

AN ABSTRACT OF THE THESIS OF

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_____ISOTHERMAL TRANSFORMATION OF ALUMINUM BRONZE_____

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The response of metals to heat treatment has been an important consideration in the development of alloys as engineering materials.

This thesis project was conducted for the purpose of studying the transformation reactions occurring in the aluminum bronze alloys as a result of heat treatment.

Several alloys of aluminum bronze were prepared for this purpose by alloying copper with aluminum. Two of these alloys, one a hypoeutectoid alloy of 10.8 per cent aluminum and the other a hypereutectoid alloy of 12.3 per cent aluminum were annealed, heat treated, and examined metallographically.

The alloys were annealed prior to heat treatment to obtain an homogeneous structure. The heat treatment was done by heating the annealed specimens to an elevated temperature in the single solid-solution beta region, quenching to temperatures at which beta cannot exist, and holding for a definite period of time before further quenching to room temperature.

The heat treatment resulted in a phase change from the single beta phase to two eutectoidal phases called alpha and delta. In addition to the eutectoidal phases, an intermediate or transitional phase called beta₁ was observed.

The influence of temperature and time on these phase transformations was determined by metallographic examination. The results of the examination of the transformation products were illustrated by means of isothermal transformation curves.

The transformation reactions of the hypo- and hypereutectoid alloys were compared to each other. The comparison was made to determine the effects of excess alpha and delta constituents on the transformation temperatures and time.

The most outstanding influences that excess alpha and delta have on aluminum bronze alloys as compared to the eutectoid alloys

were found to be:

1. The martensite start temperature is lower in the hypereutectoid alloys.
2. The martensite start temperature is higher in the hypoeutectoid alloys.
3. Alloys containing appreciable amounts of excess alpha do not form a true lamellar eutectoid structure.
4. The time necessary for the eutectoid reaction to start is shorter in the hypoeutectoid alloys containing excess alpha.
5. The transitional change from beta to β_1 takes place at a lower temperature in the hypereutectoid alloy containing excess delta.
6. Alloys at or near the eutectoid composition precipitate out delta as a proeutectoid constituent at the higher transformation temperatures. But at the lower temperatures, alpha is precipitated out as the proeutectoid constituent.
7. Alpha is nucleated first at the grain boundaries and later is nucleated within the grains.
8. Delta has an equal tendency to nucleate within the grains and at the grain boundaries.

ISOTHERMAL TRANSFORMATION
OF ALUMINUM BRONZE

by

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ISOTHERMAL TRANSFORMATION OF ALUMINUM BRONZE

CHAPTER I

INTRODUCTION

Alloys of the copper-aluminum system are designated as aluminum bronze alloys. These alloys in the range of 5 to 13 per cent aluminum are of considerable value as engineering materials.

Aluminum bronze alloys of 10 to 13 per cent aluminum are important because of their response to heat treatment with an improvement of physical properties. The improvement of the physical properties of metals such as steel and aluminum bronze is a direct result of certain transformations or phase changes that occur in the metal structure during a heat treating process.

The response of the binary alloys of copper and aluminum to heat treatment is quite similar to that of plain carbon steel. This fact not only indicates their importance commercially, but also provides an interesting topic for study in the field of physical metallurgy.

Several investigations have been made of the isothermal transformation of aluminum bronze. Nearly all of these investigations have been conducted on the binary Cu-Al system with alloys having the eutectoid composition of 88.2 per cent copper and 11.2 per cent aluminum.

Relatively little work has been done to determine the isothermal transformation reactions of these alloys having greater or lesser amounts of aluminum than the 11.8 per cent in the eutectoid alloys.

The objective of this project was to study the transformation reactions of two copper-aluminum alloys -- one a hypoeutectoid alloy containing 10.8 per cent aluminum and the other a hypereutectoid alloy containing 12.3 per cent aluminum.

In early investigations of an alloy system it is necessary to develop the equilibrium diagram. An equilibrium diagram shows the phases that are present at given temperatures. The term equilibrium refers to the existence of a phase at very stable conditions.

Although these diagrams are very important in the study of alloys, they do not give a true picture of the structures that an alloy will possess as a result of non-equilibrium cooling. In the actual applications of metals, equilibrium structures are never obtained completely. Because of this, it is necessary to study the structures that an alloy will have as a result of non-equilibrium cooling.

Bain and Davenport (1, pp.117-144) were the first investigators to do extensive work of this nature. Their work was performed on the isothermal transformation of

eutectoid steel at temperatures below the eutectoid temperature.

Alloys that form what is called a eutectoid are valuable in the study of phase transformations. They may be studied more easily than alloys of other composition since they exist as single solid-solutions at elevated temperatures.

In the eutectoid steels, studied by Bain and Davenport, the single high-temperature phase called austenite cannot exist at room temperatures. Austenite is a solid-solution of carbon in iron and has a minimum temperature of 720 C at which it may continue to exist without undergoing a phase change. Sometimes the phase change of a high-temperature constituent is referred to as a decomposition with decreasing temperature.

If austenite were allowed to cool very slowly, the resulting structure would consist of two equilibrium phases called ferrite and cementite. The intimate mixture of these two phases is called lamellar pearlite. Ferrite is the iron-rich phase capable of retaining only small amounts of carbon in solid-solution at room temperatures. Cementite is an intermetallic compound containing a definite amount of carbon.

In their study, Bain and Davenport developed the technique for quenching specimens from the austenite temperature to various temperatures below the eutectoid

point. Fundamentally their procedure involved heating small specimens to a temperature in the austenite region to obtain an homogeneous solid-solution. The specimens were quenched in a lead bath maintained at constant sub-critical temperature for a predetermined length of time. A large number of specimens were quenched in this manner at many temperature levels and for various periods of time.

It was found that the type of transformation product resulting from the decomposition of austenite depended on the temperature of the quench, and the amount of decomposition depended on the length of time held at the quench temperature. The types of non-equilibrium products found in the metal structures were of three general types: pearlite, bainite, and martensite.

The pearlite was found to exist in several different forms depending on the temperature of formation. The coarse pearlite formed at a temperature just under the eutectoid temperature, fine pearlite at a temperature slightly below this, and nodular pearlite at a temperature even lower. At a temperature just below that for nodular pearlite, bainite having a feathery appearance was formed. At temperatures considerably below that for feathery bainite, an acicular bainite structure was formed. Below the temperature of the bainite reaction, an entirely different structure called martensite was formed.

With the exception of the martensite formation, the temperature at which each product is formed is not definite, but a gradual transition from one product to the next.

It was found that with the pearlite and bainite, the amount of transformation occurring at the respective temperatures depended on time. In other words, if a specimen were quenched at a temperature in the bainite region and held for a sufficiently long period of time, the austenite would eventually transform completely to bainite.

This is not true with the martensite reaction, however, although Bain and Davenport assumed it to be true in their original work. Their assumption was that martensite at a given temperature also transformed as a function of time. Later, it was found that this was not the case and that martensite continues to form only with decreasing temperature.

A diagram has been developed for the representation of temperature and degree of transformation occurring when an alloy is cooled to subcritical temperatures. These isothermal diagrams are called T-T-T curves or S curves. The T-T-T stands for time-temperature-transformation and the S refers to the general shape of the curve.

The T-T-T curves are a plot of temperature as ordinate and time to a logarithmic scale as abscissa. The curve indicates the temperature and time at which the various

products of transformation appear in the metallographic structure.

As the isothermal curve indicates, the transformation products at different temperatures do not appear at the same time. The reason for this is that at different temperatures, the time necessary for product formation varies as a function of nucleation, growth, and atomic mobility of precipitating phases (2, p.183).

Coarse pearlite is rather slow to start because nucleation at the higher temperatures is not great, although the atomic mobility is high. At temperatures in the range of nodular pearlite, the nucleation rate is high with also a relatively high atomic mobility. This results in a much more rapid start of nodular pearlite than that of coarse pearlite. Low temperature bainite, on the other hand, is rather slow to start because of relatively low atomic mobility in this temperature range.

At the point on the isothermal curve where nodular pearlite forms, there appears the knee of the curve. The knee represents the critical cooling time for the decomposition of austenite.

It was mentioned previously that the formation of martensite is independent of time. Martensite is formed upon rapid cooling past the knee of the curve to a temperature at which it may form. The degree of formation becomes greater with a lowering of the temperature of the quench.

For eutectoid plain carbon steels the martensite starts to form at 220 C and finishes at 110 C. Therefore, if a specimen were quenched from the austenite region past the knee of the curve to room temperature the resulting product would be 100 per cent martensite.

The isothermal reactions of eutectoid steel have been briefly outlined here to serve as background for the study of aluminum bronze. This was deemed necessary since the fundamentals involved are basically the same.

Several studies have been made of the aluminum bronze alloys. Early investigations were made of the phase changes by measurement of electrical resistivity during thermal treatment. Other observations have included the measurement of volume change with temperature.

Electrical resistance and volume change determinations are usually indicative of a phase change, but do not provide sufficient information as to the resulting phase structures.

The most important work that has been done in the study of phase changes has employed metallographic and x-ray diffraction methods. The x-ray diffraction determinations afford a means by which the atomic structure of existing phases could be determined, while the metallographic analysis provided visual examination of the phase structures. A combination of these techniques has proved

invaluable in metallurgical work of this nature.

The most outstanding work conducted on aluminum bronze was that of Smith and Lindlief (9, pp.69-106). They were the first to employ the methods of Bain and Davenport to the Cu-Al system. Their investigations were primarily from the metallographic standpoint, although attempts with x-ray diffraction analysis were made to a limited extent.

Since the original work of Smith and Lindlief, other investigators have been Greninger (3, pp.204-221), Mack (7, pp.1-16), and Klier and Grymko (5, pp.611-619).

Greninger was mainly interested in the martensite reaction that was found to exist in the aluminum bronze alloys quenched to low temperatures. The martensite reaction in aluminum bronze was discovered after the original work of Smith and Lindlief. Mack reported in much greater detail and clarity the isothermal reactions reported by Smith and Lindlief. Mack's work was carried out later and therefore he was able to employ better techniques for product identification. Klier and Grymko were the first and apparently the only investigators to publish information regarding the transformations in the hypoeutectoid and hypereutectoid alloys.

All of the previous work reported on the aluminum bronze alloys seems to be in good agreement as to the

transformation reactions in general. However, due to more recent developments in technique and equipment, the latter investigations have given more valid results.

CHAPTER II

BACKGROUND

In all binary alloys that form eutectoids, there are certain basic similarities. It has already been pointed out that steel and aluminum bronze are similar in their reaction to heat treatment.

Binary alloys of eutectoid composition exist as single solid-solutions above the eutectoid temperature. Subsequent equilibrium cooling to room temperature causes a transformation to two new phases. Also, if the temperature is decreased at a low enough rate through the eutectoid temperature, the low temperature equilibrium phases will be formed. If, however, the rate of cooling is relatively rapid, as is usually the case for metals, the resulting phases will not be in equilibrium and will contain certain intermediate or metastable phases.

Figure 1 shows the equilibrium diagram for the Cu-Al system. The eutectoid point for the system is at 11.8 per cent aluminum and 565 C. It should be kept in mind that the equilibrium diagram represents only the phases that will exist at very stable conditions. The conditions resulting from non-equilibrium cooling are not represented in any way by this diagram.

When aluminum bronze is cooled slowly from the beta region, the single solid-solution beta transforms to

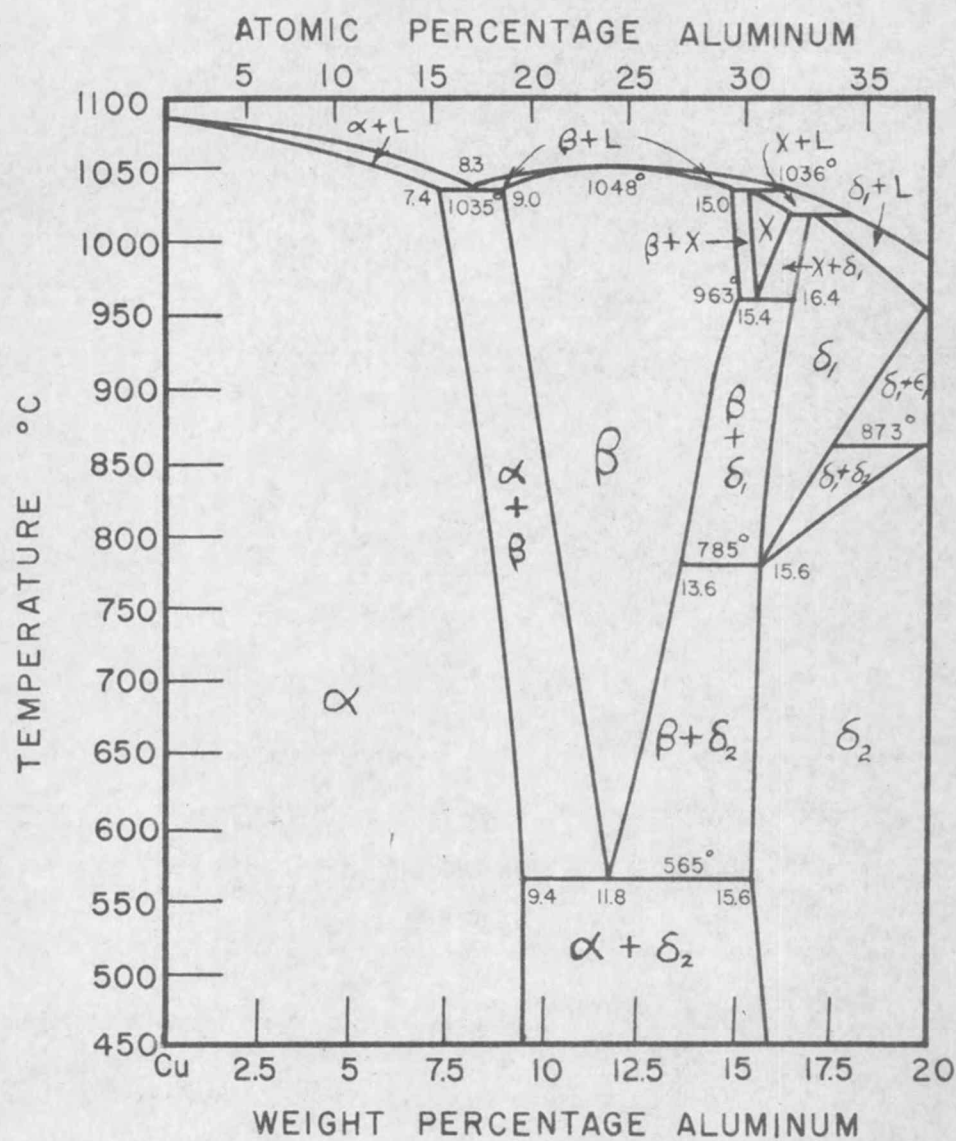


Figure 1. Copper-Aluminum equilibrium diagram

alpha and delta. The transformation is similar to the transformation of austenite to ferrite and cementite.

Alpha is a substitutional solid-solution of aluminum in copper and delta is an intermetallic compound of copper and aluminum.

If an alloy of eutectoid aluminum bronze were cooled at a high cooling velocity, certain intermediate phases would be formed. The intermediate phases are sometimes similar in appearance to the equilibrium phases, but are different in composition due to the effects of supercooling.

The more rapidly cooled beta rejects alpha and delta at a rate proportional to the severity of cooling. The rate of cooling has considerable effect on the transformation products. The rate of cooling affects such factors as nucleation of the individual phases, concentration gradients as a result of nucleation, atomic mobility due to a change of energy level, and the growth of the precipitate from the nuclei. The influence of these factors on the resulting structures in the metal has been observed by previous investigators.

The isothermal transformation technique described in Chapter I for steel has been used to a great advantage in the study of these factors on the Cu-Al system.

The products of transformation as observed by previous investigators are defined as follows:

Alpha is a face-centered-cubic structure having at equilibrium approximately 9.5 per cent aluminum in solid-solution.

Delta is a body-centered-cubic structure of the aluminum-rich intermediate phase capable of retaining up to 18.5 per cent aluminum.

Beta is the high-temperature solid-solution phase having a disordered body-centered-cubic structure. It is believed by some investigators to be a compound of Cu_3Al having a wide range of solubility.

Beta₁ is an intermediate transitional phase having an ordered body-centered-cubic structure capable of retaining a minimum of 12.8 per cent aluminum in solid-solution.

Beta' is a martensite structure with an aluminum content less than 13.0 per cent, and a crystal structure nearly that of a hexagonal-close-packed lattice.

Alpha, the face-centered-cubic structure, is a substitutional type solid-solution. When cooled to sub-critical temperatures, alpha is nucleated by the rejection from either the beta or beta₁ phase. It appears as the low-temperature proeutectoid constituent. During severe non-equilibrium cooling, alpha is precipitated at a high

rate and has a tendency toward supersaturation.

Alpha is capable of retaining at lower temperatures up to 12.5 per cent aluminum in solid-solution. As a result of its tendency to become supersaturated, its lattice parameter is expanded. The expansion of its parameter is proportional to the degree of saturation and increases with decreasing temperature.

Delta may retain up to a maximum of 18.5 per cent aluminum in solid-solution. Similar to alpha, it has a tendency to form a supersaturated solution. At the higher temperatures, just below the eutectoid point, delta is rejected as the proeutectoid constituent.

Figure 2 is the isothermal curve developed by Mack for the eutectoid aluminum bronze, and shows the time and temperature at which the proeutectoid constituents are rejected.

The reasons for these proeutectoid rejections are not definitely understood. An explanation might be that at the higher temperatures, where the atomic mobility is greater, delta nucleates more rapidly than alpha and partially depletes beta of the aluminum in solution. Whereas, at the lower temperatures, the atomic mobility or energy level is lower and allows only enough aluminum to diffuse to form alpha. Several researchers have attempted to explain this, but without definite proof of the theory.

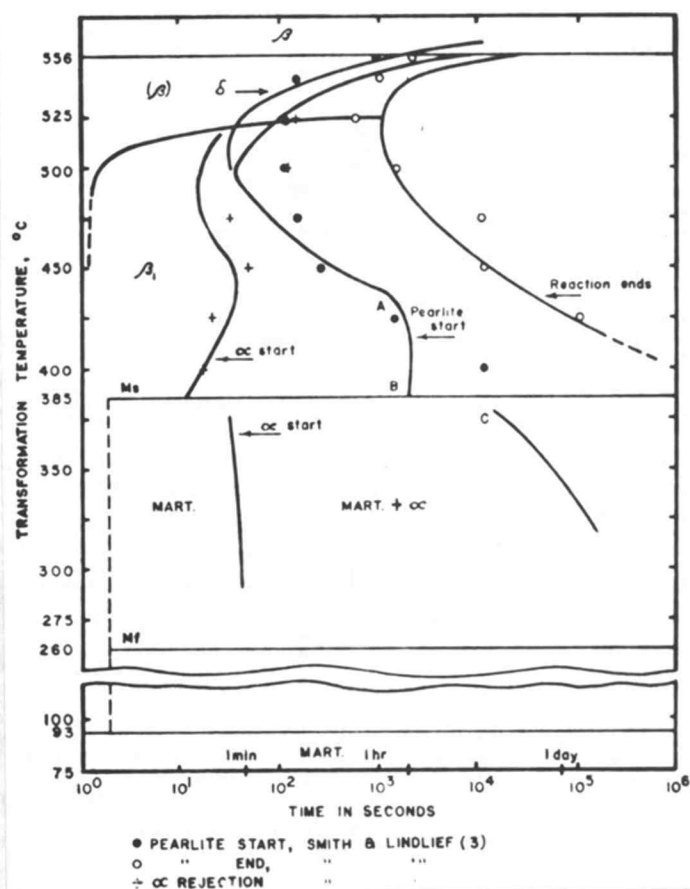


Figure 2. Isothermal transformation diagram for eutectoid aluminum bronze as determined by Mack.

Several reactions have been found to occur in the aluminum bronze alloys which are characteristic to these alloys in particular. Smith and Lindlief, in their original work, found that as beta was cooled rapidly an intermediate reaction took place. This reaction occurred in the vicinity of 535 C. They observed that beta undergoes a change, but could not identify it as a definite phase change. Their results offered no indication as to what happened except that the transitional constituent could retain more aluminum in solution than beta. In later investigations, it was determined that this transitional constituent was a result of a change in atomic arrangement. This change in atomic arrangement has been further substantiated by more recent investigations of Mack (7, p.14) and Klier and Grymko (5, p.616).

It was found that the change in atomic arrangement resulted in an ordering of the body-centered-cubic structure. A crystal change from disorder to order only results in a re-shuffle of the atoms in solution (2, p.171).

Other reactions occurring that are characteristic to this system, are the various ways in which alpha and delta form during transformation. Sometimes the alpha and delta formation resembles pearlite of lamellar structure and at other times forms as large massive particles. The pearlitic formation has been explained as an alternate

precipitation of alpha and delta. For example, as delta precipitates, the area adjacent becomes depleted of aluminum until the composition of alpha is reached and alpha forms. This is generally the manner in which the pearlitic structure is formed. With aluminum bronze alloys this reaction does not always occur in this manner. Often it is observed that the alpha and delta phases form as large massive structures, nearly independent of each other. Klier and Grymko reported this as being especially true of aluminum bronze alloys of hypo- and hypereutectoid composition. No reference to the reason for this type formation was found in the published literature for the aluminum bronze alloys.

The martensite reaction has been found to occur in the aluminum bronze alloys. The formation of martensite in the Cu-Al system is again comparable to the similar reaction in steel. Greninger (3, p.204) observed that the martensite reaction is due to rapid cooling of the beta phase. As a result of the rapid cooling, the beta lacked sufficient time in which to decompose, therefore forming a supersaturated solution. Martensite does not form as a function of time, but only forms with a decrease in temperature. In the formation of martensite, the body-centered-cubic structure of beta is changed to a distorted hexagonal structure.

The formation of martensite results from a rapid quench from the beta region to relatively low temperatures. At these low temperatures, the atomic mobility is low and the concentration gradients cannot be set up to allow transformation of any appreciable degree.

The martensite start temperature varies with the composition of the alloy. Hypereutectoid alloys form martensite at a much lower temperature than the hypoeutectoid alloys. This appears to be true for all binary alloys that form martensite.

Transformation reactions for alloys having compositions other than the eutectoid composition have fundamentally the same type reactions, except that the rates of reaction and the time for start and finish of the eutectoid formation are different.

Generally the effect of excess alpha in an alloy is to shift the isothermal curve to the left. Also, an effect of excess alpha is to increase the temperature at which the martensite reaction starts. The effects of the excess delta constituent in an alloy seem to be similar to the effects of excess alpha, except that the martensite temperature is lowered instead of raised.

It was the objective of this project to determine these effects, and to determine to what extent the microstructures of the aluminum bronze alloys were altered.

CHAPTER III

EXPERIMENTAL WORK

The two metal components used for the alloying of the aluminum bronze were commercial bus bar copper and transmission line aluminum conductor.

Bus bar copper has a composition of 99.92 per cent copper and 0.04 per cent oxygen with very small amounts of other elements accounting for the remainder.

Aluminum conductor used for transmission lines has a composition of 99.4 per cent aluminum or greater, 0.20 to 0.40 per cent copper, and small amounts of magnesium and manganese. No attempt was made to determine the exact analysis of these components and were assumed to be sufficient for the objectives of this project.

The equipment used for alloying the two metals consisted of a high-frequency induction furnace, an adjustable strip-mold, tongs, and powdered carbon. This equipment is shown in Figure 3.

The Ajax induction furnace consisted of a water-cooled induction coil, a silica liner for shielding the coil, a graphite crucible and a layer of conducting material between the graphite crucible and the silica liner. The crucible was approximately 2 inches in diameter and 4 inches in depth. The aluminum bronze alloys were made by melting 180 grams of copper and adding 20 to

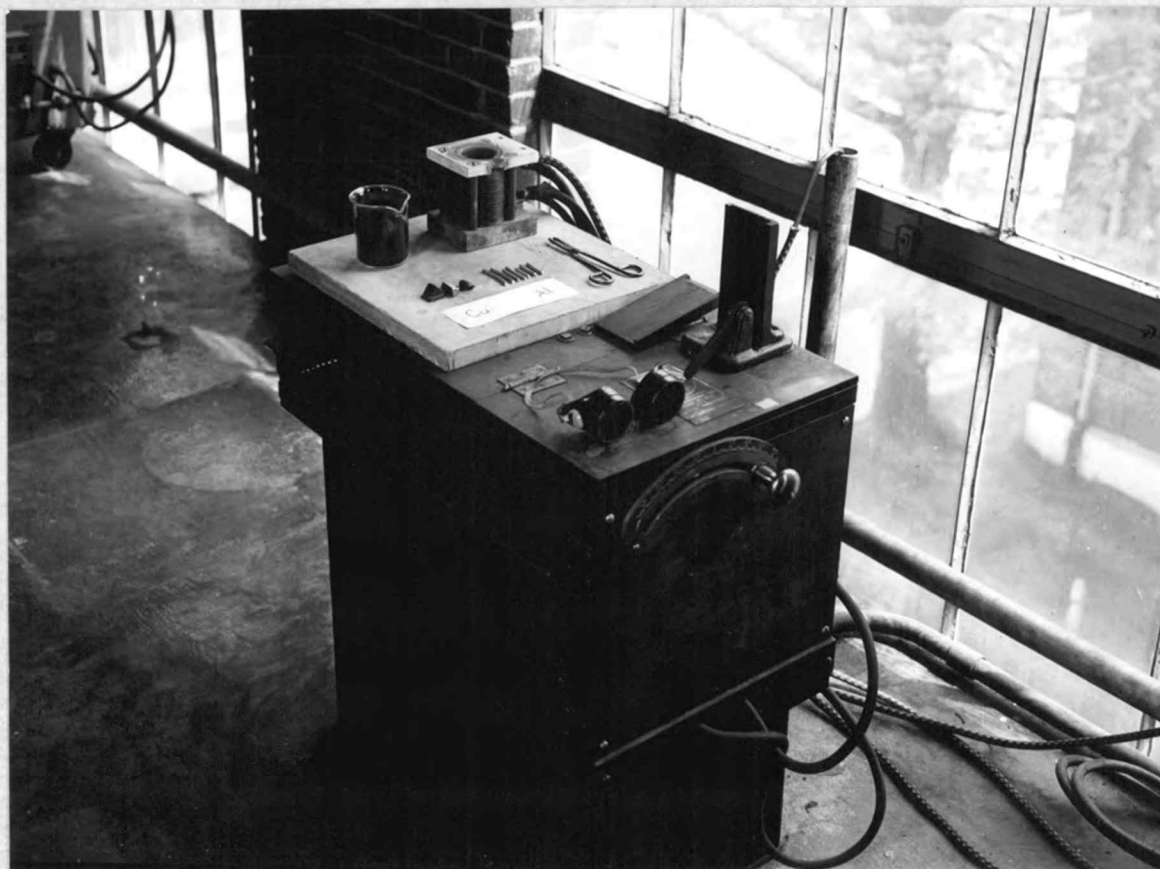


Figure 3. Ajax induction furnace

24.5 grams of aluminum.

The copper used was originally in the form of flat bars or wire. The large pieces were cut into small pieces and melted in the crucible. After the copper was melted, a powdered carbon was poured over the molten copper to prevent or at least minimize oxidation of the copper before addition of the aluminum. The carbon cover not only minimized the oxidation of copper, but also prevented serious oxidation of the aluminum as it was added to the molten copper.

The aluminum was in the form of shot lengths of wire and was added to the copper by placing one end of the wire through the carbon cover and into the molten copper. The aluminum melted readily and with the aid of tongs it was possible to completely limit the melting of the aluminum to the region beneath the carbon cover. This procedure prevented a direct exposure of the molten aluminum to the atmosphere.

In early attempts at alloying these metals, the carbon cover was not used. The absence of this protection from the atmosphere resulted in excessive oxidation of the aluminum and gave alloys of varying composition.

After an alloy was thoroughly melted, it was necessary to allow it to cool before pouring into the mold. Considerable difficulty was encountered with the castings because of shrinkage that occurred while cooling from the

liquid to the solid state. The shrinkage caused the casting to be porous at the center of the casting. The porous or piped structure at the center of the casting resulted in an alloy of non-uniform composition.

The greatest single factor in obtaining a good sound casting was the pouring temperature. If an alloy were cast from a temperature considerably above the melting point, the severe piping at the center of casting resulted. This piping not only caused the casting to be porous, but also caused a great deal of segregation of the two component metals. Observations made of the crystal structure of the piped area in the casting showed that this area was rich in aluminum. This fact was also brought out when the piped alloys were annealed. The aluminum in the center of the castings would melt and diffuse leaving large areas of nearly pure aluminum.

Another factor that was important in the casting operation was the rate of pouring. Rapid pouring resulted in the formation of gas bubbles within the melt. Slow pouring from a temperature slightly above the melting point provided sound castings with a suitable homogeneous structure.

All alloys were cast from the pouring temperature to room temperature into a strip mold. The mold was one-quarter inch thick, two inches wide, and six inches in

height. The shape of the castings were especially suitable for sectioning into smaller pieces for annealing and heat treating.

The castings were annealed before heat treatment to obtain a more homogeneous structure and to remove concentration gradients resulting from severe cooling during the casting operation. The annealing was done by heating the castings in an electric furnace to a temperature of 900 C for approximately 8 hours. At this temperature the metal was in the single solid-solution beta phase. From this temperature the alloys were furnace cooled to 565 C and held for 12 hours to form a structure consisting mainly of alpha and delta in the eutectoid form. Holding the alloys at this eutectoid temperature resulted in a close approximation of the equilibrium structure. From the eutectoid temperature, the furnace was turned off and the alloys were furnace cooled to room temperature. The annealing and heat treating furnaces are shown in Figure 4.

Specimens cut from the annealed alloys were observed with the metallographic microscope as a check on the effectiveness of the annealing operation. The microstructures indicated that the procedure for annealing was satisfactory.

The alloys were cast using definite amounts of copper and aluminum, but due to the losses of both the copper and aluminum as a result of oxidation, an analysis

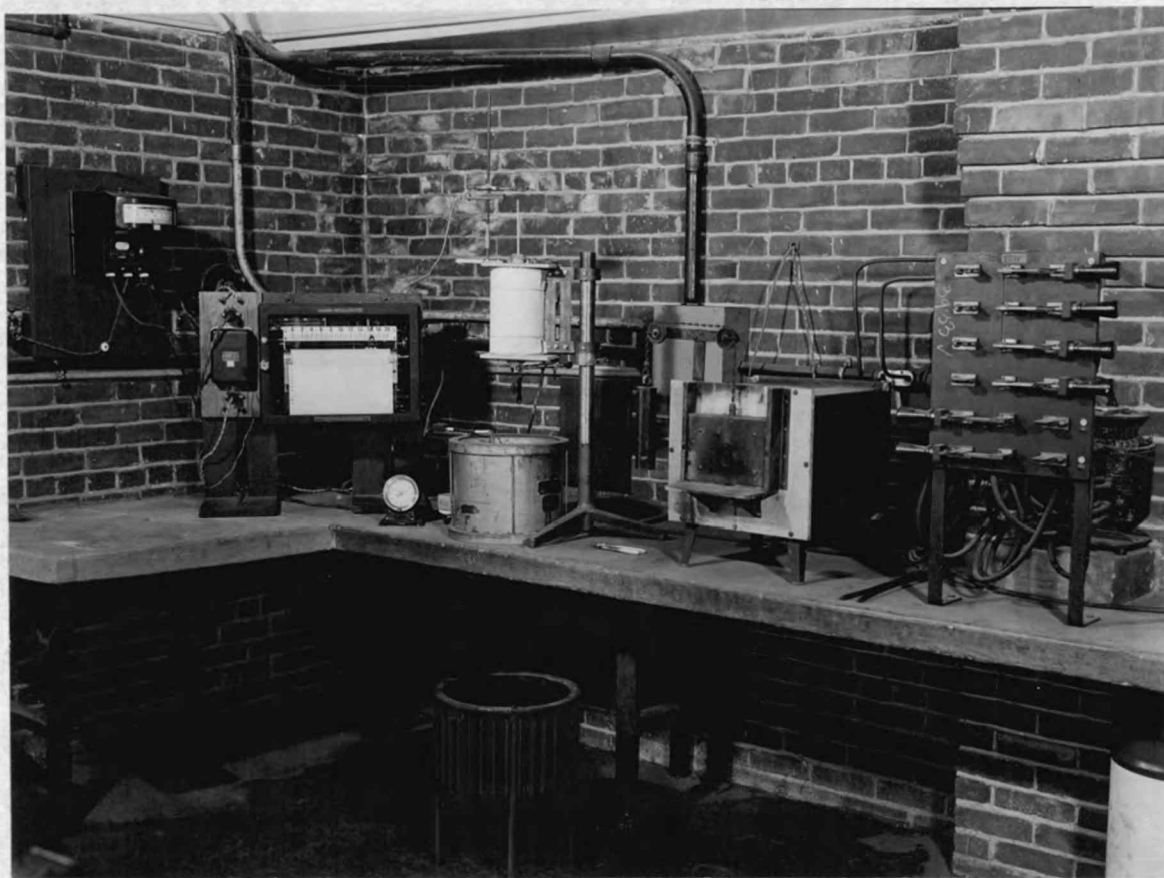


Figure 4. Annealing and heat treating furnaces

of each alloy had to be made. This check of the final analysis was made by electrolytic deposition of copper from an aluminum bronze and nitric acid solution.

The procedure for determination of the analysis of the alloys was that recommended by the American Society for Testing Materials--ASTM E 54-46T. The procedure was as follows:

A 2.0000 gram sample of aluminum bronze drill shavings was placed in a 250 ml beaker. The drill shavings were dissolved with 25 ml of a 1:1 nitric acid solution. This was heated over a steam bath for one hour to drive off the brown fumes. Fifty ml of hot water were added to the solution and allowed to stand for one hour. One drop of 0.1 normal hydrochloric acid was added and the solution diluted to 150 ml. Two platinum electrodes were inserted in the solution and covered with a split watch-glass. A 6-volt direct-current was applied to the electrodes and the copper plated-out at a current density of 4 amperes per square decimeter. The copper that plated onto the electrode was weighed and the percentage aluminum was determined by difference.

The percentage aluminum in the alloys were as follows:

<u>Alloy No.</u>	<u>Per cent Al As Cast</u>	<u>Per cent Al by Analysis</u>
1	12.0	13.10
4	10.0	12.45
5(a)	10.0	9.83
6	10.0	12.80
7 *	12.0	14.60
8 *	12.0	12.30
9 *	10.4	10.10
10 *	10.9	10.52
11 *	11.1	10.80

* Alloys melted under carbon cover

Early attempts with the electrolytic analysis gave results that did not compare very closely with the analysis as cast. This was attributed to non-homogeneous structures existing in the first alloys observed. With the improvement of alloying and casting techniques, a better correlation was obtained between the electrolytic analysis results and metallographic observations of the annealed structures. Alloys No. 8 and No. 11 were selected for this study primarily from their metallographic appearance. They appeared to have homogeneous structures of the two compositions desired as well as a favorable comparison with their electrolytic analysis results.

ADVANCE BOND

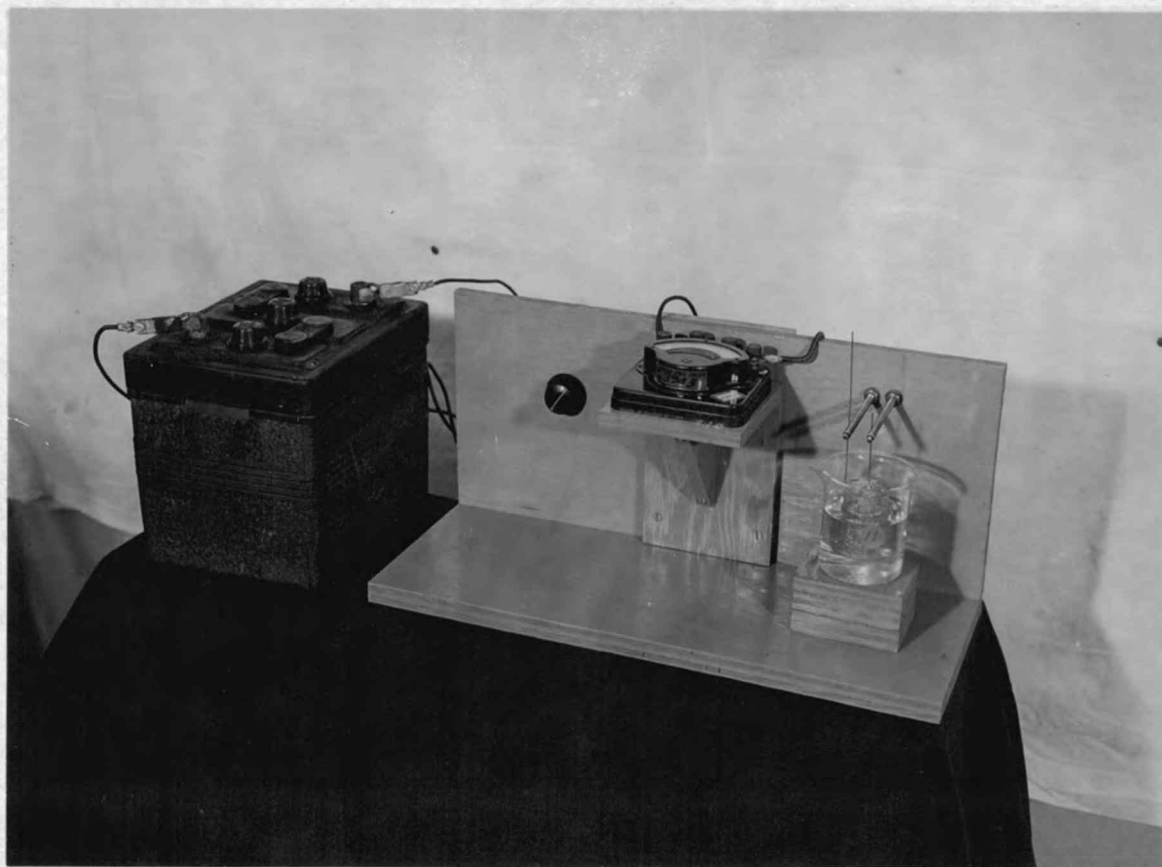


Figure 5. Electrolytic analysis equipment

After annealing, the alloys were prepared for heat treatment by cutting them into small rectangular specimens.

The original castings were rectangular strips 0.25 inches thick, 1.5 inches wide, and 5 inches in length. These strips were cut in half longitudinally. The two halves were cut transversely into small specimens 0.125 inches thick. The final specimen size was 0.25 inches wide, 0.75 inches long, and 0.125 inches thick.

Each specimen was notched on both sides at one end to permit attachment of a sling wire around the specimen. The sling wire served as a means for suspending the specimen in the vertical furnace during the initial heat treating process.

The heat treating process consisted of three main operations. The first operation was that of heating the specimens in the vertical furnace for a minimum of 15 minutes. This was assuming that the specimen required 5 minutes to come up to furnace temperature, therefore the specimen would be at the furnace temperature of 900 C for at least 10 minutes. The second operation was the quenching of the specimens from the vertical furnace to the babbit metal bath directly beneath the vertical furnace. The specimens were allowed to transform isothermally in the babbit metal bath at a given temperature for a

predetermined length of time. The third and final operation was quenching from the babbit metal bath to water at room temperature. The heat treating furnace, the babbit metal bath, and the quenching tub are shown in Figure 4.

All specimens reported in the results of this study were alloyed, cast, annealed, and heat treated in the same manner. These procedures served as the standard for the determination of the isothermal transformation of the aluminum bronze alloys.

It is very important in work of this nature to have standardized procedures. All specimens used for heat treatment should have the same annealed structure to insure more uniform grain size. Also the length of time the specimens are held at the high temperatures for obtaining a beta structure is important to prevent excessive grain growth. These factors of grain growth and grain size as well as many other factors have considerable influence on the rate of nucleation and ultimate transformation at constant subcritical temperatures. Because of these inherent factors, it was necessary to treat all specimens alike in order to limit the number of variables affecting the results.

Following the heat treatment, the specimens were prepared for microscopic examination. The procedure for preparation involved polishing and etching. The polishing

procedure consisted of successive grinding on a 120 and 240 grit belt sander, No. 1, No. 2/0, and No. 3/0 emery paper. Additional polishing was done on two laps. The first lap was canvas covered and used a 600 grit alundum powder suspended in water for the abrasive. The second lap was velvet covered and used powdered alumina suspended in water as the abrasive.

After polishing to a smooth flat surface, the specimens were etched. Two etching reagents were used for this purpose. A general purpose etch was made from 5 grams of cupric chloride in 120 cubic centimeters of water. The etchant used for final identification of all constituents was a 1 per cent chromic acid solution used with an electrolytic etching machine. The electrolytic etching machine was regulated to have an output of 5 volts direct-current with an aluminum cathode. Etching time varied from 3 to 10 seconds depending on the amount of transformation in the specimen. Generally, specimens having more transformation required less time for etching.

For additional information regarding the effects of isothermal transformation on the aluminum bronze alloys, hardness data were taken. Hardness readings were made of alloys quenched at several temperatures and for varying periods of time. Determinations of hardness were made on both the hypo- and hypereutectoid alloys at four temperatures for purposes of comparison. These four temperatures

were: 400 C, 450 C, 500 C, and 525 C.

There are several methods available for determining the hardness of a metal, therefore, it was necessary to select by trial and error method the most suitable one for use with the aluminum bronze alloys. Several Rockwell hardness scales were tried. The Rockwell D hardness scale was the only one that would cover the entire range of hardness readings. This was the basis for selecting the Rockwell D scale. The Rockwell D scale employs the diamond brale as the penetrator with an applied load of 100 kg.

CHAPTER IV

RESULTS

The results of the isothermal transformation of the alloys of aluminum bronze are illustrated by the isothermal diagrams in Figures 6 and 16. These diagrams were plotted from observations made of the metallographic structures of the heat treated alloys. The photomicrographs shown in Figures 7 through 15 and Figures 17 through 24 are typical of the structures obtained by the various heat treatments.

All specimens used for plotting the isothermal diagrams and making the photomicrographs were given the same initial treatment. The only variables used were the temperatures to which the specimens were quenched and the time held at these temperatures.

The two alloys used for this study were made from the same basic materials and only differed in composition by 1.5 per cent aluminum. This seemingly small 1.5 per cent difference in composition resulted in a considerable difference in the transformation reactions of the two alloys. The isothermal transformation curves for the two alloys are quite different and the resulting transformed structures do not have the same appearance.

It was mentioned in Chapter II that the copper-aluminum system at equilibrium conditions form phases having definite compositions for any given temperature.

But when a non-equilibrium condition exists, phase changes occur at rates proportional to the degree of temperature change. The amount of phase change is proportional to the time allowed for nucleation and growth of the precipitating phase.

It has been found in the study of these aluminum bronze alloys that the excess amounts of either alpha or delta constituents have a considerable influence on the final structure. Not only do the excess constituents affect the rate of nucleation and ultimate transformation, but also alter the temperature at which the various constituents appear in the structure.

A study of the equilibrium diagram for the copper-aluminum system will show that upon slow cooling of a hypoeutectoid alloy from the beta region the first constituent to appear will be the proeutectoid alpha. This proeutectoid alpha would be similar to that shown in Figure 18. Also, if a hypereutectoid alloy were cooled slowly, the first constituent to appear would be the proeutectoid delta. This proeutectoid delta would be similar in appearance to that shown in Figure 8.

The proeutectoid constituents in both the hypo- and hypereutectoid alloys were formed on isothermal quenching to temperatures above the eutectoid temperature. These constituents were in excess of the remaining eutectoid constituents. It is the presence of these excess

constituents that alters the reaction time for nucleation and growth of the transformation products.

Figure 7 shows the annealed structure of the hyper-eutectoid alloy No. 8. Specimens of this alloy, if cooled rapidly from the beta region to successively lower temperatures, will begin to transform at different periods of time. The curves in Figure 6 show the temperature and time at which the various constituents begin to form.

It should be noted that at temperatures above 475 C, the first constituent to precipitate from beta is the pro-eutectoid delta. But below this temperature the first constituent to precipitate is proeutectoid alpha. The reason for this has never been definitely understood by previous investigators. The only explanation that can be offered here is that at the higher temperatures the atomic mobility is greater, resulting in diffusion of the aluminum-rich delta phase. Whereas, at the lower temperatures, there is only sufficient atomic mobility to diffuse smaller amounts of aluminum to form alpha.

There is perhaps another reason for this change of initial precipitate from delta to alpha with decreasing temperature. It may be due to the transitional change from beta to β_1 . As beta is cooled below the eutectoid temperature, it cannot retain all of the aluminum present, therefore, it rejects aluminum in the form of the delta

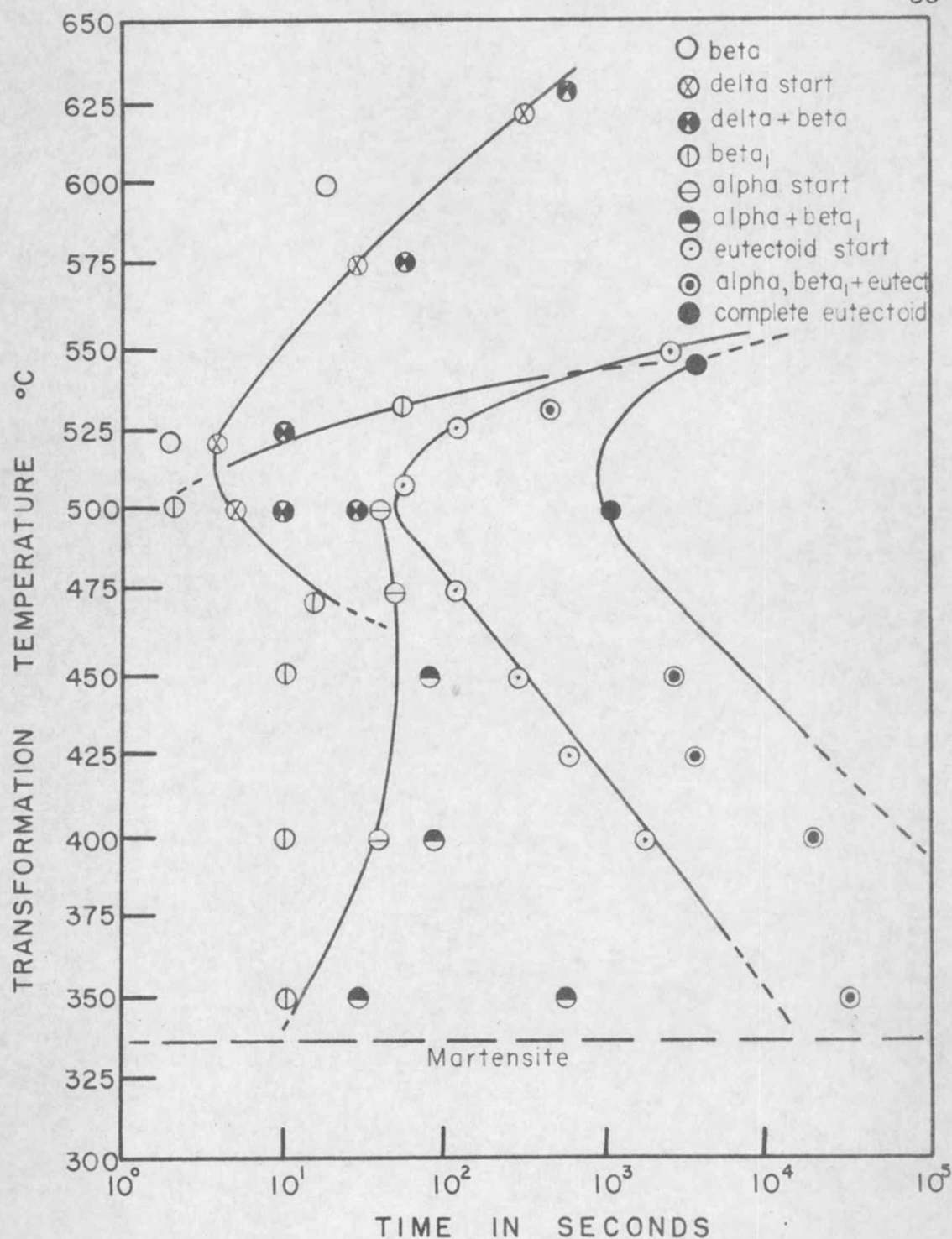


Figure 6. Isothermal transformation diagram for the hypereutectoid alloy No. 8.

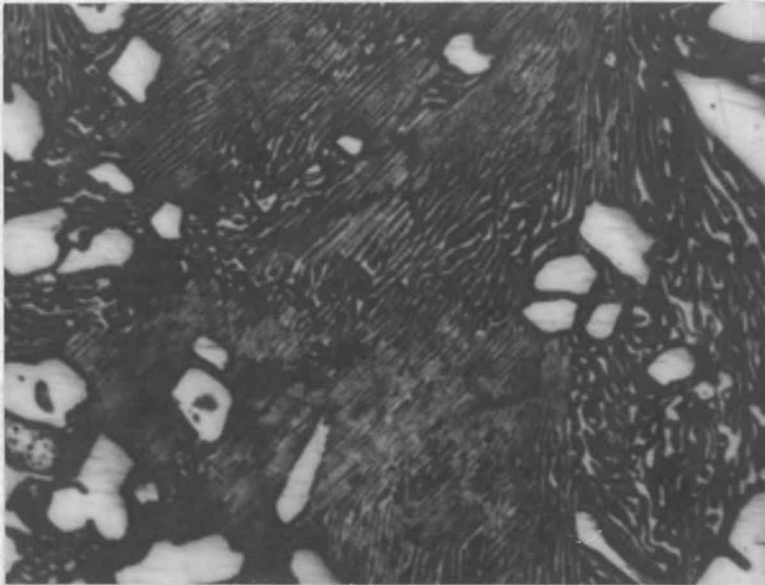


Figure 7. Specimen 8-0. Annealed at 565 C for 12 hours. The structure consists of lamellar eutectoid plus excess delta(gray particles). x 500.

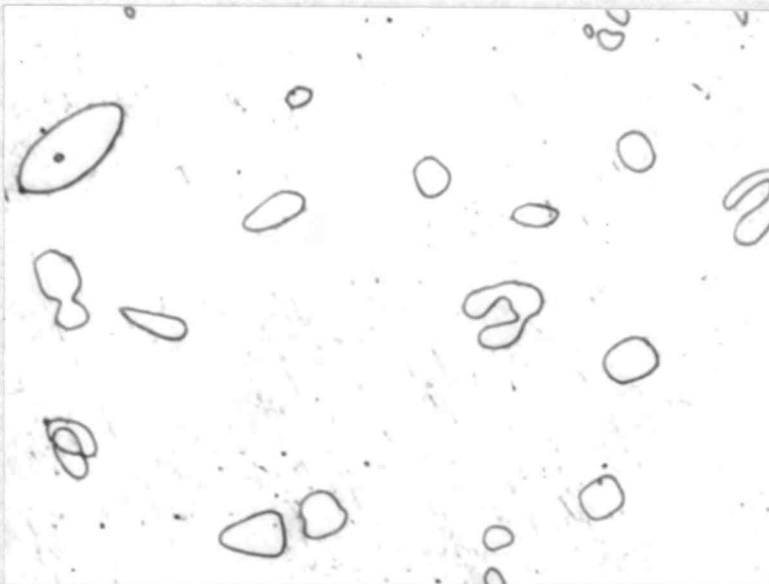


Figure 8. Specimen 8-66, 600 seconds at 600 C. The structure is proeutectoid delta(gray areas) in untransformed beta. x1000.

phase. At temperatures between 500 and 525 C, however, the beta undergoes an atomic rearrangement of its lattice from disordered body-centered-cubic to an ordered body-centered-cubic. This ordering of beta allows greater solubility of aluminum, therefore not requiring as much rejection of the aluminum from β_1 as from beta.

The proeutectoid rejection of delta in the hyper-eutectoid alloys appears to nucleate at random throughout the original beta grain as well as at the grain boundary. This may be seen in Figure 9. The proeutectoid alpha on the other hand nucleates first at the original beta grain boundaries as is shown by Figure 12. Upon further transformation, it also nucleates throughout the grain body as shown by Figure 13.

The eutectoid start in the hypereutectoid alloys is initiated primarily at the original beta grain boundaries where the first alpha was formed. Alloy No. 8 had a composition rather close to the eutectoid composition. The eutectoid structure for this alloy was a lamellar structure consisting of alternate layers of alpha and delta as illustrated in Figure 13.

Figures 12, 13, and 14 show progressive steps of transformation of β_1 to proeutectoid alpha and lamellar eutectoid at a quench temperature of 450 C.

Figures 9, 10, and 11 show the progressive steps in

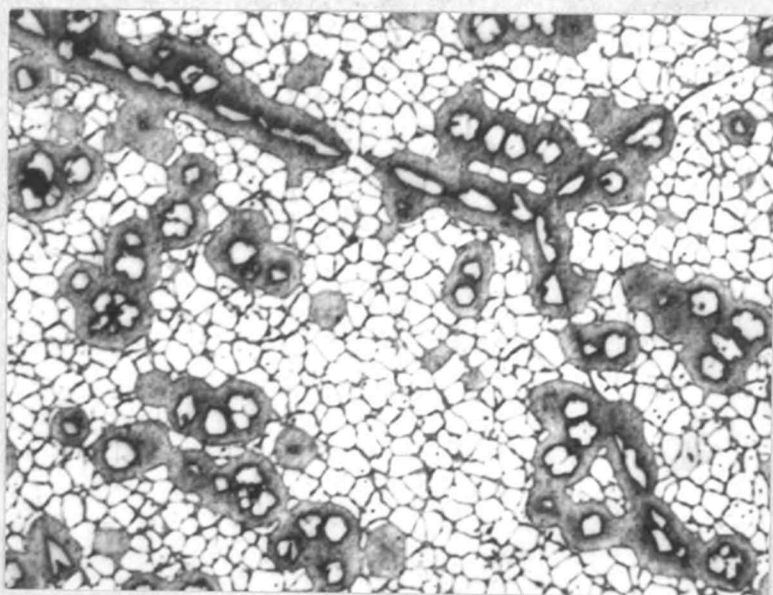


Figure 9. Specimen 8-35, 40 seconds at 500 C. Delta has precipitated at the grain boundaries and within the grains (gray circular areas). The dark structure surrounding the delta is untransformed beta and the white background area is β_1 . x1000

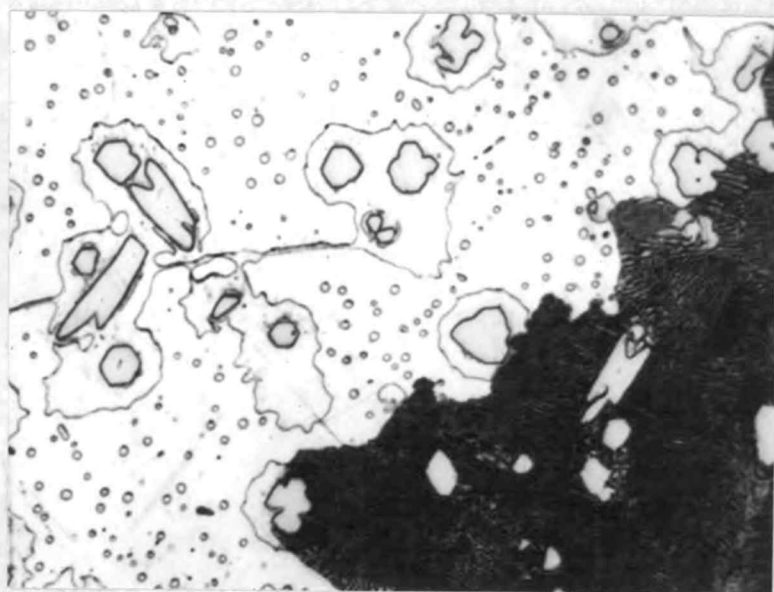


Figure 10. Specimen 8-38, 600 seconds at 500 C. The structure is proeutectoid delta, untransformed beta surrounding the delta, large white areas of β_1 , and dark lamellar eutectoid. Note that the eutectoid grows in either beta or β_1 . x1000.



Figure 11. Specimen 8-40, 1,920 seconds at 500 C.
Complete transformation from beta to the
dark lamellar eutectoid and proeutectoid
delta. x1000.

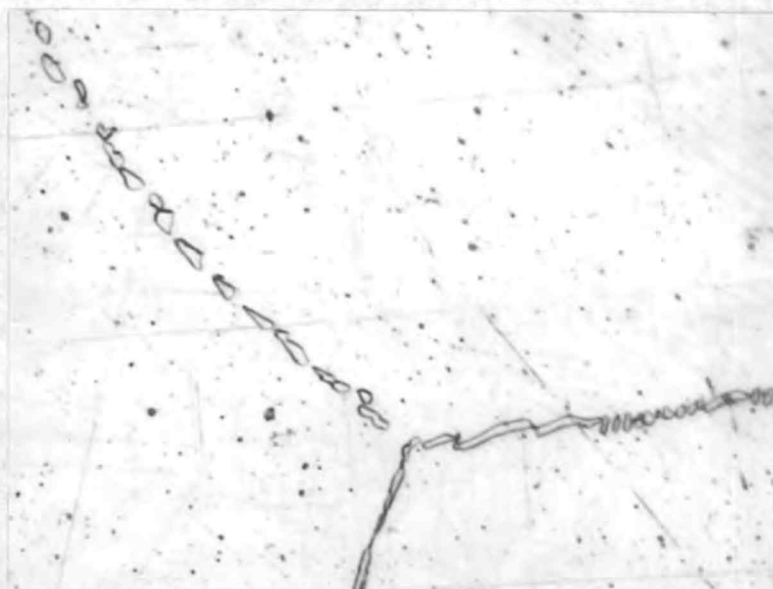


Figure 12. Specimen 8-52, 1,800 seconds at 400 C.
Alpha has precipitated at the original
beta grain boundaries. x1000.

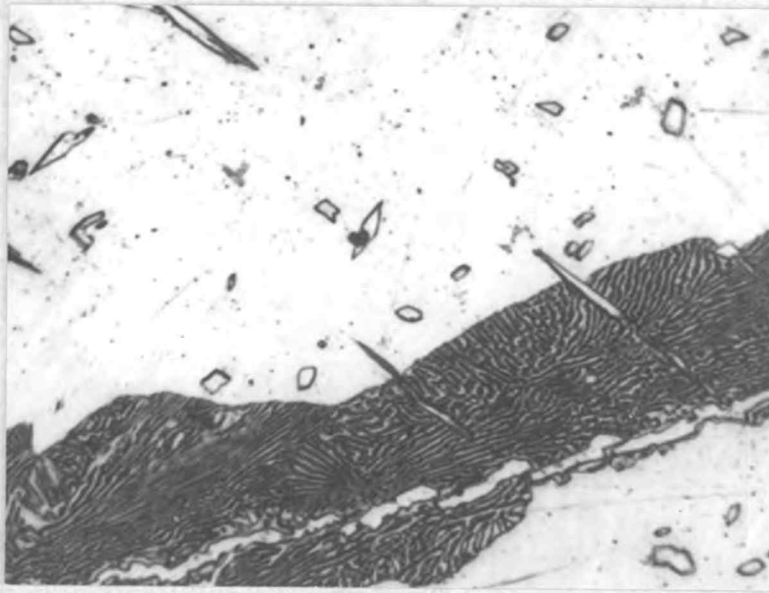


Figure 13. Specimen 8-53, 6000 seconds at 400 C. Alpha has precipitated at the original beta grain boundaries and within the original beta grains. Eutectoid has grown around the alpha from the grain boundaries. x1000.

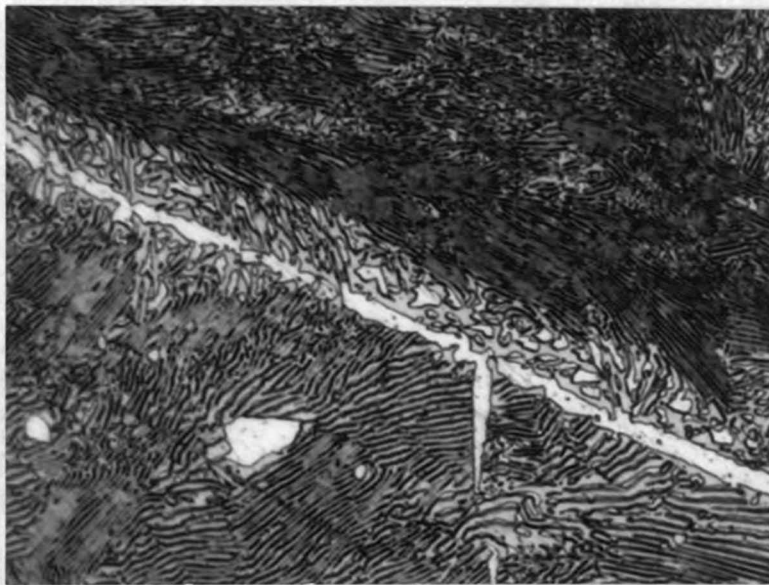


Figure 14. Specimen 8-55, 165,300 seconds at 400 C. The transformation is complete from beta₁ to the lamellar eutectoid and proeutectoid alpha. x1000.

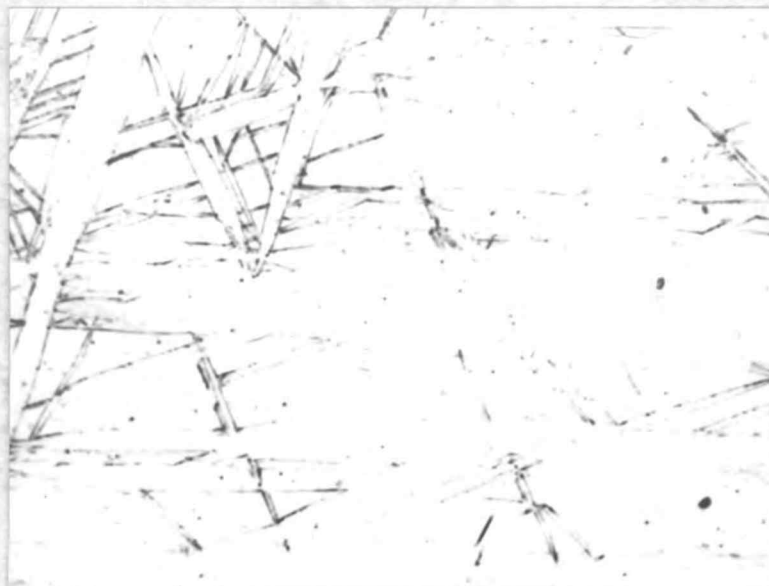


Figure 15. Specimen 8-64, 1,800 seconds at 325 C.
Martensite structure with small particles
of alpha within the martensite needles.
x1000.

the transformation of the hypereutectoid alloy quenched to 500 C and held for definite lengths of time. Note the various stages of transformation. Figure 10 shows four phases existing together. Also note that the eutectoid grows from either the beta or the β_1 phase.

Figure 15 shows the martensite structure formed by rapid quenching from beta to 325 C. The acicular or needlelike structure is also characteristic of martensite in steel.

The isothermal transformation diagram for the hypoeutectoid alloy No. 11 is shown in Figure 16. Upon cooling from the beta region the first constituent to form was the proeutectoid alpha. The composition of alloy No. 11 is further removed from the eutectoid composition than the composition of alloy No. 8.

Nucleation of proeutectoid delta was not observed at all in the metallographic structures of this alloy. The effect of the excess alpha in this alloy is to initiate the start of the eutectoid formation, also resulting in an earlier completion of the eutectoid reaction. The martensite start temperature is considerably higher than it was for the hypereutectoid alloy.

A peculiar characteristic of the aluminum bronze alloys is that after martensite is formed, it also will eventually transform to the eutectoid structure if allowed sufficient time. This is especially noticeable in the hypoeutectoid alloys where martensite temperatures are higher. On this one point, the reactions in steel and aluminum bronze do not compare.

Figure 17 shows the annealed structure of hypoeutectoid alloy No. 11. The large light areas of excess alpha are plainly seen.

Figures 19, 20, and 21 show the progressive steps in the transformation of this alloy at 500 C. The eutectoid

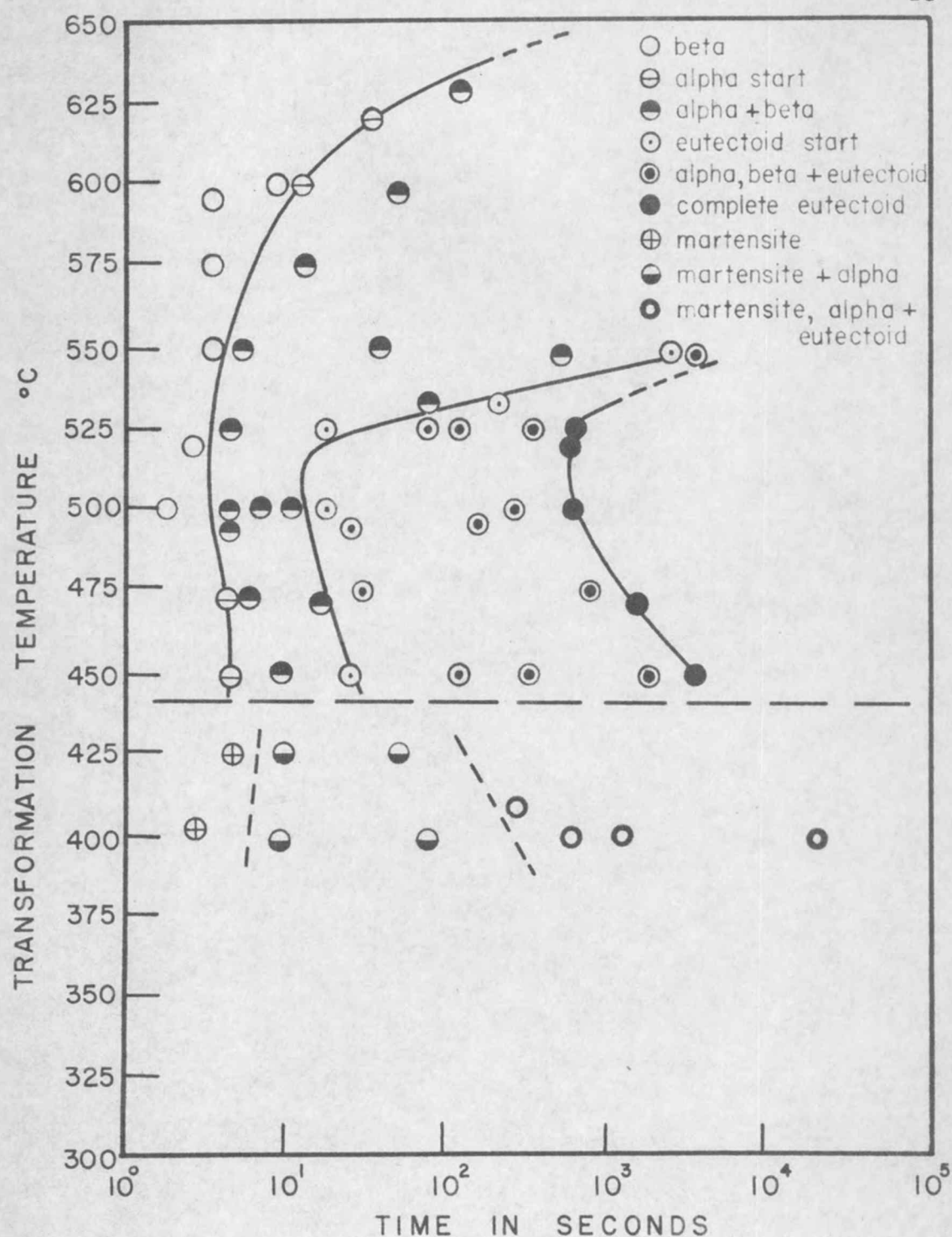


Figure 16. Isothermal transformation diagram for the hypoeutectoid alloy No. 11.

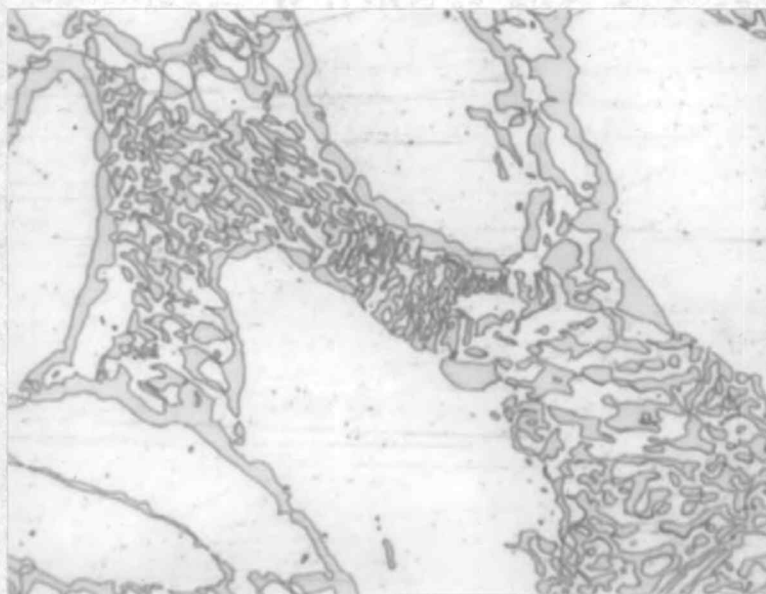


Figure 17. Specimen No. 11-0 annealed at 565 C for 12 hours. Eutectoid structure of excess alpha(light area) and coarse alpha and delta mixture. Delta(gray area). x500.

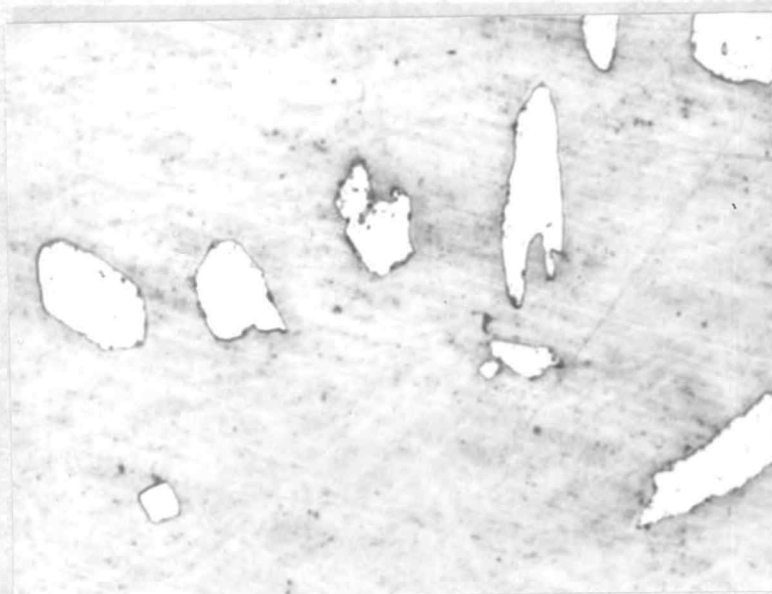


Figure 18. Specimen No. 11-89, 150 seconds at 630 C shows proeutectoid alpha(light area) in untransformed beta. x500.

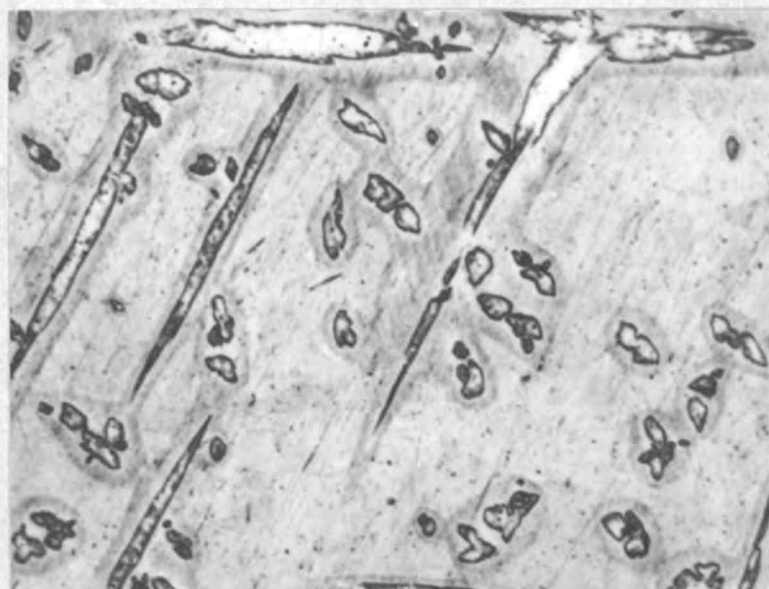


Figure 19. Specimen 11-78, 12 seconds at 500 C. Proeutectoid alpha in untransformed beta. The shaded area around the alpha indicates a concentration gradient caused by the precipitation of the alpha phase. x1000.

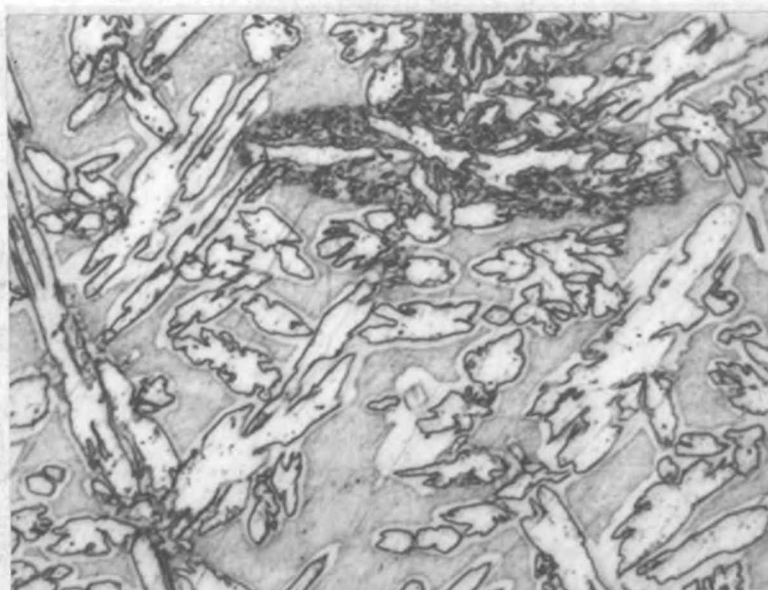


Figure 20. Specimen 11-80, 60 seconds at 500 C. Proeutectoid alpha plus eutectoid (dark area) at top of figure. The lighter areas surrounding the alpha again indicates the concentration gradient caused by the precipitation of the alpha. x1000.

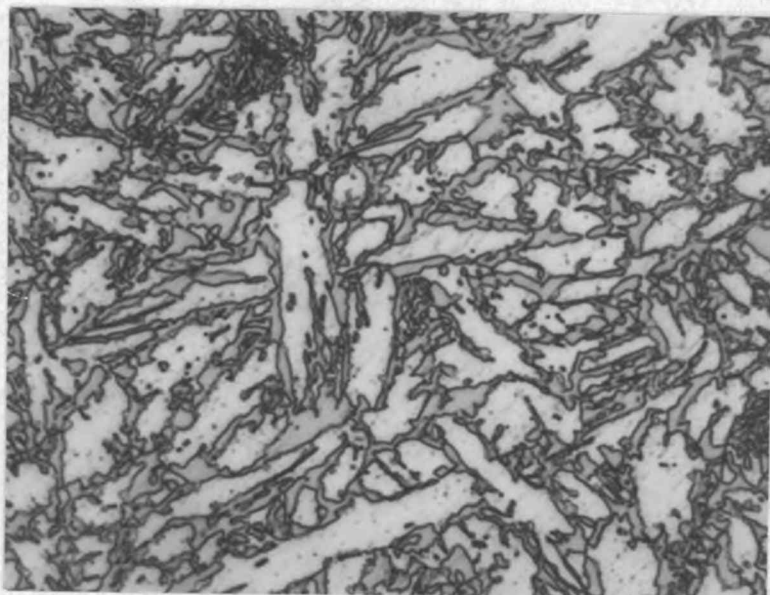


Figure 21. Specimen 11-82, 600 seconds at 500 C. Complete transformation of beta to a coarse eutectoid structure of alpha and delta. x1000.

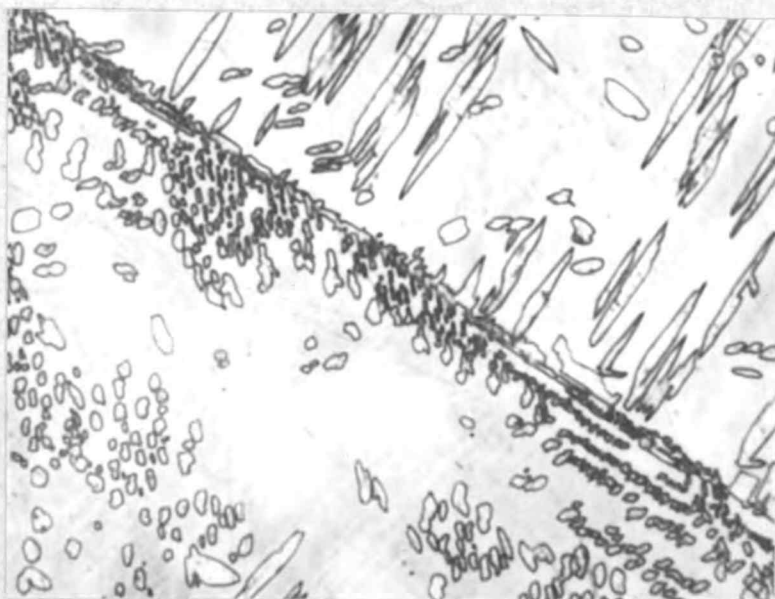


Figure 22. Specimen 11-84, 20 seconds at 525 C. Alpha has precipitated at the original beta grain boundaries and through the grains. Note the two distinct shapes of the alpha particles. x500.



Figure 23. Specimen 11-70, 40 seconds at 400 C. Martensite formation with small amounts of alpha. Note the needlelike structure of the martensite. x500.



Figure 24. Specimen 11-75, 23,400 seconds at 400 C. Martensite with a considerable amount of alpha precipitated. The eutectoid structure is visible at the grain boundary. Note the coring in alpha in the upper left-hand corner of the figure. x1000.

structure is rather coarse and has relatively large masses of alpha and delta tending to form independent structures. Figure 22 shows two distinct forms of proeutectoid alpha. Some of the alpha particles are long and slender and others are circular in appearance.

Figures 23 and 24 illustrate two progressive steps in the transformation of martensite to the eutectoid. Figure 23 is primarily martensite with small particles of alpha having been rejected.

Figure 24 shows the martensite with considerable amounts of alpha already rejected with small amounts of eutectoid present.

Martensite consists of a supersaturated solid-solution aluminum in copper. As the alpha is rejected from the martensite, it also is in a supersaturated condition. As the martensite continues to transform the supersaturated alpha has a tendency to reject some of its aluminum, therefore resulting in high concentration gradients in its structure. The concentration gradients cause coring in the alpha. This coring may be observed in Figure 24 in the large alpha particles in the upper left-hand and lower right-hand corners of the photomicrograph. The etching characteristics of the cored alpha particles is conclusive evidence of the concentration gradients present.

The transformation structures obtained from the hypoeutectoid alloy were quite different from the structures found in the hypereutectoid alloy. Specimens of the hypoeutectoid alloy did not indicate a definite change from beta to β_1 as observed in the hypereutectoid alloy. The differences in the structures may be seen by a comparison of the photomicrographs of both alloys quenched to 500 C. Compare Figures 9, 10, and 11 with Figures 19, 20, and 21.

The hypoeutectoid alloy was rich in alpha and precipitated large amounts of this constituent throughout the original beta grains. The rate of alpha nucleation and the number of alpha particles growing from the nuclei accelerated the formation of the eutectoid. The greater number of alpha particles in the hypoeutectoid alloy relatively more surface area from which the eutectoid could nucleate and grow. This accounted for the shorter time necessary for the start of the eutectoid formation in the hypoeutectoid alloy as compared to the time required for the hypereutectoid alloy.

A comparison of the isothermal curves for alloys No. 8 and No. 11 is shown in Figure 25. Note specifically the difference in time necessary for the start of the eutectoid formation for the two alloys. Also the temperature of the start of martensite formation for the two alloys should be noted.

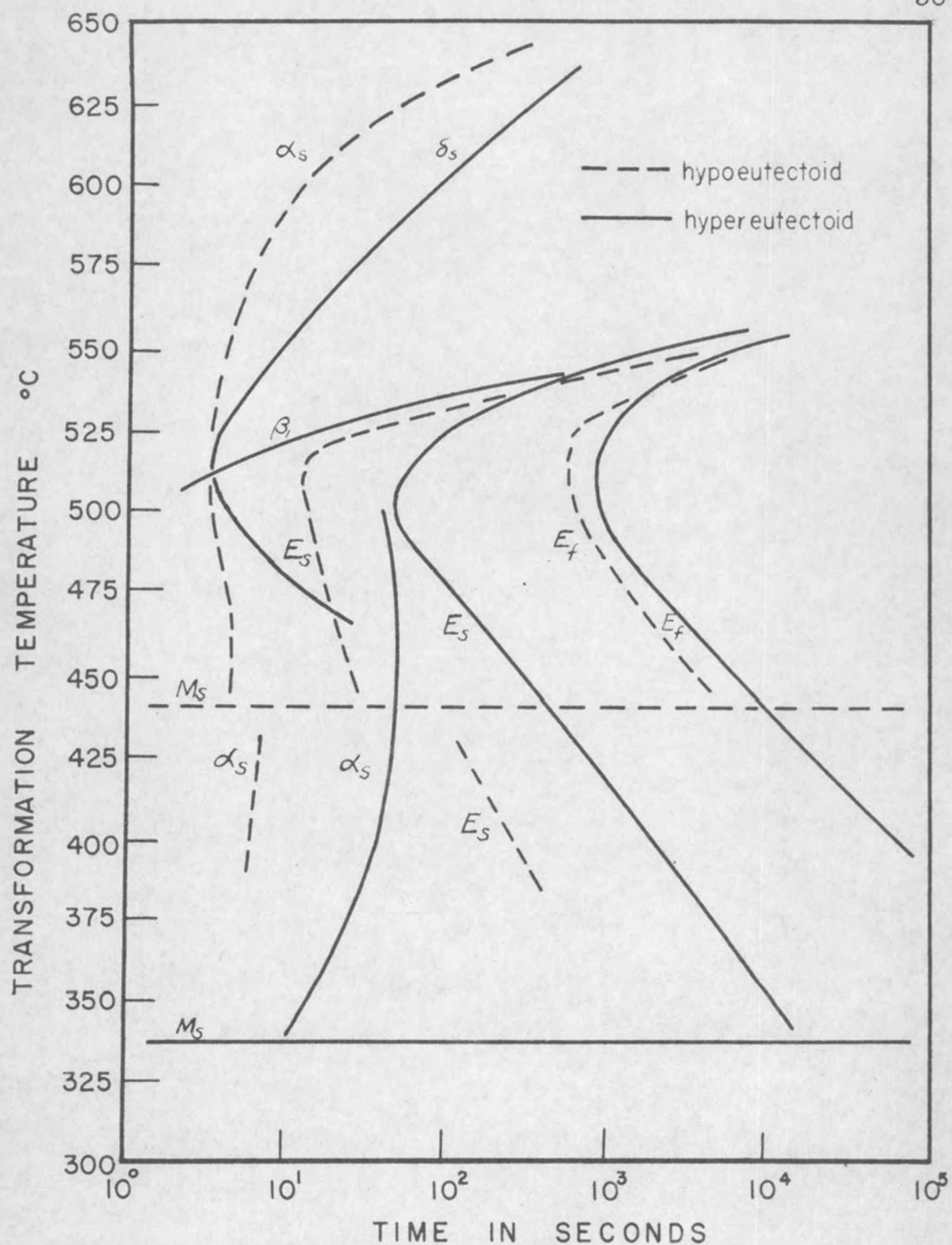


Figure 25. Combined isothermal transformation diagrams for alloys No. 8 and No. 11

Perhaps the greatest difference that was observed between the two alloys was the relative size of the transformation products. The hypereutectoid alloy formed a very fine lamellar eutectoid structure plus the excess alpha or delta constituents. The excess delta was present in the specimens transformed above 475 C and the excess alpha was present in the specimens transformed below the temperature of 475 C. The hypoeutectoid alloy formed a rather coarse eutectoid structure plus the large particles of excess alpha. Compare Figures 11 and 14 with Figure 21.

Hardness measurements were taken of specimens from both the hypo- and hypereutectoid alloys. The hardness readings were taken of specimens quenched to four representative temperatures. Each specimen contained a different amount of transformation products.

The hypoeutectoid alloy indicated a general decrease in hardness with an increase in transformation. The hypereutectoid alloy indicated just the opposite. The hardness increased with an increase in transformation. The trend of hardness versus transformation time at the four representative temperatures is shown in Figures 26 and 27.

The hardness values of the hypereutectoid specimens quenched to 525 C for short periods of time were considerably higher than the hardness values of specimens quenched to 500 C, 450 C, and 400 C. No attempt was made to deter-

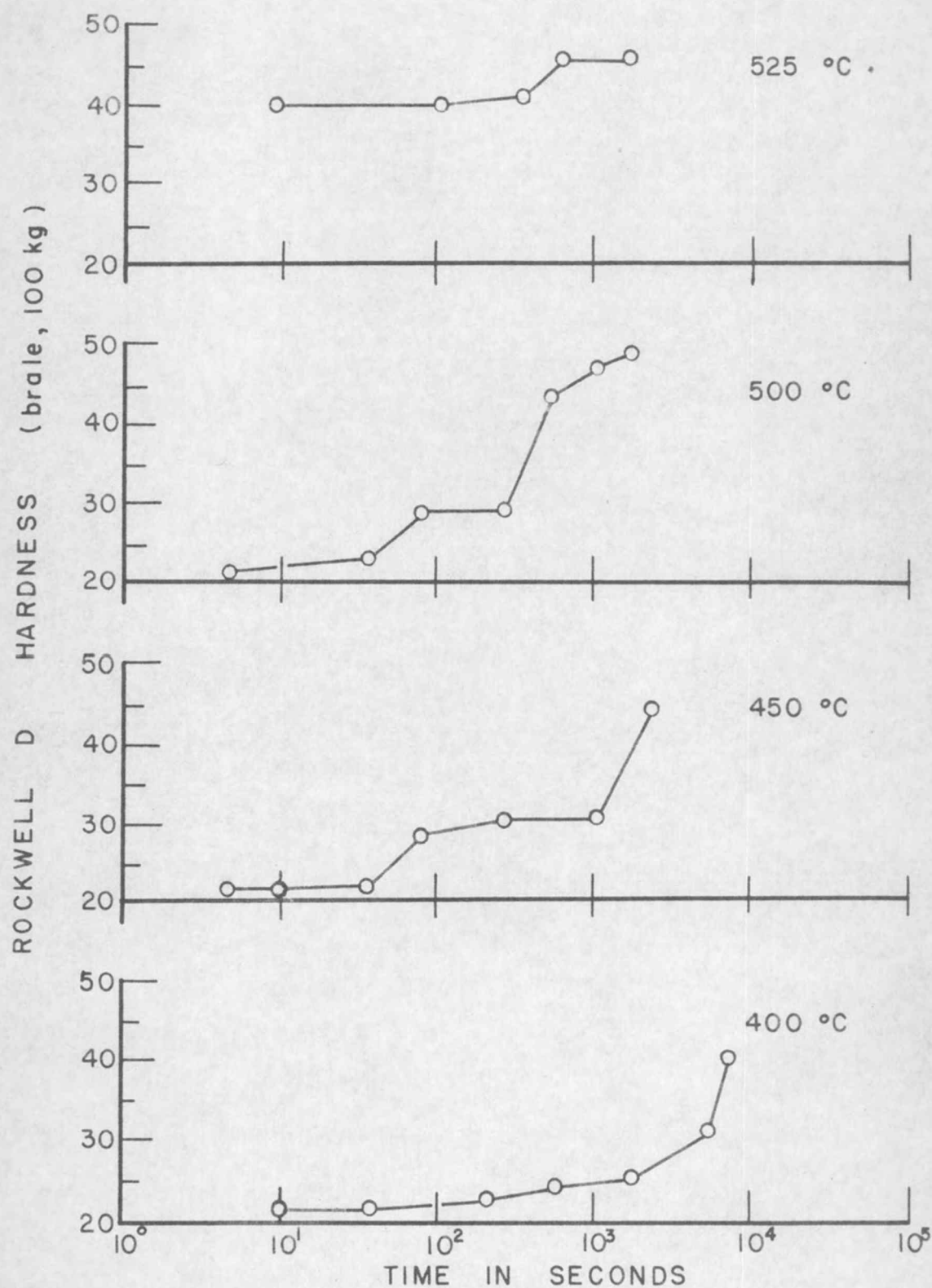


Figure 26. Hardness vs. transformation time - alloy No. 8

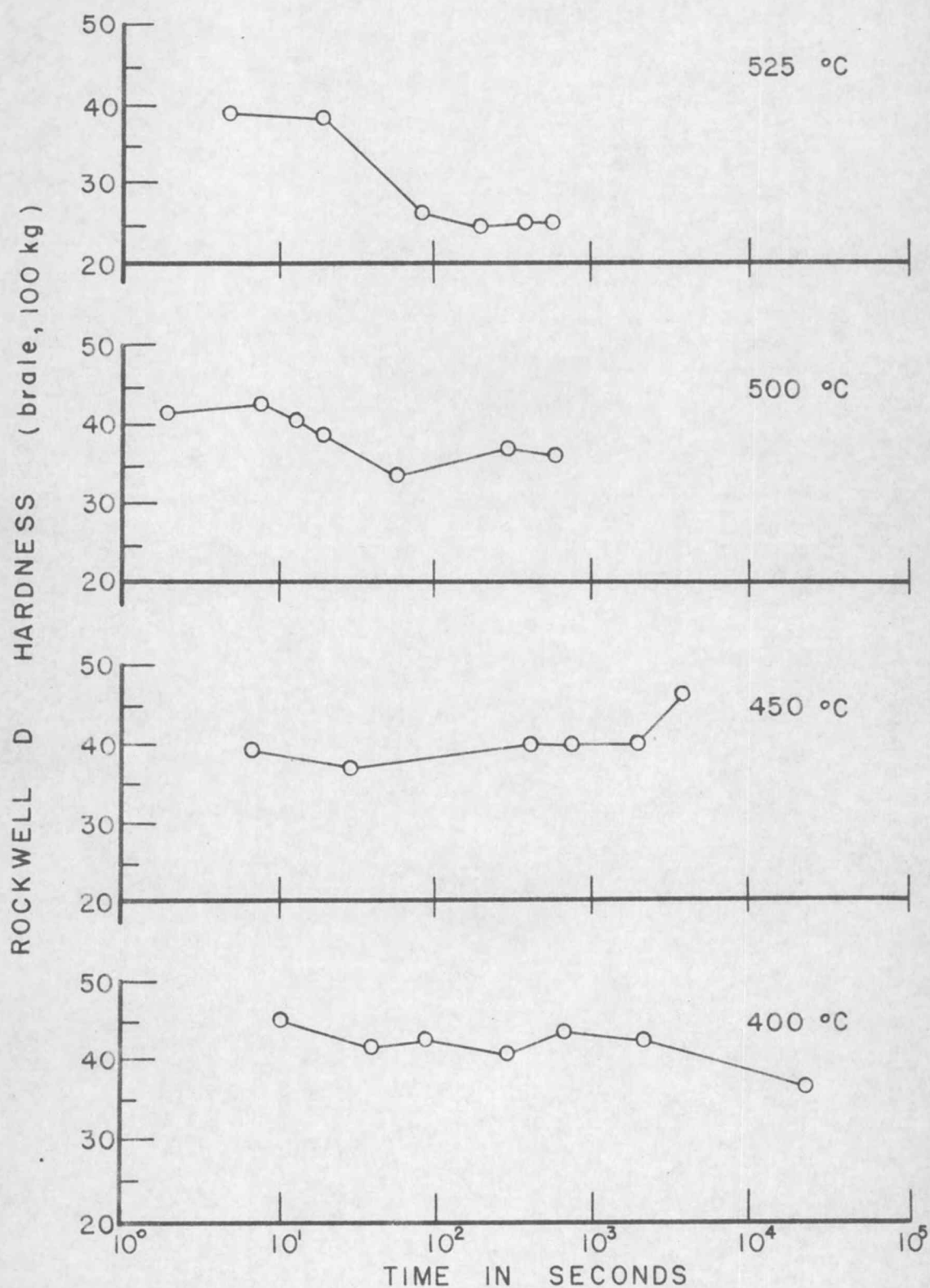


Figure 27. Hardness vs. transformation time - alloy No. 11

mine the reason for this although it was assumed to be due the transitional change from beta to β_1 .

Specimens quenched to 525 C gave higher hardness values and consisted of a quenched beta structure while specimens quenched to 500 C, 450 C, and 400 C had low hardness values and consisted of a quenched β_1 structure. The hypoeutectoid hardness values seemed to support this supposition. They indicated high hardness values for all specimens quenched to the four representative temperatures for short periods of time and did not indicate in their structure the transitional change from beta to β_1 .

The improvement of hardness with increasing transformation in the hypereutectoid alloy was attributed to the growth of the fine lamellar eutectoid. The decrease in hardness of the hypoeutectoid alloy was attributed to the formation of the coarse eutectoid.

These observations seem to be in good agreement with the general theory that metals having a fine metallographic structure exhibit higher hardness and greater strength than the same metals having a coarse metallographic structure.

CHAPTER V

CONCLUSIONS

From the results presented in the previous chapter, several conclusions may be made.

Alloys of aluminum bronze, differing only by a small percentage of aluminum, exhibit certain outstanding differences in their response to an isothermal heat treatment. The major differences in the two alloys observed in this respect may be listed as follows:

1. The martensite start temperature was lower in the hypereutectoid alloy than in the hypoeutectoid alloy.
2. A hypoeutectoid alloy containing appreciable amounts of excess alpha does not form a true lamellar eutectoid structure.
3. The transitional change from beta to β_1 takes place at a slightly lower temperature in the hypereutectoid alloy as compared to a eutectoid alloy.
4. Alloys at or near the eutectoid composition precipitate out delta as a proeutectoid constituent at the higher temperatures. But at the lower temperatures, alpha precipitates out as the proeutectoid constituent.

5. Alpha is nucleated at the original beta grain boundaries and later is nucleated within the grains.
6. Delta has an equal tendency to nucleate first within the grains and at the grain boundaries.
7. The time necessary for the eutectoid reaction to start is shorter for the hypoeutectoid alloy containing excess alpha than for the hypereutectoid alloy.
8. The hypereutectoid alloy increased in hardness with an increase in transformation, whereas the hypoeutectoid alloy decreased in hardness with an increase in transformation.

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ADVANCE BOND



APPENDICES

APPENDIX A

ALLOYING DATA

Alloy No.	Weight of Copper (grams)	Weight of Aluminum (grams)	Percentage Aluminum (as cast)	Percentage Aluminum (by analysis)
1	180	24.5	12.0	13.10
4	180	20.0	10.0	12.45
5(a)	180	20.0	10.0	9.83
6	180	24.5	12.0	12.80
7	180	24.5	12.0	14.60
8	180	24.5	12.0	12.30
9	180	21.0	10.4	10.10
10	180	22.0	10.9	10.52
11	180	22.5	11.1	10.80
12	180	20.5	10.2	-----
13	180	21.5	10.6	-----
14	180	23.0	10.7	-----
15	180	24.0	11.9	-----

HEAT TREATING AND HARDNESS DATA FOR
THE HYPEREUTECTOID ALLOY NO. 8

Specimen No.	Quenching Temperature C	Quenching Time Seconds	Rockwell D Hardness (brale, 100kg)
65	630	600	
30	620	330	
28	600	20	
29	600	600	
66	600	600	
6	575	30	
31	575	60	
3	550	2700	
4	540	3600	
5	535	990	
2	530	480	
1	530	60	
9	525	90	
59	525	10	40
60	525	120	40
61	525	420	41
62	525	780	47
63	525	1800	47
10	520	10	
11	520	2	
26	510	60	
25	500	40	
32	500	5	21
35	500	40	23
36	500	90	29
37	500	300	29
38	500	600	44
39	500	1020	47
40	500	1920	48
56	500	2	
57	500	10	
58	500	30	
27	490	60	
21	475	50	
13	475	120	
12	470	15	
14	465	300	
15	450	400	
20	450	90	
41	450	5	21
42	450	10	21
43	450	40	22
44	450	90	29

HEAT TREATING AND HARDNESS DATA FOR
ALLOY NO. 8 (continued)

60

Specimen No.	Quenching Temperature C	Quenching Time Seconds	Rockwell D Hardness(brale,100kg)
45	450	300	31
46	450	1080	31
47	450	2700	45
18	425	3000	
19	425	600	
23	425	180	
22	400	90	
48	400	10	21
49	400	40	21
50	400	240	22
51	400	600	24
52	400	1800	26
53	400	6000	31
54	400	18000	40
55	400	165300	49
24	390	210	
67	350	10	
68	350	30	
69	350	300	
70	350	600	
71	350	36000	
64	325	1800	

HEAT TREATING AND HARDNESS DATA FOR
THE HYPOEUTECTOID ALLOY NO. 11

61

Specimen No.	Quenching Temperature C	Quenching Time Seconds	Rockwell D Hardness(brale,100kg)
11	675	10	
12	675	20	
13	675	30	
14	650	30	
15	650	60	
16	650	300	
17	650	600	
18	650	1680	
19	650	1200	
89	630	150	
23	620	40	
22	600	10	
21	600	15	
20	590	60	
50	575	15	
49	570	3	
31	550	4	
32	550	/6	
33	550	10	
34	550	30	
35	550	120	
37	550	600	
38	550	3600	
51	550	45	
52	550	90	
53	550	2700	
4	535	60	
2	530	240	
1	525	120	
55	525	120	
83	525	5	39
84	525	20	38
85	525	90	27
86	525	200	25
87	525	400	26
88	525	660	26
56	520	600	
57	520	3	
39	500	5	
41	500	120	
40	500	600	
43	500	1800	
45	500	60	
66	500	20	

HEAT TREATING AND HARDNESS DATA FOR
ALLOY NO. 11 (continued)

62

Specimen No.	Quenching Temperature C	Quenching Time Seconds	Rockwell D Hardness (brale, 100kg)
76	500	2	42
77	500	8	43
78	500	12	40
79	500	20	38
80	500	60	34
81	500	300	37
82	500	600	36
40	490	60	
46	490	180	
47	490	30	
48	490	5	
61	475	35	
62	475	900	
60	470	20	
44	470	5	
58	470	6	
59	470	1200	
24	450	10	
25	450	5	
90	450	7	39
91	450	30	37
92	450	420	40
93	450	840	40
94	450	2000	40
95	450	4000	46
96	450	120	
63	425	5	
64	425	10	
65	425	60	
29	410	300	
26	405	3	
30	405	1200	
69	400	10	45
70	400	40	42
71	400	90	43
72	400	300	41
73	400	720	44
74	400	2100	43
75	400	23400	37
28	400	600	