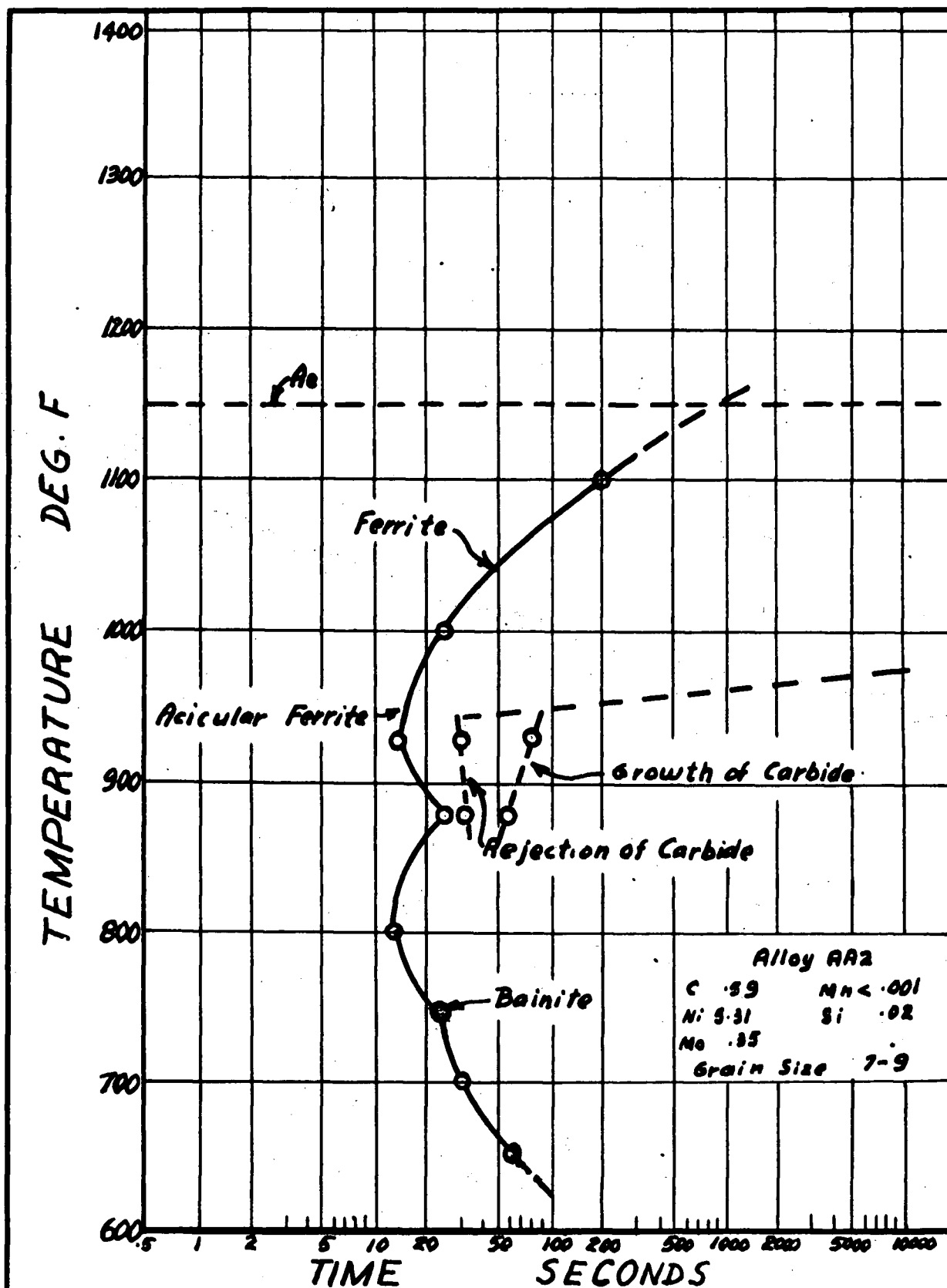


Fig 13 Beginning of Transformation of Alloy Containing 5.31%Ni.
 Isothermally Held After Quenching From 1550 F.

Alloy A (0 percent nickel)

A very fine dendritic pattern is produced on casting alloy A (fig. 14) which is a regular pattern of Widmanstaaten ferrite and fine pearlite (fig. 15). Annealing by heating for 30 minutes at 1550 deg. F. and cooling slowly in five hours to room temperature produces a homogeneous fine-grained structure (fig. 16) of ferrite and coarse lamellar pearlite (fig. 17), the structure which is used for isothermal work.

The transformation product between 650 and 880 deg. F. is feathery lower bainite (fig. 18 to 25). At 930 deg. F. upper bainite grows nodularly (fig. 26), the structure of which is not resolved at 1800 magnifications. At 1000 deg. F. two products form and grow simultaneously (fig. 27, 28 and 29), the light-etching phase being acicular ferrite, and a dark-etching phase nodular in formation and very rapid-growing. At 1100 deg. F. acicular ferrite forms at two seconds (fig. 30) and a dark-etching phase begins to form at five seconds near adjoining groups of ferrite fingers (fig. 31). At 1200 deg. F. Ferrite begins at five seconds (fig. 32) and has an acicular structure which becomes more rounded by the time pearlite forms at 15 seconds (fig. 33). The time of beginning of reaction between 800 and 1000 deg. F. is undetermined because it is below the limit of accurately measuring time at temperature.

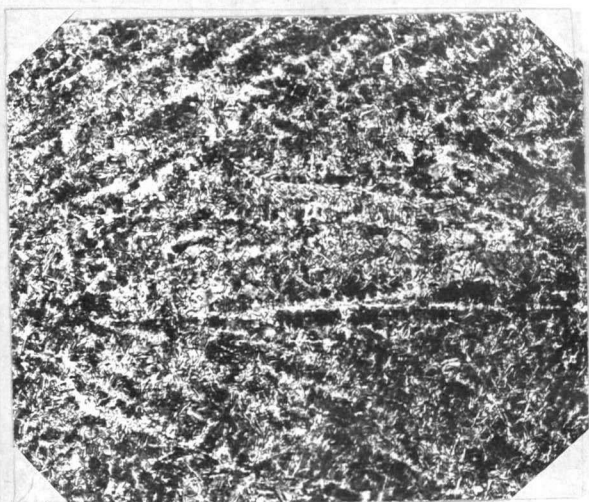


Fig. 14 Alloy A as cast X100
Fine dendritic pattern of ferrite(white) and pearlite(black).

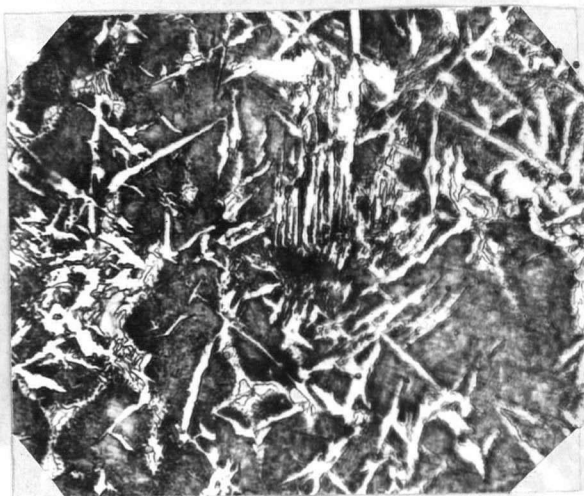


Fig. 15 Alloy A as cast X850
Widmanstaaten ferrite(white)
pearlite(dark).

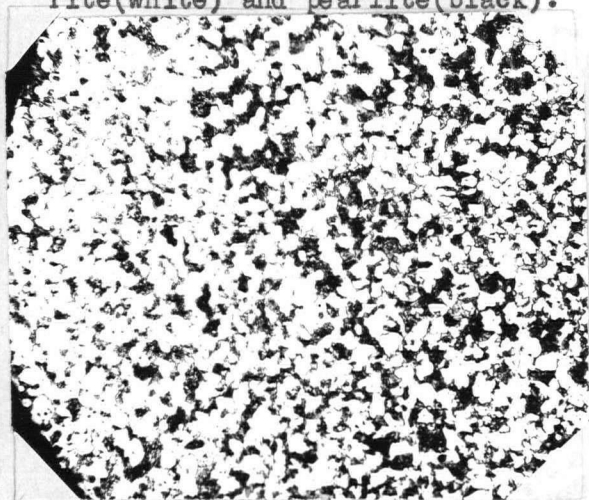


Fig. 16 Alloy A annealed X100
Fine grain structure of ferrite
(white) and coarse pearlite(dark).



Fig. 17 Alloy A annealed X850
Lace network of coarse and
fine pearlite plus ferrite.

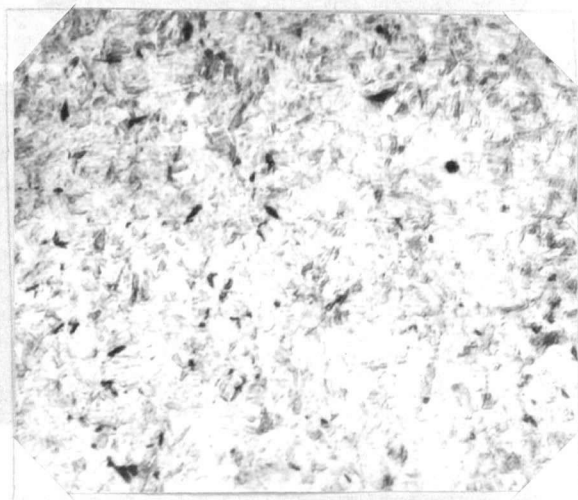


Fig. 18 Alloy A 3 sec. 650
deg. F. shows bainite (dark
specks) and martensite X850.

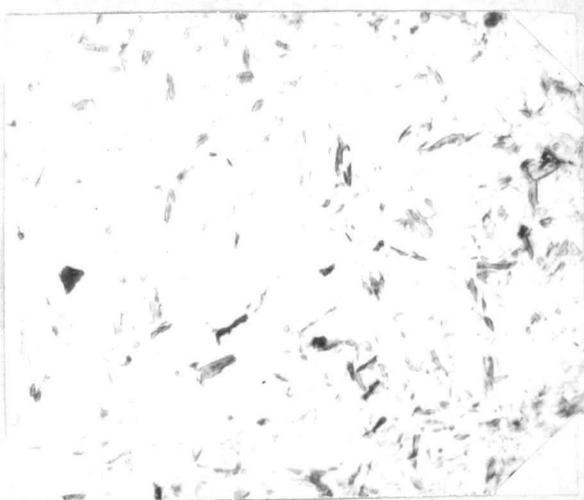


Fig. 19 Alloy A 5 sec. at
650 deg. F. shows growth of
bainite. X850

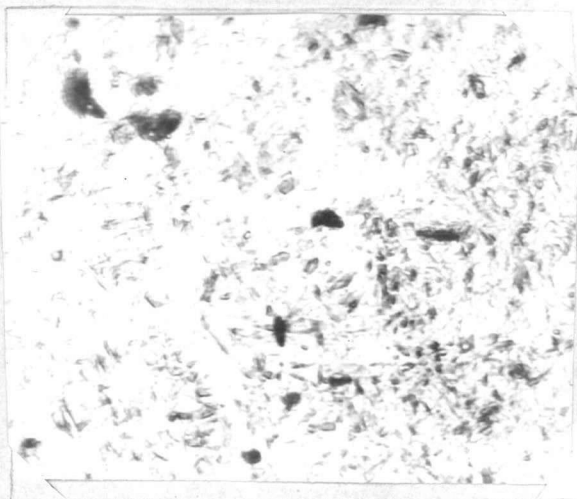


Fig. 20 Alloy A 2 sec. at 700 deg. F. Bainite(black) begins. Matrix martensite. X850



Fig. 21 Alloy A 3 sec. at 700 deg. F. Bainite grows. X 850

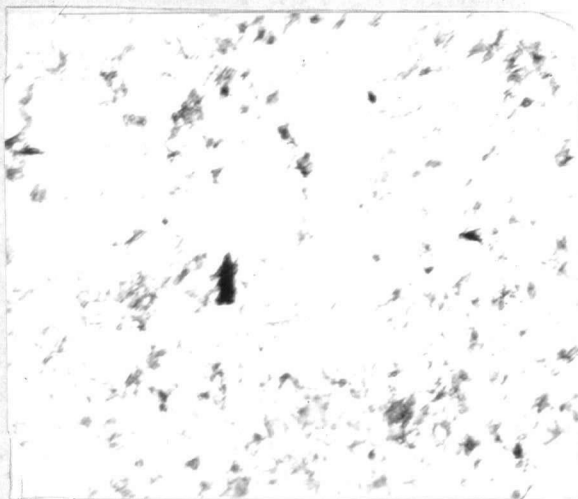


Fig. 22 Alloy A 1 sec. at 750 deg. F. Bainite forms. X1000

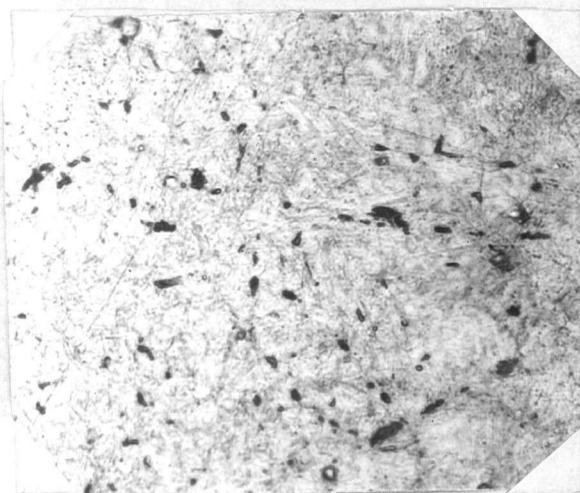


Fig. 23 Alloy A Bainite after 3 sec. at 750 deg. F. X 850

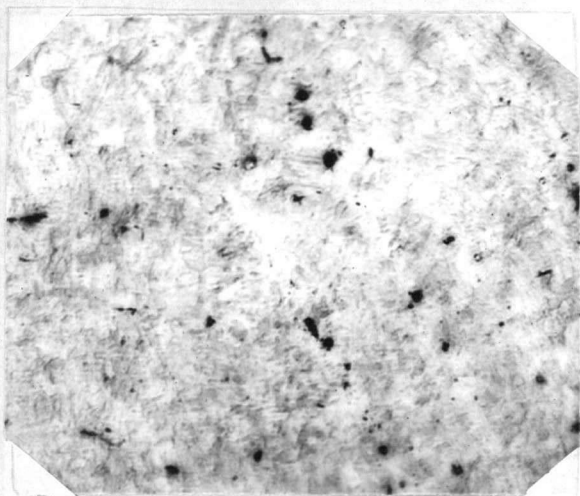


Fig. 24 Alloy A Bainite formed at 1 sec. 800 deg. F. X850

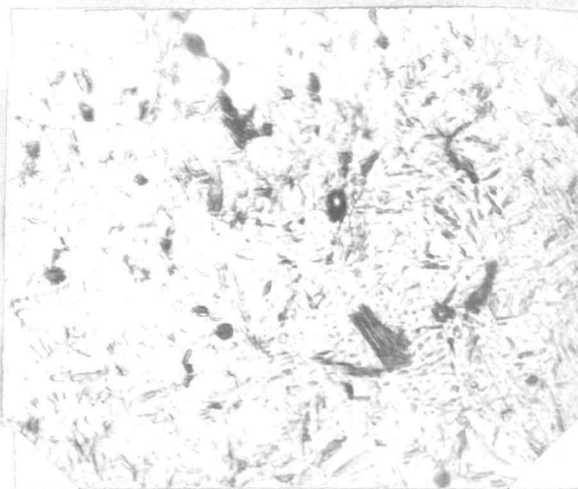


Fig. 25 Alloy A transformed 1 sec. at 880 deg. F. X1000

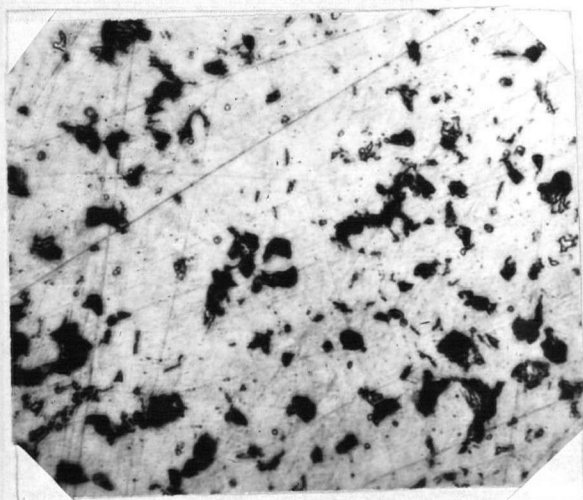


Fig. 26 Alloy A transformed 1 sec. at 930 deg. F. to upper bainite. X1000

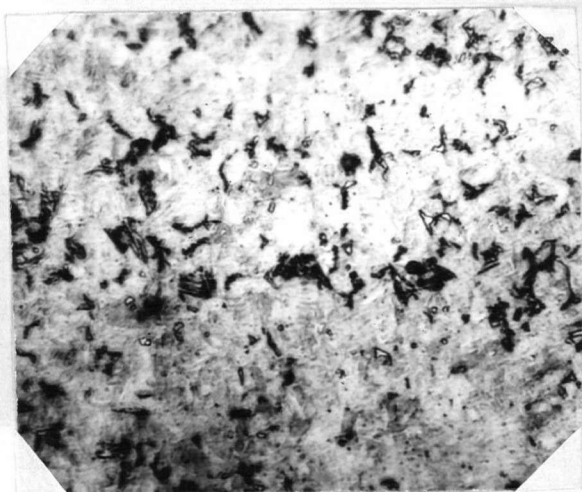


Fig. 27 Alloy A transformed 1 sec. at 1000 deg. F. Acicular ferrite(light)and dark phase. X850

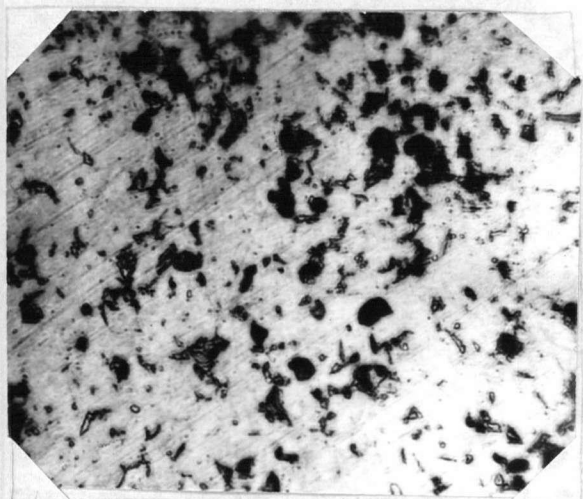


Fig. 28 Alloy A transformed 2 sec. at 1000 deg. F. Dark-etching phase grows. X850

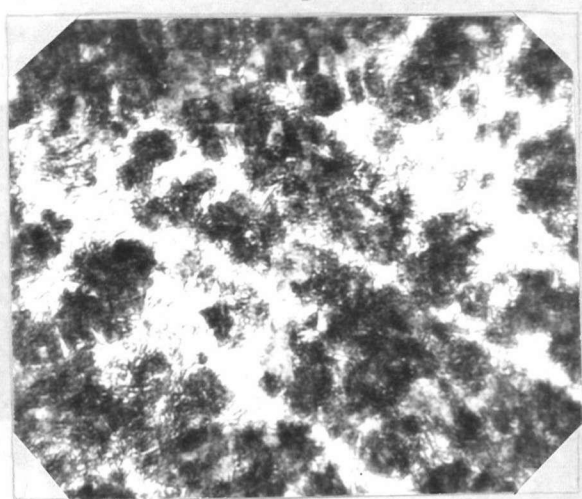


Fig. 29 Alloy A transformed 5 sec. at 1000 deg. F. X850



Fig. 30 Alloy A transformed 3 sec. at 1100 deg. F. to acicular proeutectoid ferrite. X850

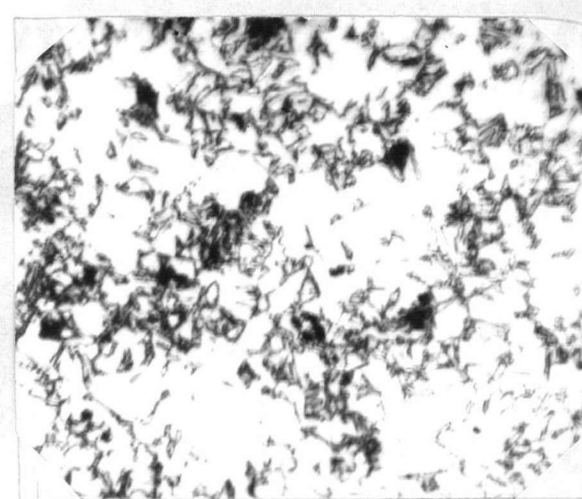


Fig. 31 Alloy A transformed 5 sec. at 1100 deg. F. pearlite begins to form. X850

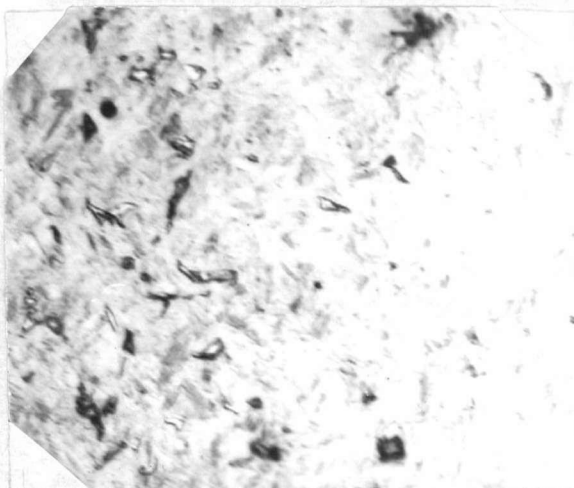


Fig. 32 Alloy A transformed
5 sec. at 1200 deg. F.
Proeutectoid ferrite begins
to form. X850

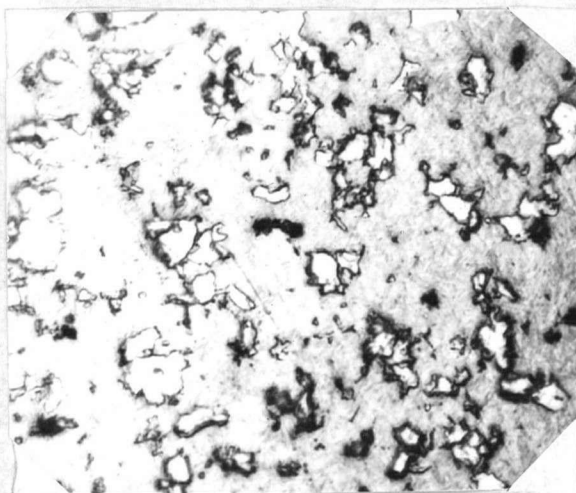


Fig. 33 Alloy A transformed
15 sec. at 1200 deg. F.
Pearlite begins to form(center).
X850

Alloy AA₁ (2.13 percent nickel)

A very fine dendritic pattern is developed in the cast ingots (fig. 34) which is an intricate pattern of ferrite fingers and pearlite (fig. 35). Annealing the alloy removes the dendritic pattern giving a fine grained (fig. 36), homogeneous mixture of ferrite and fine lamellar pearlite (fig. 37) which is the structure previous to isothermal heat treatment.

Between 650 and 880 deg. F. feathery bainite forms (fig. 38 to 45). At 930 deg. F. a nodular dark-etching product forms (fig. 46) and is probably upper bainite. At 1000 deg. F. two products appear simultaneously (fig. 47), acicular ferrite and a nodular, dark-etching constituent which grows more rapidly than ferrite (fig. 48). At 1100 deg. F. ferrite precipitates at 5 seconds (fig. 49) and grows alone until 400 seconds when pearlite appears (fig. 50). At 1200 deg. F. ferrite begins to form at 20 seconds (fig. 52) but pearlite was not found up to 20,000 seconds.

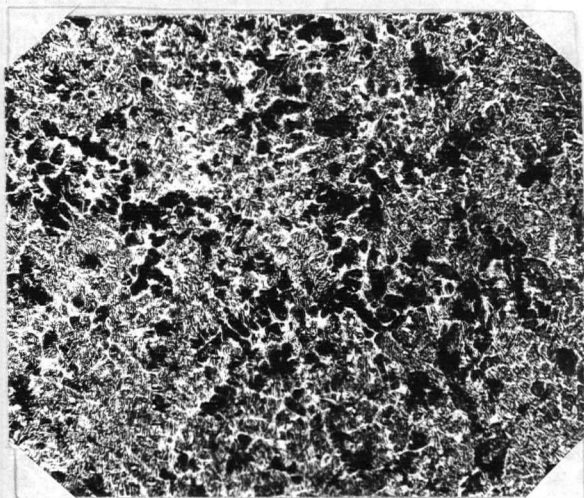


Fig. 34 Alloy AA₁ as cast
Ferrite(white),pearlite(black),
fine dendrites. X100

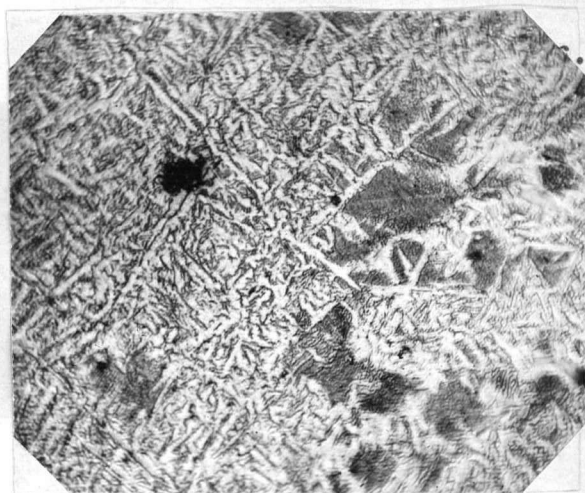


Fig. 36 Alloy AA₁ as cast
shows feathery interlacing
Widmanstaaten ferrite X850.

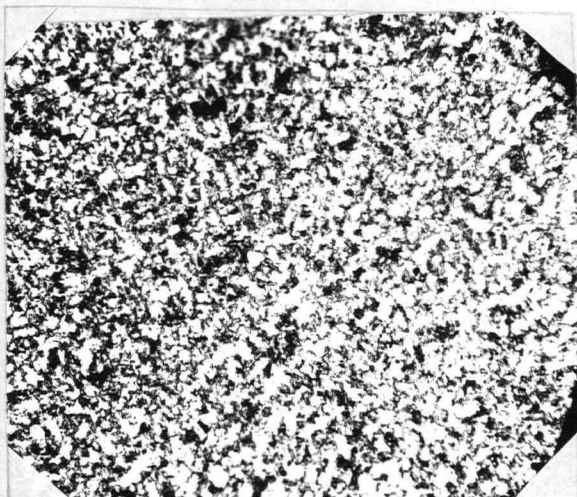


Fig. 36 Alloy AA₁ Annealed
Fine-grained structure of ferrite
(white) and pearlite(dark). X100

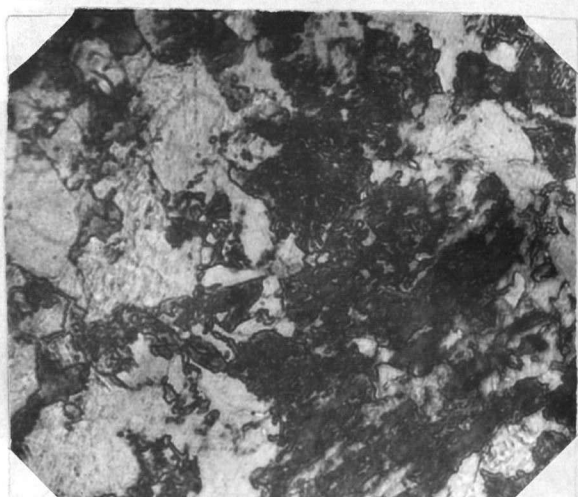


Fig. 37 Alloy AA₁ annealed
Fine pearlite and ferrite
X850



Fig.38 Alloy AA₁ transformed
15 sec. at 650 deg. F. to
show begin of bainite X1200

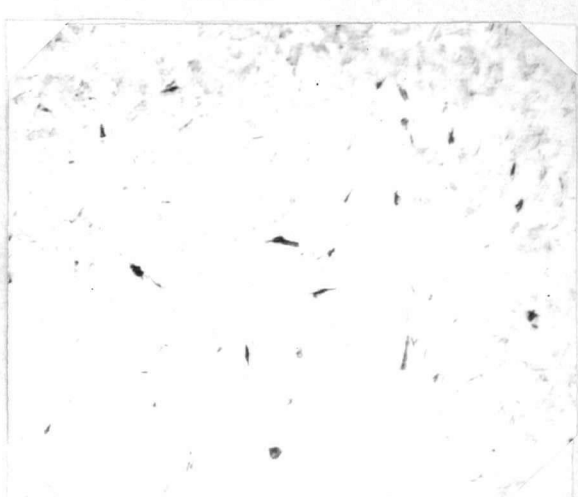


Fig. 39 Alloy AA₁ transformed
17 sec. at 650 deg. F. X850

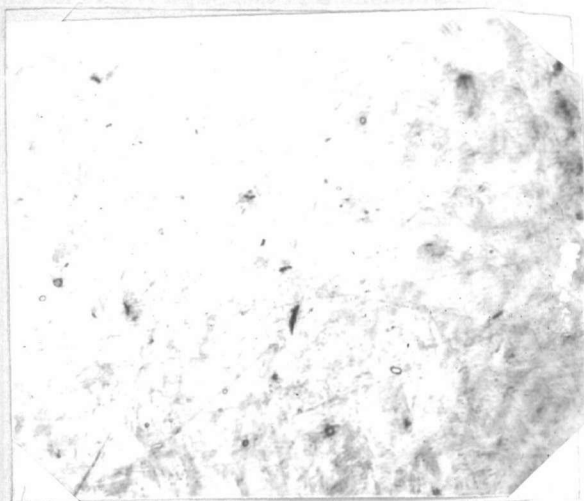


Fig. 40 Alloy AA₁ transformed
10 sec. at 700 deg. F.
Bainite begins to form. X850

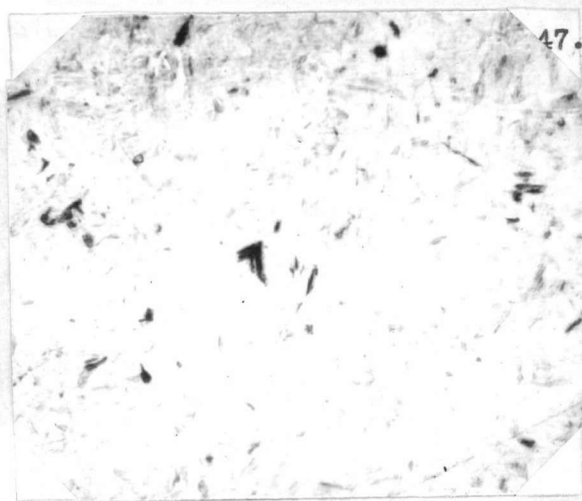


Fig. 41 Alloy AA₁ transformed
12 sec. at 700 deg. F.
X850

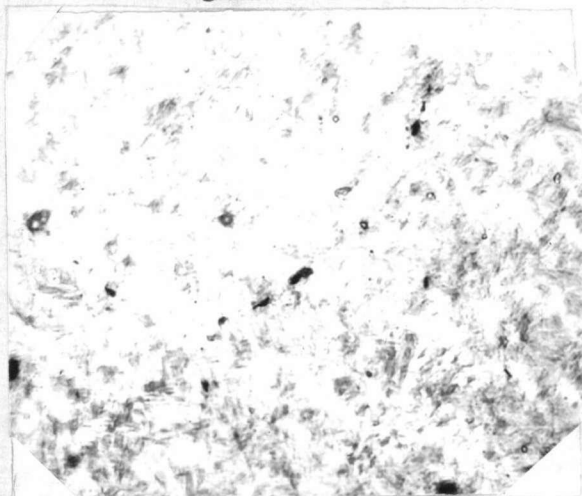


Fig. 42 Alloy AA₁ transformed
4 sec. at 750 deg. F.
Bainite begins to form. X850

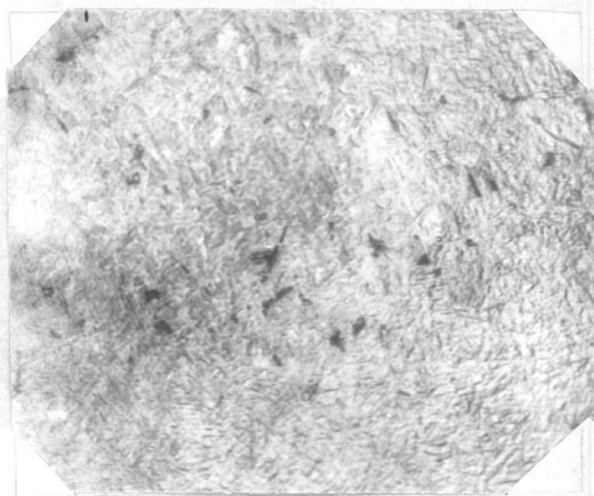


Fig. 43 Alloy AA₁ transformed
3 sec. at 800 deg. F.
Bainite begins to form. X850

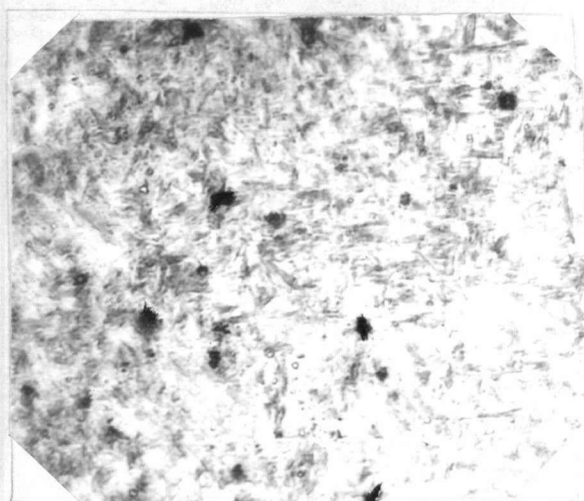


Fig. 44 Alloy AA₁ transformed
2 sec. at 880 deg. F.
Bainite begins to form. X850

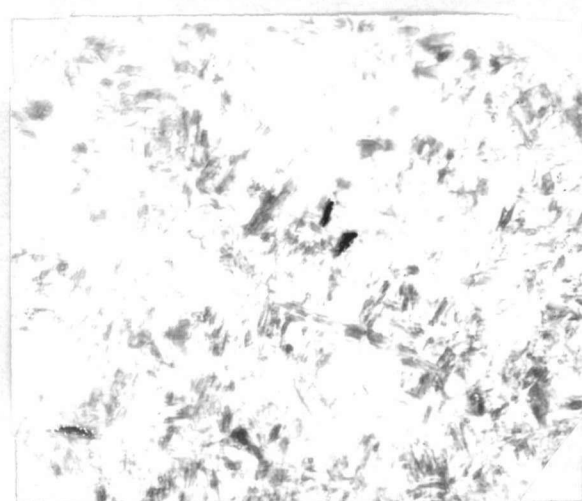


Fig. 45 Alloy AA₁ transformed
3 sec. at 880 deg. F.
X850.

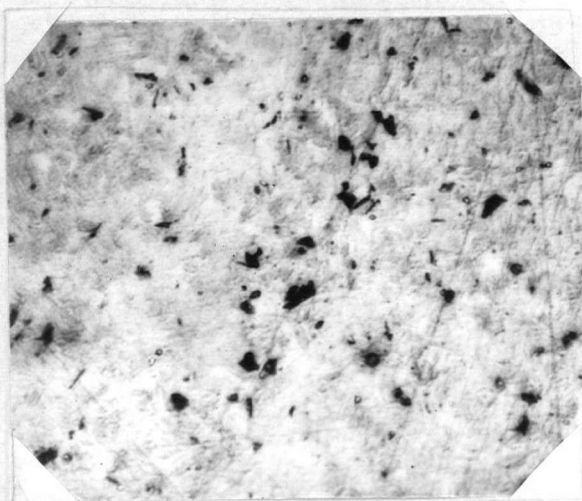


Fig. 46 Alloy AA₁ transformed
3 sec. at 930 deg. F. X850
Upper bainite begins to form

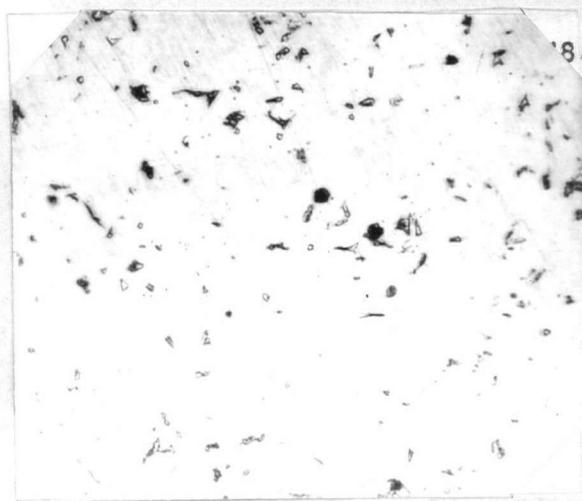


Fig. 47 Alloy AA₁ transformed
3 sec. at 1000 deg. F. Acicular
ferrite and a dark-etching phase
X850

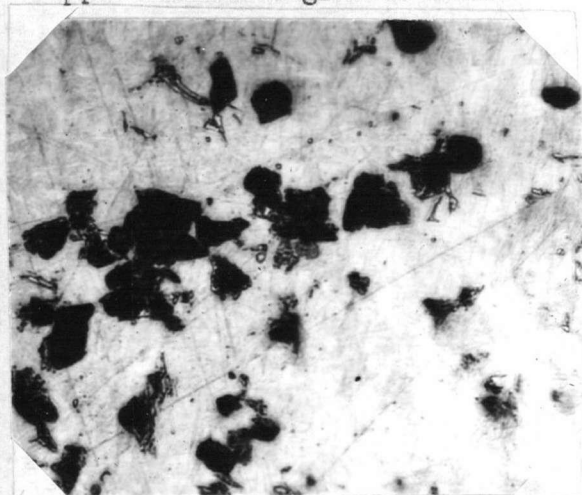


Fig. 48 Alloy AA₁ transformed
5 sec. at 1000 deg. F. Dark phase
grows faster than ferrite. X850

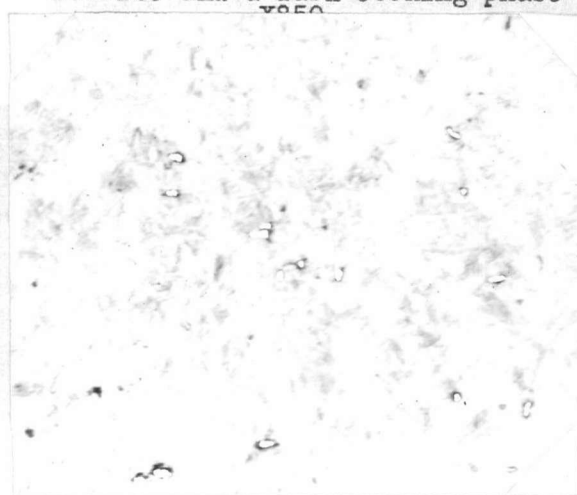


Fig. 49 Alloy AA₁ transformed
5 sec. at 1100 deg. F. Ferrite
begins to form. X850

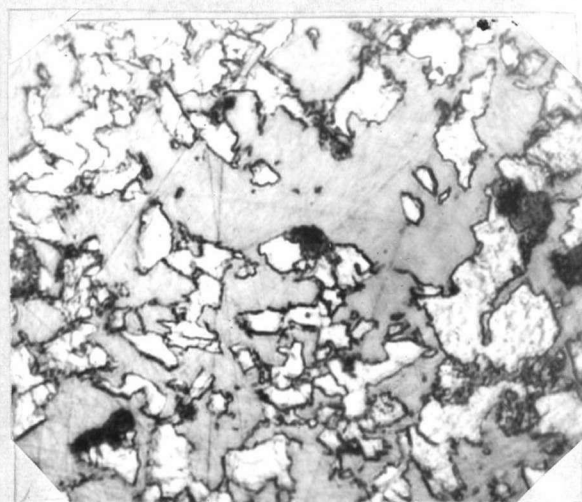


Fig. 50 Alloy AA₁ transformed
400 sec. at 1100 deg. F. Pearlite
begins to form. X850

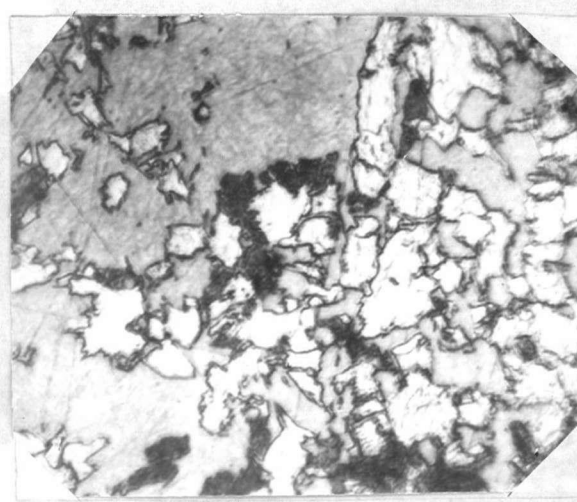


Fig. 51 Alloy AA₁ transformed
500 sec. at 1100 deg. F.
X850

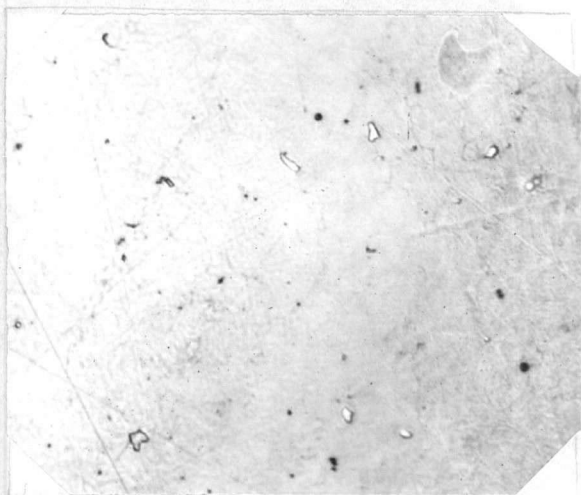


Fig. 52 Alloy AA₁ transformed
20 sec. at 1200 deg. F. Ferrite
begins to form. X850

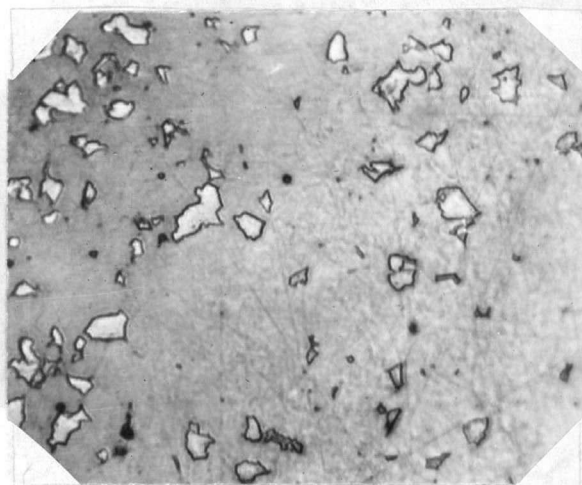


Fig. 53 Alloy AA₁ transformed
40 sec. at 1200 deg. F. X850

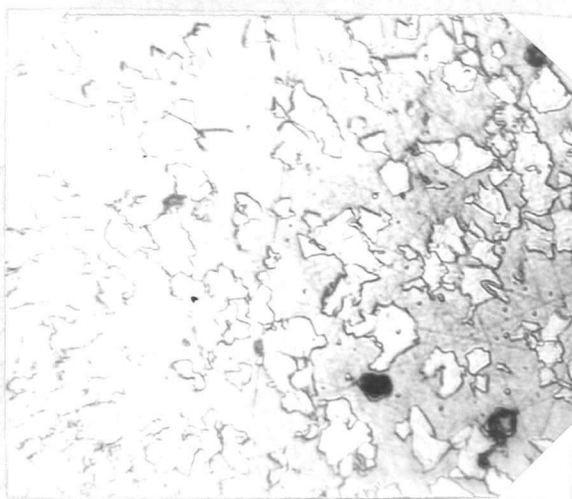


Fig. 54 Alloy AA₁ transformed
5000 sec. at 1200 deg. F. X850

Alloy AA₂ (3.61 percent nickel)

A very fine dendritic pattern is produced on casting (fig. 55) which is a very intricate pattern of acicular ferrite and bainite (fig. 56). Annealing the alloy removes the dendrite pattern, producing a uniform fine-grained structure (fig. 57). Several products form during annealing, among which are proeutectoid ferrite, fine pearlite, acicular ferrite, and a secondary carbide produced at the same temperature range as the acicular ferrite and bainite (fig. 58).

Feathery bainite forms between 650 and 800 deg. F. (fig. 59 to 62). At 880 deg. F. the first product after 9 seconds appears to be acicular ferrite (fig. 63). Further progress of transformation at 880 deg. F. shows two products, the feathery or acicular product being ferrite with rejection of a carbide between 20 and 25 seconds (fig. 64 and 65), the carbide then growing separately within areas of ferrite (fig. 66). Similar growth is found at 930 deg. F.; after 10 seconds acicular ferrite precipitates (fig. 67) followed at 15 seconds by rejection of carbide (fig. 68) and growth of the carbide phase separately within groups of acicular ferrite at 20 seconds (fig. 69) and eventually away from ferrite groups by 30 seconds (fig. 70). At 1000 deg. F. ferrite precipitates after 20 seconds (fig. 71) and grows

until at 400 seconds carbide precipitates (fig. 72) and grows as a separate phase between 500 and 1000 seconds (fig. 73 and 74). At 1100 deg. F. ferrite forms at 25 seconds (fig. 75) and grows until 2000 seconds when fine lamellar pearlite begins to grow (fig. 76). At 1200 deg. F. ferrite precipitates at 500 seconds (fig. 77) and grows rounded and agglomerated by 10000 seconds (fig. 78). Pearlite was not found up to 20000 seconds.

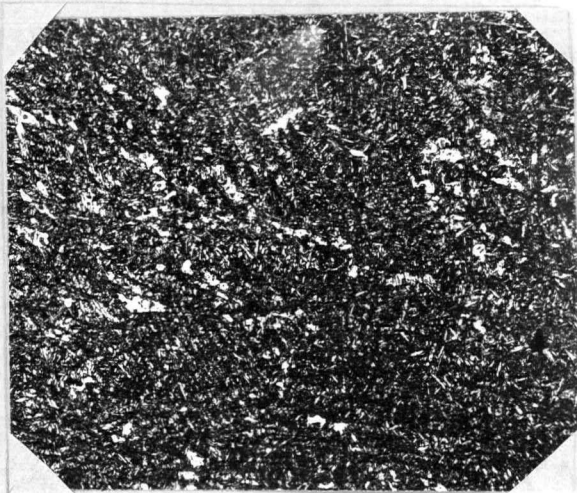


Fig. 55 Alloy AA₂ as cast
showing extremely fine den-
drites. X100

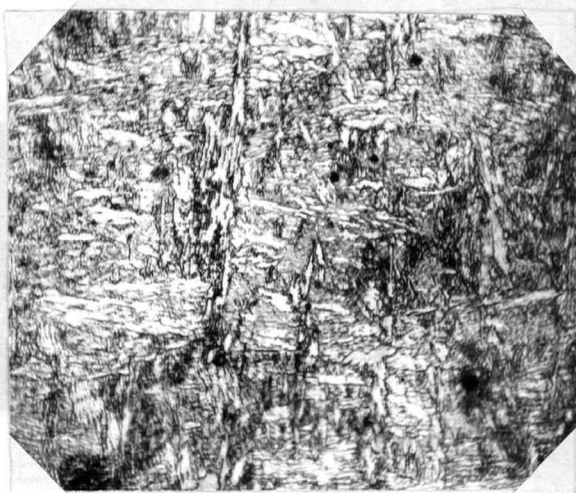


Fig. 56 Alloy AA₂ as cast
showing acicular ferrite and
bainite. X850

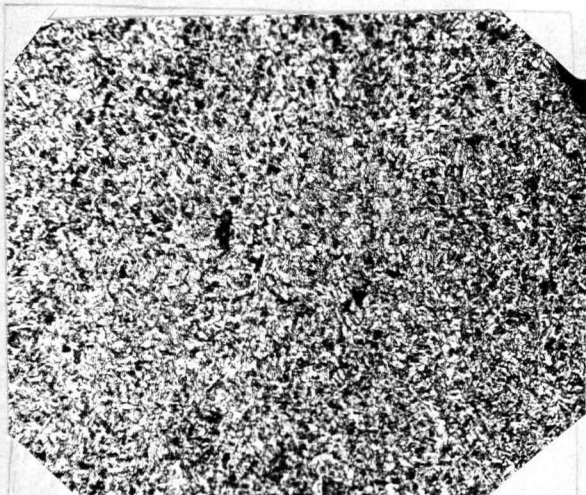


Fig. 57 Alloy AA₂ annealed
shows extremely fine grain
structure. X100



Fig. 58 Alloy AA₂ annealed X850
Proeutectoid and acicular ferrite
Pearlite and secondary carbide.

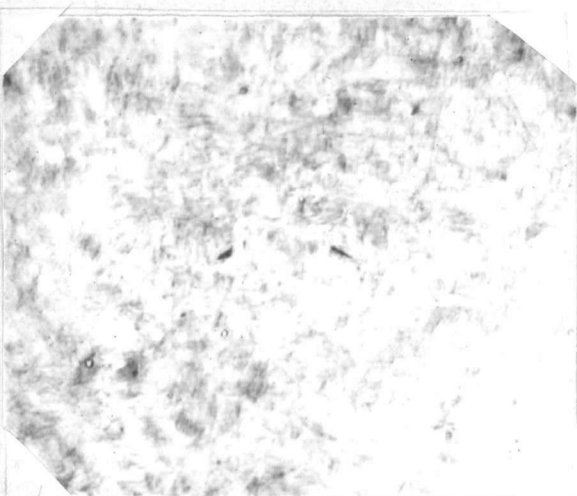


Fig. 59 Alloy AA₂ transformed
30 sec. at 650 deg. F.
Bainite begins to form. X850

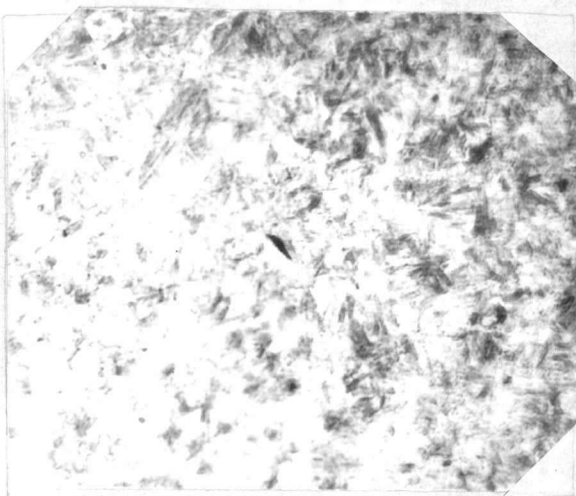


Fig. 60 Alloy AA₂ transformed
25 sec. at 700 deg. F.
Bainite begins to form. X850

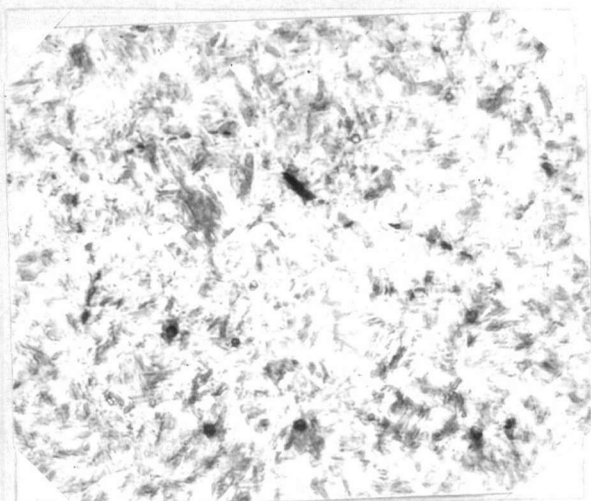


Fig. 61 Alloy AA₂ transformed
9 sec. at 750 deg. F.
Bainite begins to form. X850

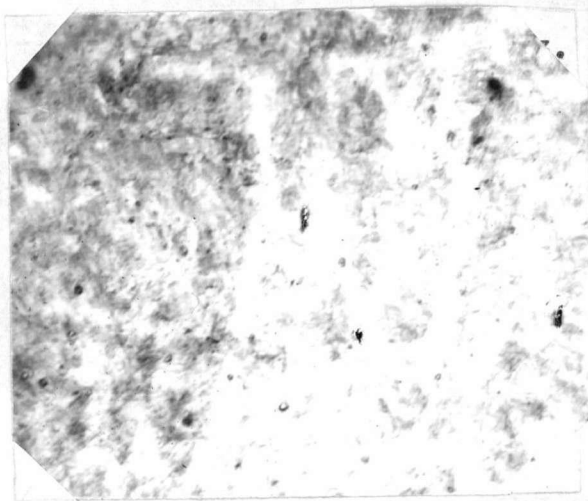


Fig. 62 Alloy AA₂ transformed
7 sec. at 800 deg. F.
Bainite begins to form. X850

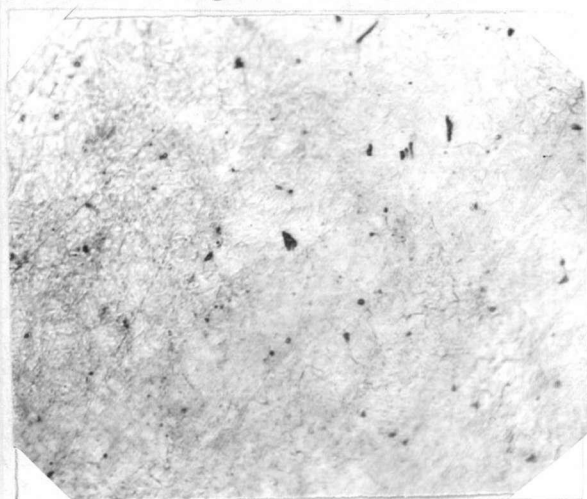


Fig. 63 Alloy AA₂ transformed
9 sec. at 880 deg. F. Acicular
ferrite begins. X850 Picral.

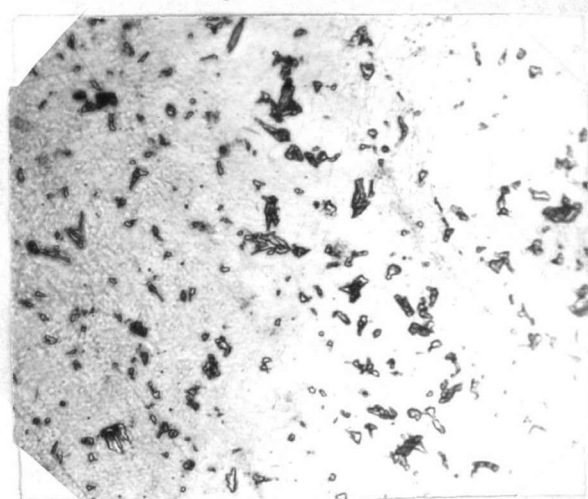


Fig. 64 Alloy AA₂ transformed
20 sec. at 880 deg. F. acicular
ferrite grows. X850

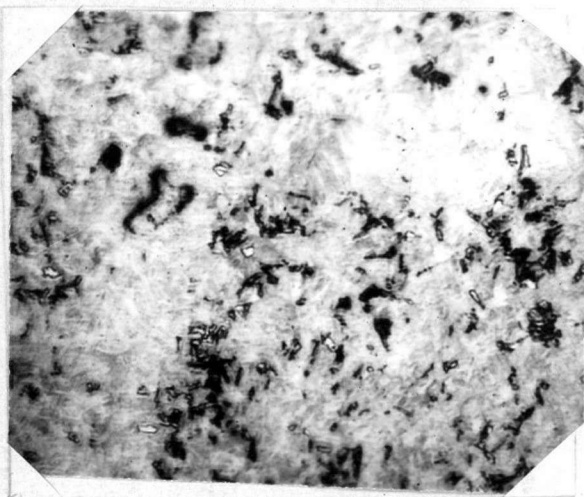


Fig. 65 Alloy AA₂ transformed
25 seconds at 880 deg. F. shows car-
bide rejection from ferrite. X850

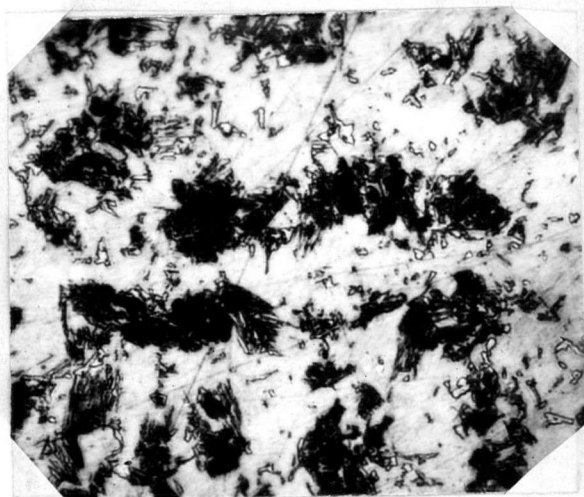


Fig. 66 Alloy AA₂ transformed
40 sec. at 880 deg. F. shows growth
of the carbide as a separate phase.
X850

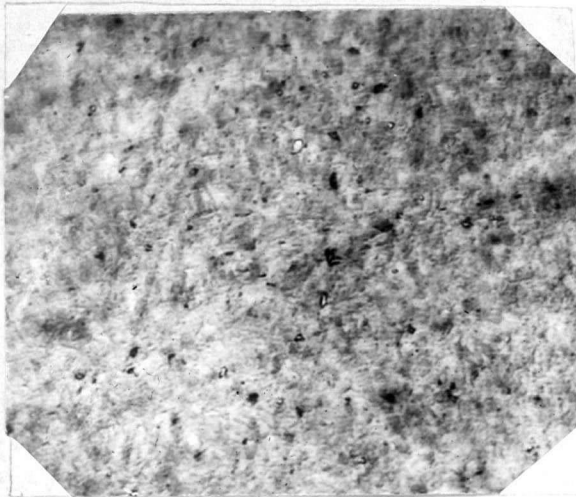


Fig. 67 Alloy AA₂ transformed
10 sec. at 930 deg. F.
Ferrite begins to form. X850

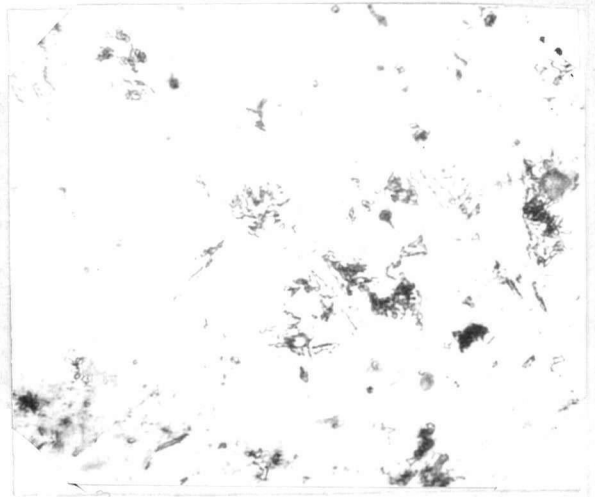


Fig. 68 Alloy AA₂ transformed
15 sec. at 930 deg. F. Carbide
rejected from acicular ferrite.
X850.

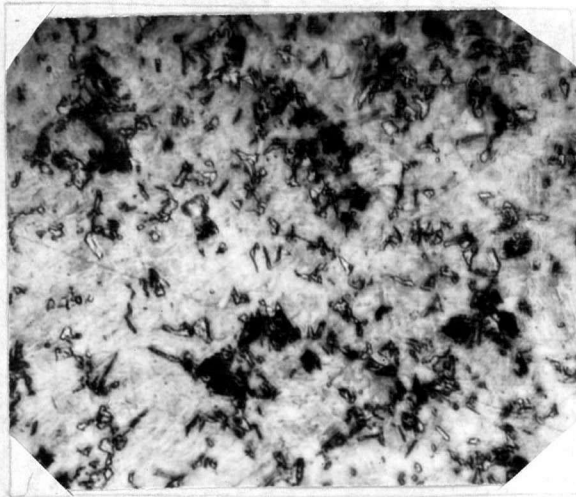


Fig. 69 Alloy AA₂ transformed
20 sec. at 930 deg. F. Carbide
begins to grow. X850

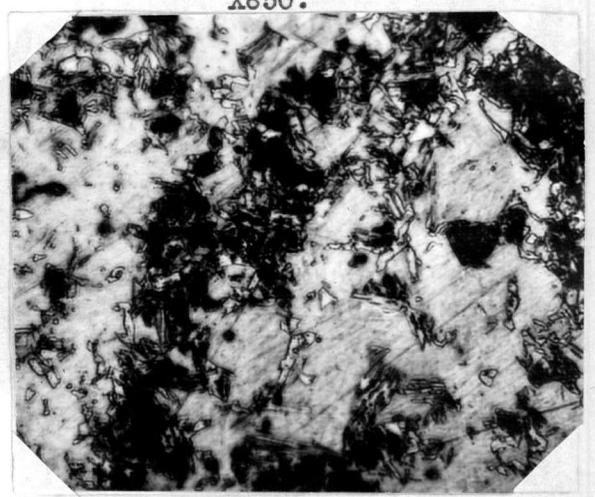


Fig. 70 Alloy AA₂ transformed
30 sec. at 930 deg. F. Carbide
grows rapidly. X850

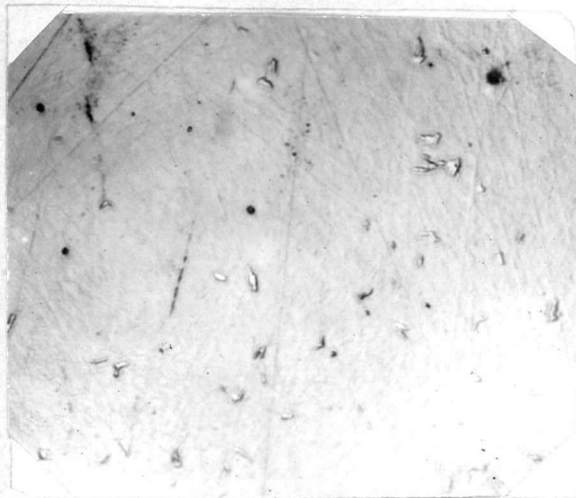


Fig. 71 Alloy AA₂ transformed
10 sec. at 1000 deg. F.
Ferrite begins to form. X850

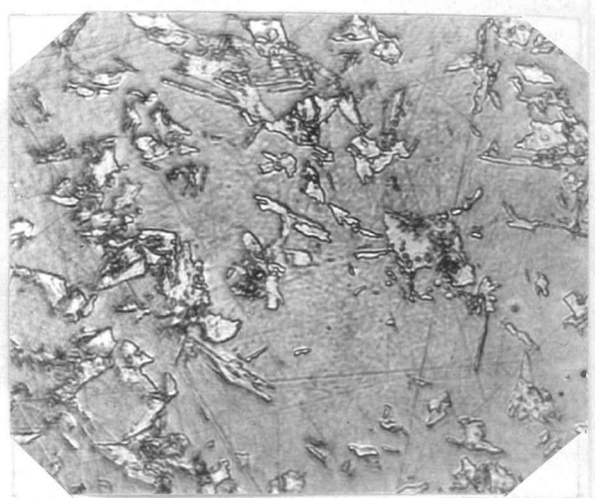


Fig. 72 Alloy AA₂ transformed
400 sec. at 1000 deg. F. Carbide
begins to precipitate. X850

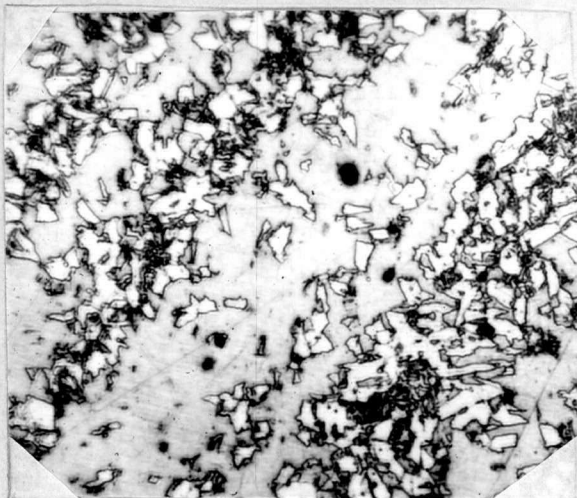


Fig. 73 Alloy AA₂ transformed
500 sec. at 1000 deg. F. X850
Carbide begins to grow.

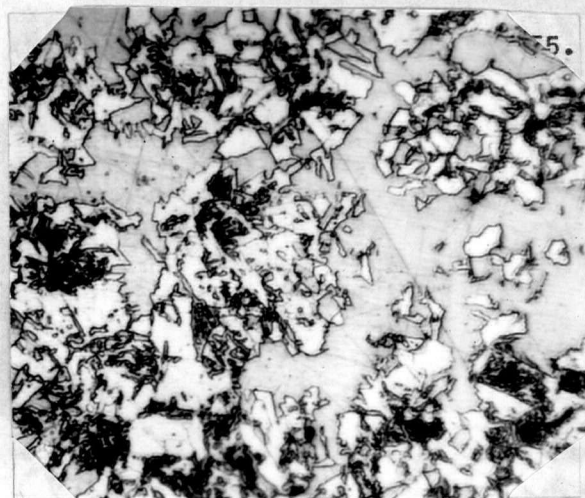


Fig. 74 Alloy AA₂ transformed
1000 sec. at 1000 deg. F. X850
Further carbide growth.



Fig. 75 Alloy AA₂ transformed
20 sec. at 1100 deg. F.
Ferrite begins to form. X850

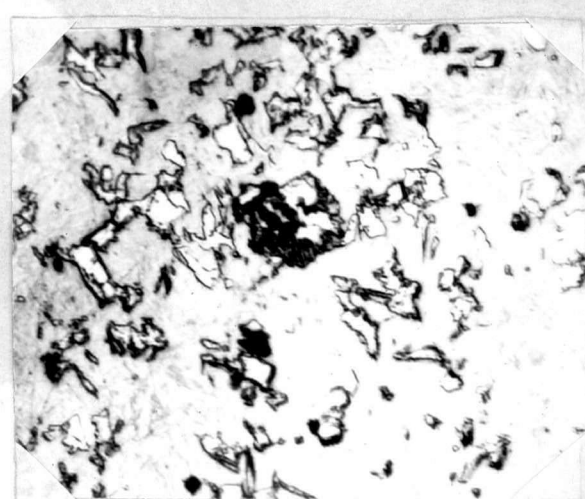


Fig. 76 Alloy AA₂ transformed
2000 sec. at 1100 deg. F. X850
Fine pearlite begins to form.

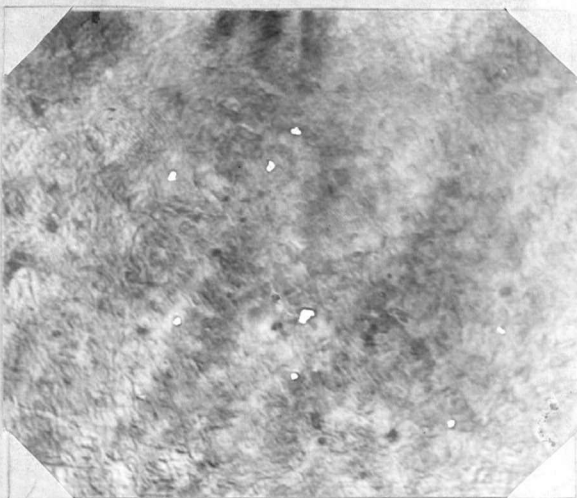


Fig. 77 Alloy AA₂ transformed
500 sec. at 1200 deg. F.
Ferrite begins to form. X850

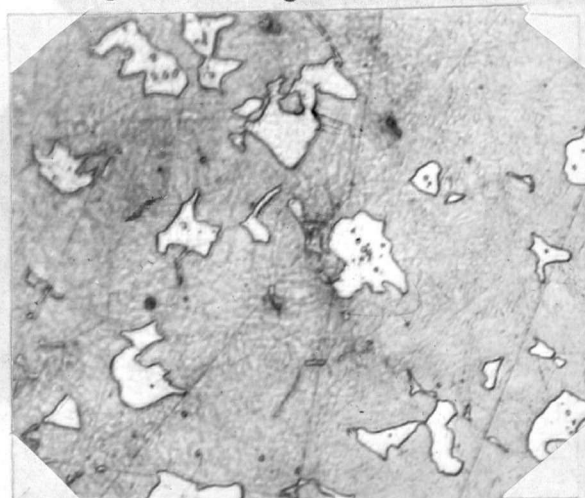


Fig. 78 Alloy AA₂ transformed
10000 sec. at 1200 deg. F.
X850

Alloy AA₃ (5.31 percent nickel)

The structure developed on casting is a very fine dendritic pattern (fig. 79) of feathery ferrite along Widmanstaaten planes (fig. 80) bainite and martensite. Annealing the cast ingot does not remove entirely the dendritic pattern (fig. 81) but leaves a very fine network of Widmanstaaten ferrite, acicular ferrite, carbide rejected and grown from acicular ferrite, bainite and martensite (fig. 82). Between 650 and 800 deg. F. feathery bainite forms and grows (fig. 83 to 87). At 880 deg. F. Ferrite particles precipitate at 25 seconds (fig. 88) followed by carbide rejection at 30 seconds (fig. 89) as the ferrite grows acicularly, and the carbide phase begins to grow at 60 seconds (fig. 90 and 91). At 930 deg. F. acicular ferrite forms after 15 seconds (fig. 92), followed by carbide rejection at 30 seconds on growth of the ferrite (fig. 93 and 94), and the carbide phase begins to grow at 80 seconds (fig. 95) within groups of ferrite and extends beyond ferrite groups by 120 seconds (fig. 96). At 1000 deg. F. ferrite fingers form at 30 seconds (fig. 97) and grows rounded (fig. 98 to 102). Pearlite was not found at 20000 seconds, at which temperature ferrite forms as a line marking grain boundaries as well as the large particles (fig. 103). At 1100 deg. F. ferrite begins after 100 seconds (fig. 104), and grows rounded by 10000 seconds (fig. 105). The pearlite reaction does not appear at 20000 seconds.



Fig. 79 Alloy AA₃ cast and drawn 1100 deg. F. X100
Fine dendritic pattern



Fig. 80 Alloy AA₃ cast and drawn 1100 deg. F. X850 Ferrite and tempered bainite & martensite.

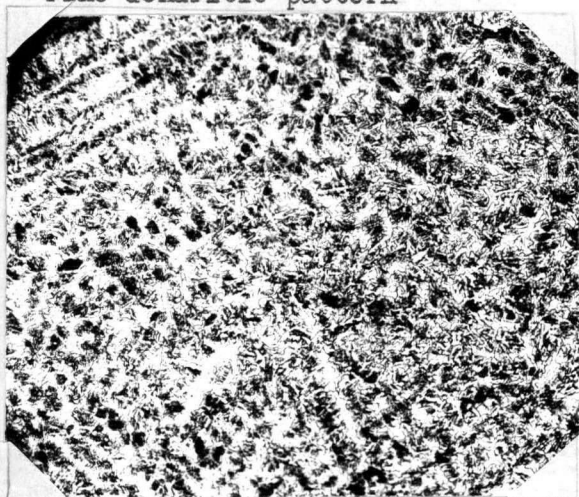


Fig. 81 Alloy AA₃ annealed X100
Dendritic pattern not entirely removed.



Fig. 82 Alloy AA₃ annealed. X850
Ferrite, secondary carbide, bainite and martensite.

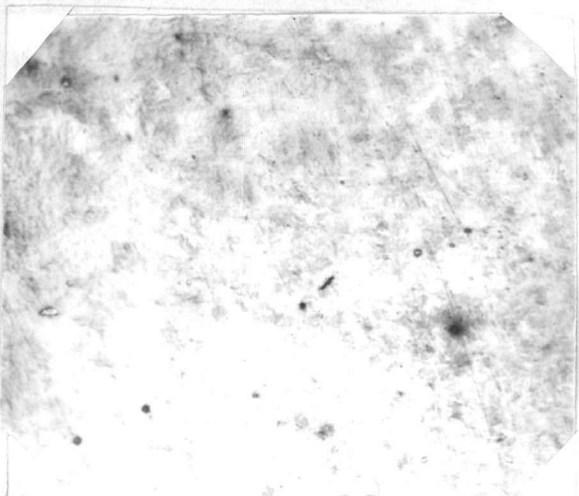


Fig. 83 Alloy AA₃ transformed 60 sec. at 650 deg. F.
Bainite begins to form. X850

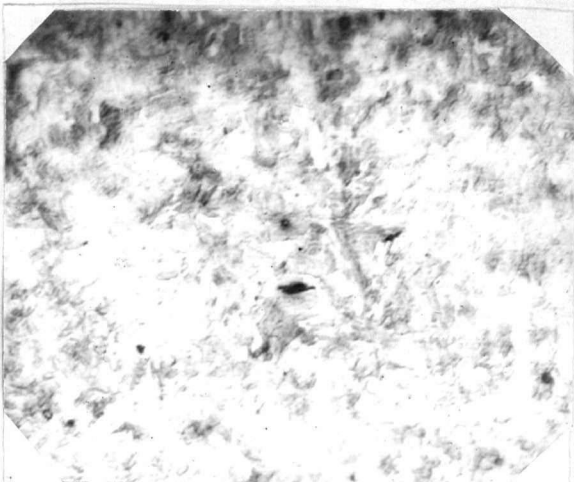


Fig. 84 Alloy AA₃ transformed 30 sec. at 700 deg. F.
Bainite begins to form. X850

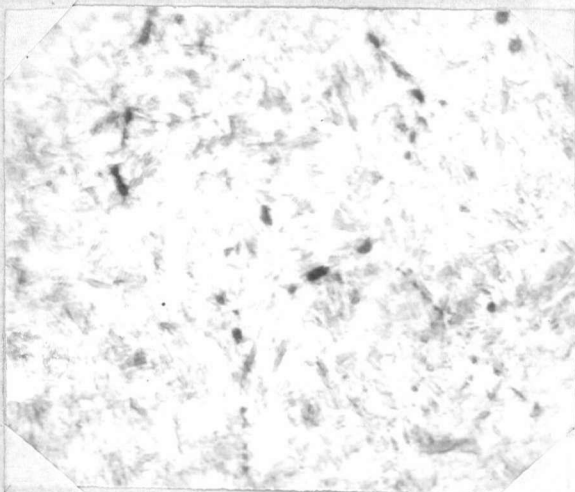


Fig. 85 Alloy AA₃ transformed
25 sec. at 750 deg. F.
Bainite begins to form. X850

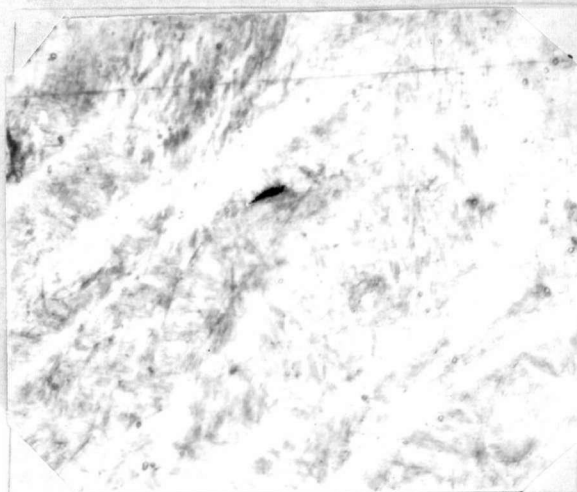


Fig. 86 Alloy AA₃ transformed
14 sec. at 800 deg. F.
Bainite begins to form. X850



Fig. 87 Alloy AA₃ transformed
20 sec. at 800 deg. F.
Bainite begins to form. X850



Fig. 88 Alloy AA₃ transformed
25 sec. at 880 deg. F.
Ferrite begins to Form. X1000

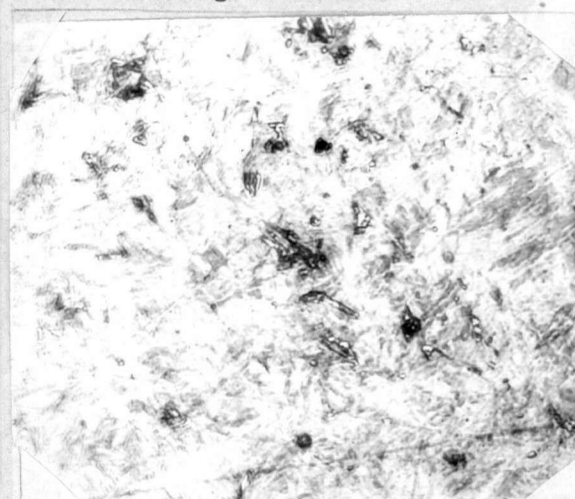


Fig. 89 Alloy AA₃ transformed 30
sec. at 880 deg. F. X850 Ferrite
grows acicularly, rejecting carbide.

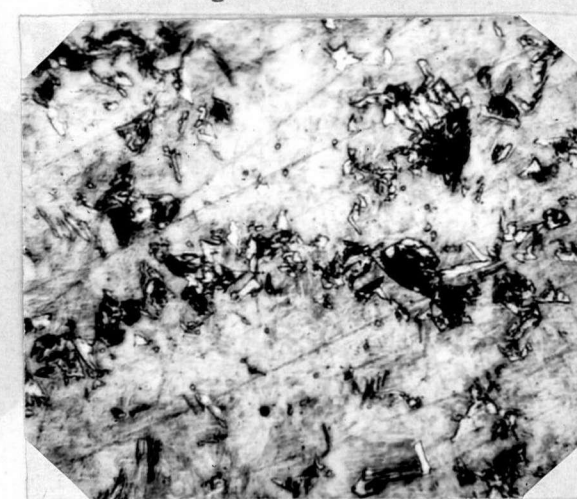


Fig. 90 Alloy AA₃ transformed
60 sec. at 880 deg. F. X850
Carbide begins to grow.

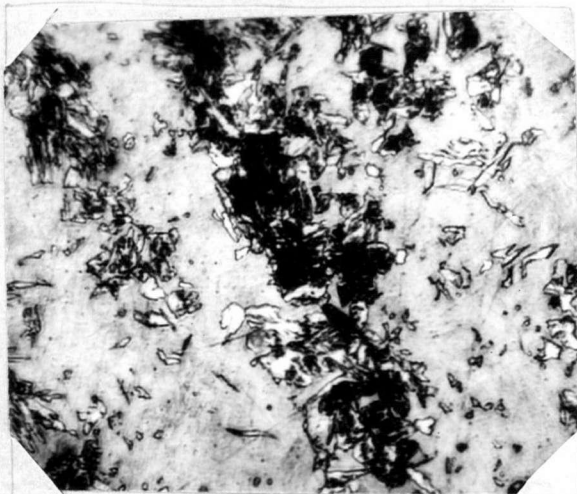


Fig. 91 Alloy AA₃ transformed
120 sec. at 880 deg. F. X850
Further growth of carbide.

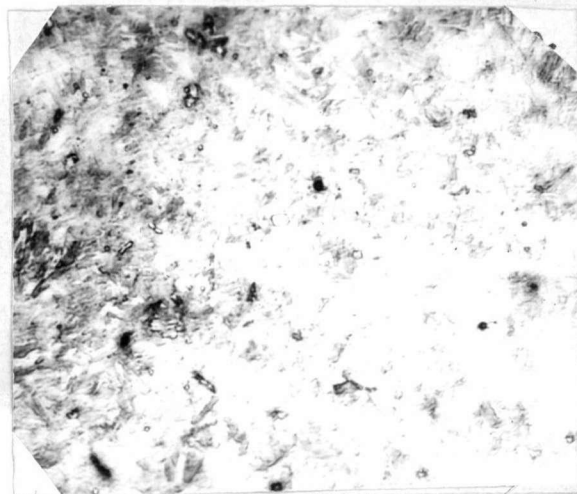


Fig. 92 Alloy AA₃ transformed
15 sec. at 930 deg. F.
Ferrite begins to form. X850



Fig. 93 Alloy AA₃ transformed
30 sec. at 930 deg. F. X850
Carbide rejected as ferrite grows

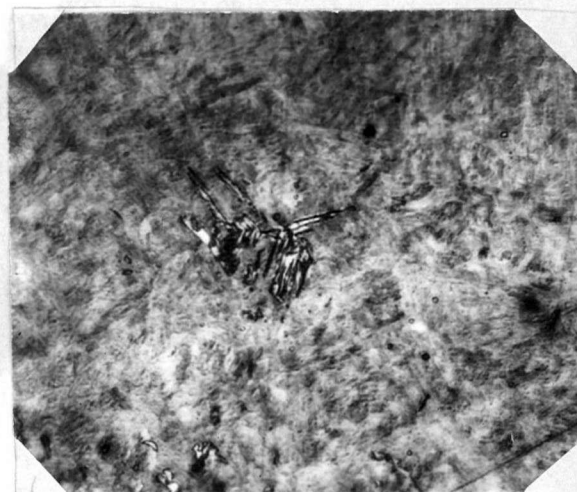


Fig. 94 Alloy AA₃ transformed
40 sec. at 930 deg. F. X1000
Further carbide rejection.

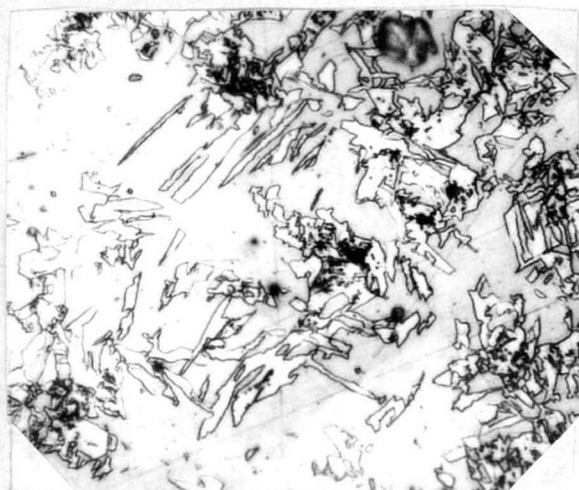


Fig. 95 Alloy AA₃ transformed
80 sec. at 930 deg. F. X850
Carbide phase begins to grow.

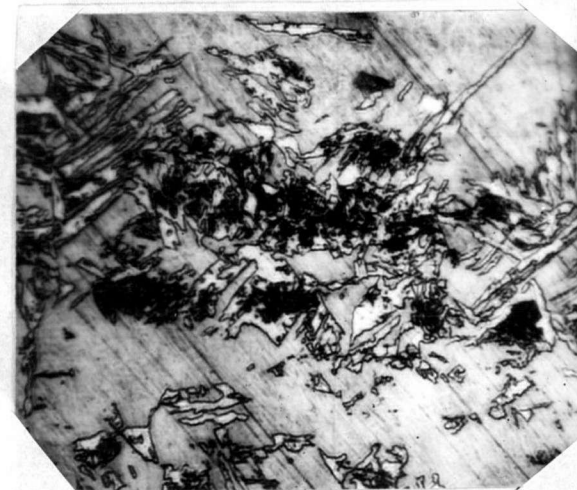


Fig. 96 Alloy AA₃ transformed
120 sec. at 930 deg. F. X850
Carbide growth much greater.

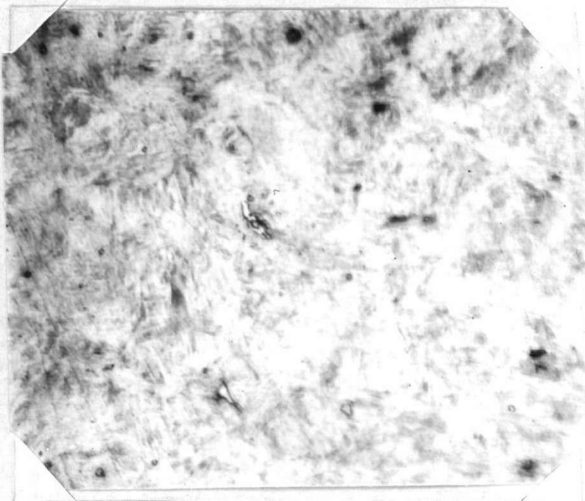


Fig. 97 Alloy AA₃ transformed
30 sec. at 1000 deg. F.
Ferrite begins to form. X850

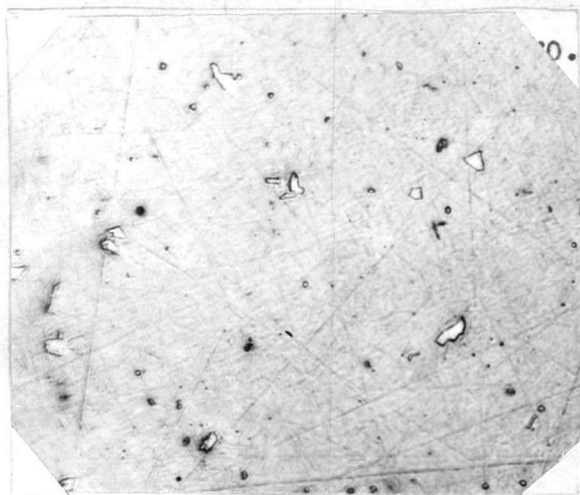


Fig. 98 Alloy AA₃ transformed
150 sec. at 1000 deg. F.
Ferrite grows rounded. X850

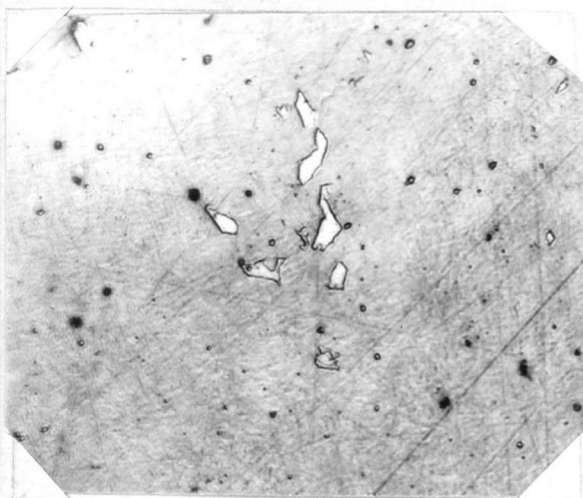


Fig. 99 Alloy AA₃ transformed
300 sec. at 1000 deg. F. X850
Ferrite grows further.



Fig. 100 Alloy AA₃ transformed
500 sec. at 1000 deg. F. X850

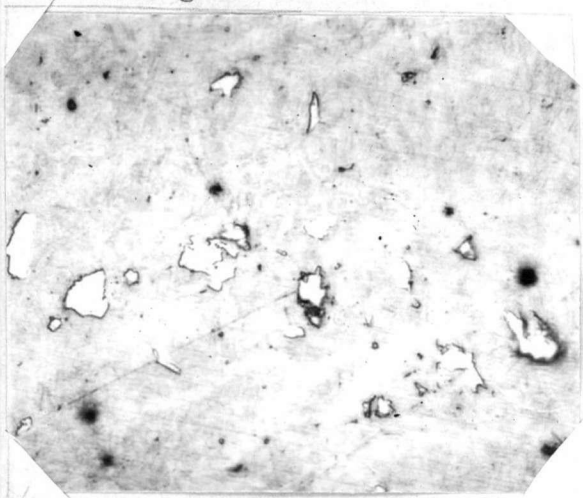


Fig. 101 Alloy AA₃ transformed
1000 sec. at 1000 deg. F. X850

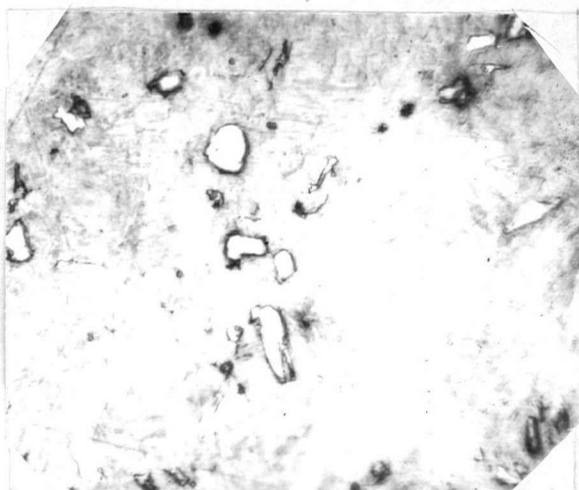


Fig. 102 Alloy AA₃ transformed
2000 sec. at 1000 deg. F. X850

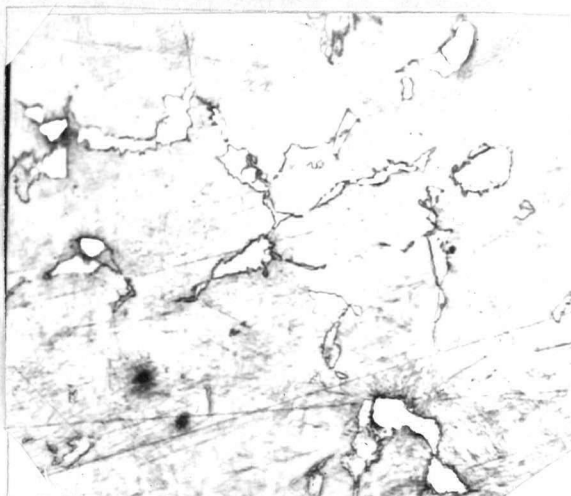


Fig. 103 Alloy AA₃ transformed 20000 sec. at 1000 deg. F. showing ferrite outlining grain boundaries. X850

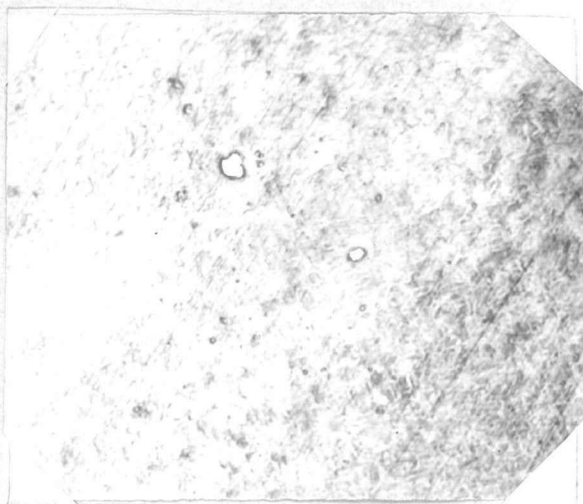


Fig. 104 Alloy AA₃ transformed 100 sec. at 1100 deg. F. Ferrite begins to form. X850

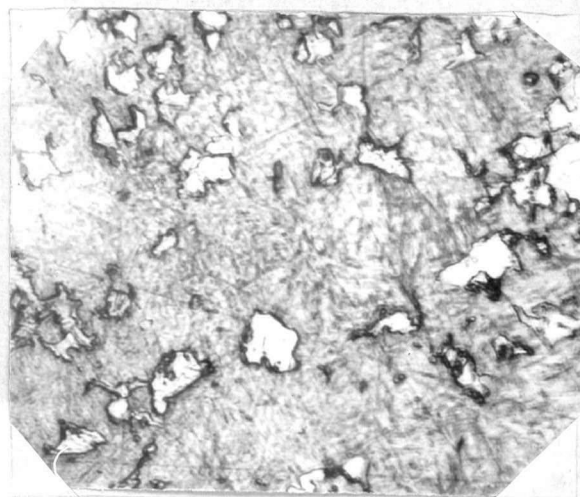


Fig. 105 Alloy AA₃ transformed 10000 sec. at 1100 deg. F. Ferrite grown similar to that at 1000 deg. F. X850

DISCUSSION OF RESULTS

Several investigators have reported that nickel shifts the whole isothermal transformation curve to the right, and that all portions of the curve are shifted similar amounts. The present investigation has found (fig. 10 to 13) that the pearlite curve is pushed to the right much more than any other part of the isothermal transformation curve with increasing nickel content. The effect on the pearlite reaction cannot therefore be directly related to the increase in nickel content. To find the direct effect of nickel on the pearlite reaction a series of pure iron-nickel-carbon alloys shall be investigated. If the pearlite reaction could be explained by the lowering of the eutectoid temperature the curves of this reaction drawn with a common A_e temperature would be identical. It can therefore only be assumed that nickel intensifies greatly the effect of molybdenum on the pearlite reaction.

By extrapolation of data given by Wells and Mehl³⁵ and Ham¹⁷ the approximate values of diffusion coefficients of nickel and molybdenum at 1000 deg. F. in austenite containing 0.6 percent carbon are 9×10^{-14} and 8×10^{-13} cm² per second respectively, compared with 8×10^{-9} cm² per second for carbon¹⁵. The ratio of diffusion rates is $\frac{D_{MO}}{D_N} = \frac{9}{1}$. The ratio at 1550 deg. F. is 4 to 1; thus, in the range of temperature which

pearlite forms nickel diffuses more slowly than does molybdenum. Increasing the nickel content should increase the preference in forming ferrite nuclei, because nickel is an element partitioned almost entirely in ferrite. The delay in forming ferrite at equivalent temperatures below the equilibrium (the gamma to gamma plus alpha equilibrium is lowered proportionally to the eutectoid lowering with increasing nickel₃₁) may be explained on a basis of lowered diffusion. But the delay in the pearlite reaction may not entirely be the result of lowered diffusion.

The increase in the ferrite nucleation rate by nickel and the increase in the carbide nucleation rate by molybdenum are two opposing factors which depend on free energy and diffusion rates before growth of nuclei can occur. Because the pearlite reaction in the higher nickel alloys tested isothermally did not appear within the time limits investigated (assuming the reaction does appear at longer times according to Bain's equilibrium phase diagram₃₁) even after the ferrite has apparently grown to its full amount, some other cause besides diffusion is necessary to explain the delay. This suggests two possible hypotheses; (1) that nucleation sites for carbides are increasingly more difficult to find as the austenite nickel content is increased, and that these carbide nucleation sites cannot exist until ferrite

transformation and further nickel diffusion from austenite to ferrite lowers the nickel content of the remaining austenite, or (2) that nickel increases the tendency for carbide nuclei to be less than the critical size for growth according to free energy relationships.

The accepted theory of nucleation and growth of nuclei^{5,9,10,11,13,27}, in solid-solid reactions (based on analogy of gas-liquid-solid reactions) is as follows. During the random migrations of atoms in austenite, volumes are established from time to time of the required lattice for a precipitating phase; the number of these embryo lattices or potential nuclei depends on diffusion relationships; and the size of the potential nuclei is statistically distributed. Free energy relationships determine the minimum size potential nucleus which has a surface energy equivalent to the difference in free energy between austenite and a phase of the potential nucleus lattice. If this condition is met by a potential nucleus it can remain in situ as a stable nucleus, and growth of this nucleus into a phase of the new lattice can occur as diffusion in austenite brings other atoms appearing in the new phase to lattice positions adjoining the nucleus. If this condition is not met the embryo lattice is broken up by continued diffusion of the atoms. But the accepted theory has been questioned to explain some discrepancies, the argument being that thermodynamics does not tell us exactly what happens,

but what is most likely to happen. Hultgren₉ has suggested growth from an embryo lattice smaller than the accepted minimum, or, for isothermal transformation, growth from zero time.

This leads to the hypothesis discussed earlier that nickel intensifies formation of smaller embryo lattices or "quasi-nuclei" of carbides, and that growth of these smaller nuclei must necessarily take longer than growth from much larger nuclei, which results in transformation time to visible amounts being extremely long; or that the "quasi-nuclei" themselves have to diffuse before growth can occur, and diffusion rate of a "quasi-nucleus" is smaller than that of nickel and molybdenum. This hypothesis may explain some of the facts better than other hypotheses and can only be proven by indirect means.

The effect of nickel in increasing both the amount and time of formation of acicular ferrite at intermediate temperatures can readily be explained by the increased tendency toward ferrite nucleation and the low diffusion rate of nickel causing slower growth of ferrite nuclei. Lower diffusion rates of all elements at these temperatures and the increased nucleation rate of ferrite results in the formation of a high carbon ferrite. As the acicular ferrite grows further, diffusion of carbon and carbide-forming elements causes precipitation of carbides, both within the ferrite

and at the ferrite-austenite interface. Eventually, the carbide grows as a separate phase. This type of precipitation has been discussed before in the literature. Davenport²⁰ calls acicular ferrite the "X" constituent and notes the secondary carbide reaction in low and medium alloy steels. This type of transformation was also noted³⁹ in transformations of low and medium carbon N E steels, and in all alloys discussed the pearlite reaction was delayed greatly.

The bay which appears in the curve has not been noted before for nickel steels. The lower bainite reaction is evidently separate from the ferrite reaction. The upper bainite reaction has been displaced by the acicular ferrite reaction, and the bay in the curve between the acicular ferrite and lower bainite reactions illustrates the separation in maxima of the two reactions.

CONCLUSIONS

(1) Nickel shifts the isothermal transformation curve generally to the right in a 0.55 carbon, 0.35 molybdenum alloy of iron.

(2) Nickel delays the pearlite reaction more than can be explained by the lowering of the eutectoid temperature. To find the actual effect of nickel and molybdenum, as single alloying elements and together, isothermal transformation data will have to be obtained for pure iron-nickel-carbon alloys and pure iron-molybdenum-carbon alloys, and the results of these investigations compared with those of the present investigation.

(3) Nickel produces a tendency toward formation of high carbon acicular ferrite at intermediate temperatures, accompanied on further growth of the ferrite by carbide precipitation and agglomeration, and by eventual growth of the carbide as a separate phase formed directly from austenite.

(4) The upper bainite reaction is suppressed as nickel content is increased, and is displaced by the acicular ferrite reaction.

(5) The lower bainite reaction as represented on the curve becomes separated from the rest of the curve by the appearance of a bay between the acicular ferrite and bainite reactions, a fact which has never been reported in

earlier investigations of alloys containing nickel.

(6) The upper temperature of formation of bainite is not lowered as rapidly as the eutectoid temperature with increasing nickel.

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