A TIME - TEMPERATURE - TRANSFORMATION STUDY OF THE β EUTECTOID OF THE COPPER - ANTIMONY SYSTEM

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A TIME-TEMPERATURE-TRANSFORMATION STUDY OF THE β EUTECTOID OF THE COPPER-ANTIMONY SYSTEM

SUMMARY

The primary objective of this investigation was to obtain time-temperature-transformation data for the β eutectoid (36.5% Sb and 63.5% Cu) of the copper-antimony system.

A 200 gram sample was prepared in a closed carbon crucible, well mixed and cast in a mold to give a casting 1/16" X 3" X 6". Samples 3/16" X 3/4" were cut from the casting with a silicon carbide cut-off wheel mounted on a high speed rotary hand tool. The samples were inserted into partially flattened steel tubes, 1/4" X 1¼", and the ends of the tubing were crimped to form air and liquid tight seals. A β structure was obtained by first heating the samples to 1450°F for ten to fifteen minutes and the homogenizing them at 1100°F for about an hour. Following this homogenization period the samples were water quenched directly to room temperature.

The heat treatment temperatures employed in this investigation were 500°F, 600°F, 700°F, and 750°F, and the lengths of the treatments varied from periods of 5 seconds to 2 weeks. For heating periods of 2 minutes or more, the samples were placed in laboratory tube furnaces. However, for heat treatments of shorter duration a constantly-stirred, molten lead bath was employed. All samples were quenched directly to room temperature following the heating period.

The samples were then removed from the capsules, mounted in bakelite, and polished by standard metallographic techniques, except that the metallographic papers were lubricated with varsol and very light pressures and slow strokes were used. Etching was accomplished with a ferric chloride-hydrochloric acid-ethyl alcohol etching reagent.

The results from a study of microstructures of the samples which had been first quenched to room temperature and then reheated to various temperatures for transformation are as follows.

TRANSFORMATION TEMPERATURE	BEGINNING OF TRANSFORMATION	TRANSFORMATION COMPLETED
500°F	Less than 5 min.	1-3 hours
600°F	Less than 2 min.	12-15 minutes
700°F	Less than 5 sec.	45-60 seconds
750°F	Less than 15 sec.	1½-2 minutes

The transformation of the β phase of approximately eutectoid composition of the copper-antimony system was observed to proceed by the following steps.

(1) The nucleation of primary δ in the grain boundaries followed by

(2) The nucleation and growth of the $\delta + \epsilon$ eutectoid product in the grain boundaries. The growth of the local primary δ stops when the $\delta + \epsilon$ product is first formed.

(3) The precipitation of a fine pattern believed to be of a δ composition within the grains.

(4) The $\delta + \epsilon$ product coarsens to δ in lamellar form in a matrix ϵ. The lamellar δ grows until it breaks into a rodlike form and starts spheroidization.

(5) It is possible that the β structure transforms to tempered β, or β', upon being quenched to room temperature. This reaction has been reported by other investigations as $\beta \longrightarrow \beta' \longrightarrow \delta + \epsilon$. No concrete evidence was secured to either substaniate or disprove this point.

(6) No phase change to a structure comparable to martensite in steels was observed in quenching a sample of β in liquid nitrogen. The microhardness of the β sample quenched in liquid nitrogen was the same as the microhardness of a β sample quenched only to room temperature. (Rockwell 47C)

At transformation temperatures of 500°F, 600°, 700°F and 750°F there were initially two transformation reactions going on simultaneously. One of these nucleated and grew only from the grain boundaries, while the other nucleated and grew at random in the grains. For temperatures of 500°F and 600°F, about midway to complete transformation the reaction taking place in the grains had produced large enough quantities of precipitation to completely halt the reaction nucleated in the grain boundaries. Hence at 500°F and 600°F, the reaction in the grains was responsible for determining the length of time necessary for complete transformation.

However, at 700°F and 750°F the reaction in the grains stopped very soon after it had started growing . At these temperatures the transformation was finally completed by the reaction which had originally nucleated in and grown from the grain boundaries.

The following recommendations are made concerning further investigation which may be made on the β eutectoid of the copper-antimony system:

(1) The portion of the phase diagram containing the β eutectoid be thoroughly checked to obtain the exact composition of that point.

(2) A time-temperature-transformation study be made of the β eutectoid employing isothermal methods of transformation.

(3) The development of an electrolytic polishing mechanism which would enable more representative samples to be prepared.

(4) A determination of the accuracy of the reports of earlier investigators concerning the existance of a tempered β phase, commonly known as β'.

(5) The microhardness of the primary phases and changes of microhardness with the decomposition reaction.

(6) Analytical determinations be made of the exact composition of all samples of β eutectoid cast for study of the alloy.

A TIME-TEMPERATURE-TRANSFORMATION STUDY OF THE β EUTECTOID OF THE COPPER-ANTIMONY SYSTEM

INTRODUCTION

The present investigation of the β eutectoid of the copper-antimony system is the result of observations made during an undergraduate laboratory problem. Samples of β composition were found to decompose on cooling by the nucleation and growth of a lamellar structure similiar to the growth of pearlite in austenite.

A literature survey revealed the only major work done on the β eutectoid phase was accomplished by A. Osawa and N. Shibata[1] in an investigation of the structural changes due to quenching and tempering. Their investigation employed X-ray and dilatometric procedures and was conducted to determine the crystal classes, lattice constants, number of atoms per unit cell, and expansions and contractions resulting from the decomposition of β. No attempt was made to determine the rates of transformation as a function of time and temperature, nor to study the exact process by which the transformation took place.

Due to this lack of information regarding the β phase decompositions, M.L. Picklesimer[2] attempted an investigation by use of isothermal transformation procedures. While his results substaniated in part some of the previous work done by Osawa and Shibata, he was hindered considerably by segregation in his cast alloy. No accurate determination of the rates of transformation could be made because every time-temperature-transformation run contained at least one sample whose composition was very much out of line.

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1. Science Reports, Vol. 28, 1939-40, Tohoku Imp. Univ.

2. A Partial Investigation of The Isothermal Transformation of The Eutectoid of The Copper-Antimony System, Picklesimer, M.L., 1949.

Therefore, the first step of the present investigation was to devise a technique by which pure copper and antimony could be melted in the correct amounts and produce an alloy completely free of segregation. Securing a homogeneous alloy of the β eutectoid would enable a study of the nucleation and growth of the decomposition products to be conducted with the assurance that all observed reactions were being produced by samples of uniform composition.

The technique also had to be able to prevent the rapid oxidation of antimony which ordinarily takes place at temperatures well below the melting point of copper. As can be seen from the phase diagram, Figure 1, an increase of only 0,05% copper over the eutectoid composition will cause considerable variation in the quantity and nature of the decomposition products.

After the development of a technique which would produce cast alloys of a uniform composition, the method of obtaining time-temperature-transformation data had to be considered. Preliminary investigation indicated that a β structure containing no decomposition products could be obtained by quenching from 1100°F directly to room temperature. This fact indicated definitely that a time-temperature-transformation curve of some type does exist for the eutectoid. Otherwise, at least small portions of decomposition would have been observed following a direct quench.

In comparing this system to that of the low-carbon steels, this quenched structure would correspond to an austentic structure which has not been cooled down to the M_s line of a transformation diagram. Obviously then, if a structure exists in the copper-antimony system which could compare to martensite in steels, its formation temperature is below that of room temperature.

From this type of analogy it was reasoned that a quenched β sample was comparable to austenite, and that transformation could be obtained by merely

reheating quenched samples to desired constant temperatures for various lengths of time. The constant temperatures at which the β should be treated were also suggested by comparision with steels. The minimum time of transformation for most common low-carbon steels is from 100°F to 200°F degrees below the critical point. Following this reasoning, the optimum heat-treatment temperatures for the β eutectoid would probably fall within the same range, The various temperatures to be used for the transformation were originally chosen on this basis.

However, the heat treatment procedure outlined above is questionable on several accounts. One of these is the danger of intersecting the transformation curve while heating up to the desired constant point. Another is the chance that water quenching before reheating to the transformation temperature may alter somewhat the time required for the reactions to take place. The former mishap may be considered eliminated if a sample which has been heated to the desired point and held a short time fails to show any evidence of decomposition. The latter possibility, however, is not this easily checked, and more extended work will have to be accomplished regarding this point after the general shape of the transformation curve has been found.

This above outlined procedure for heat treatment contains the theory employed in devising a satisfactory method of studying the decomposition of the β eutectoid. Naturally a great deal of trial and error work was necessary to determine the exact times required to yeild the desired results.

EQUIPMENT AND MATERIALS

The equipment used was

(1) An Ajax electric induction furance, serial number 384035, 220 volt, for melt preparation.

(2) Standard laboratory furnaces for homogenization.

(3) Standard laboratory equipment for mounting and polishing samples.

(4) A Brown Electric Pyrometer, serial number 213374, manufactured by the Brown Instrument Co., Phila., Pa. The controller was used for the lead bath and was operated with a chromel-alumel thermocouple.

(5) A molten lead bath constructed by winding a coil of 30 feet of 18 gage, 0.4 ohms per foot, chromel A resistance wire on a 5" inside diameter, 5" high ceramic core mounted in a 12" X 12" X10" box constructed of $\frac{1}{4}$" transite and insulating with Silocell insulating brick and ground asbetos.

(6) A Bausche and Lombe Research Metalloscope.

(7) Standard ageing furnaces for heat treating.

(8) A carbon crucible, 3" O.D., 2" I.D., and 7" high, equipped with a lid which contained threads to enable a screw-type fastening.

(9) A carbon mold, 7" X 4" X 2" which contained a casting section, 1/16" X 3" X 6".

(10) Standard laboratory aging furnaces.

The materials used were

(1) Electrolytic tough pitch copper.

(2) Antimony as pure as available commericially.

(3) Steel capsules constructed by crimping the ends of $1\frac{1}{2}$" lengths of $\frac{1}{4}$" steel tubing to form a gas and liquid tight seal.

(4) Mounting wires for suspension and handling of the capsuled samples.

(5) A ferric chloride stock solution made by disolving 25 grams of ferric chloride in 20 cc of concentrated hydrochloric acid and 100cc of ethyl alcohol. The etching solution was made up fresh each time by diluting the stock solution 1 part to 10 parts ethyl alcohol.

(6) A solution of varsal containing a small amount of paraffin for lubrication on the metallographic polishing papers.

(7) Metallographic polishing papers of grits 0, 2/0, 3/0 and 4/0.

PROCEDURE

Previous investigation illustrated the need for the development of a technique by which pure copper and antimony could be melted in the correct amounts and produce an alloy completely free of segregation. The technique also had to be able to prevent the rapid oxidiation of antimony which ordinarily takes place at temperatures well below the melting point of copper. The following procedure meets the above outlined requirements.

A 200 gm. melt of the eutectoid composition, 36.5% Sb and 63.5% Cu, was prepared in an induction furnace. The carbon crucible employed in the operation was equipped with a screw-fastening lid and had been fashioned from a stick of 3" carbon electrode. The lid was squared on top to allow it to be screwed on and off with a pair of long-handled tongs. The crucible was equipped with a vent hole, 1/64" in diameter, in its side midway between the top and bottom edges.

The copper portion of the alloy was placed in the crucible and the lid left off while the metal melted, then the antimony was added in its solid state, and the lid screwed on the crucible as rapidly as possible. The crucible was allowed to remain at temperature in the induction furnace about five minutes after the antimony had been added. It was then removed and allowed to cool.

The entire apparatus was moved to a standard laboratory furnace and heated again to about 1600°F. When it was evident that the metal had become completely melted, the crucible was held by a long-handled pair of tongs and was inverted continuously for several minutes. Care was taken to keep the side of the crucible containing the vent hole always on the top to prevent molten metal from spilling out through the hole. After several minutes of complete mixing, the alloy was allowed to cool, and the

entire process was repeated. The entire cycle in the laboratory furnace was performed a total of four times.

Final casting was made in a mold fashioned from a carbon brick which had been split in half. The castings were 1/16" X 3" X 6" and were allowed to cool to room temperature in the mold.

Samples 3/16" wide and 3/4" long were cut from the castings using a silicon carbide cut-off wheel on a small, high-speed rotary hand tool. They were then inserted into flattened 1/4" steel tubes $1\frac{1}{4}$" long, and the ends of the tubing were crimped to form an air and liquid tight seal.

The capsuled samples were heated to 1450°F (the melting point is 1380°F) for ten to fifteen minutes, removed from the furnace, and cooled in air with the capsule held vertically until the molten sample had just solidified. They were then inserted into a furnace at 1100°F and were homogenized from one to two hours. After homogenization the samples were water quenched directly to room temperature.

The temperatures to which the quenched samples were reheated to transform were 500°F, 600°F, 700°F, and 750°F, and the lengths of time varied from five seconds to two weeks. For heat treatment periods of more than fifteen minutes in duration, the capsuled samples were fastened to chromel A wire and suspended in standard tube furnaces. However, for the shorter periods up to fifteen minutes, a constantly stirred molten lead bath was employed. Samples which were to be transformed for periods under two minutes were removed from the capsule and were introduced into the bath uncovered. This procedure proved acceptable since the molten lead did not attack the samples during such short lengths of time. All samples were again water quenched following their transformation heat treatment period.

The contents of the capsules were removed by filing each side through and cutting one end off. This enabled the samples to be removed whole and undamaged. It was then broken into two peices and mounted in bakelite for cross-section examination.

The polishing of the samples followed standard procedures except that varsol lubricated metallographic papers, very light pressures and slow strokes were used. Failure to employ these precautions resulted in a fine pattern of cracks covering the entire surface of the sample.

The polished samples were etched for times varying from one second to ten seconds, depending on th transformation of the sample, with the ferric chloride etching solution given in "Equipment and Materials". The etched surfaces were examined with the Research Metalloscope, and structures showing the processes of the transformation were photographed.

DATA

The experimental data recorded during this investigation consisted of photographs of the microstructures of the prepared samples. Complete coverage of the transformations at the different temperatures, including both pictures and short discussions, is presented on the following pages.

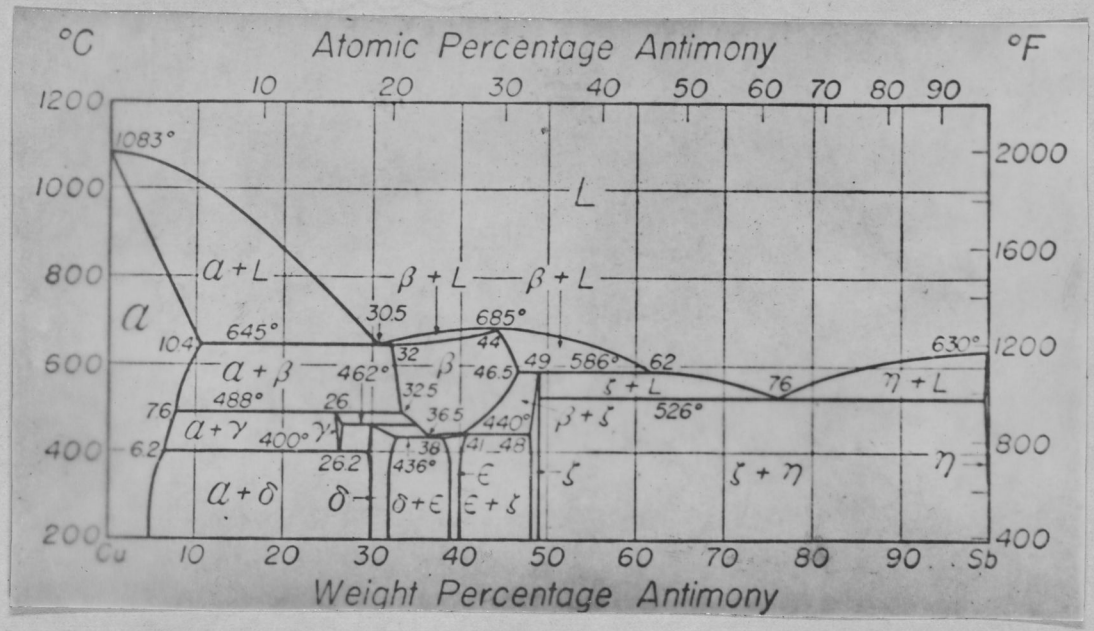


Fig. 1. EQUILIBRIUM PHASE DIAGRAM OF THE COPPER-ANTIMONY SYSTEM.

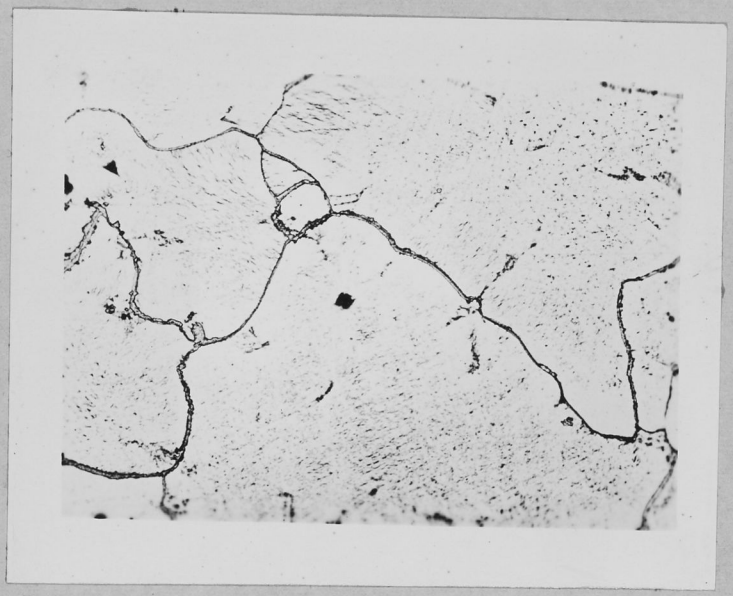


Fig. 2. Sample No. E5-1 200X
Cast, Homogenized at 1100°F 1 hr., water quenched, transformed at 500°F 5 min., water quenched.



Fif. 3 Sample No. E5-3 200X
Cast, homogenized at 1100°F 1 hr., water quenched, transformed at 500°F $\frac{1}{2}$ hr., water quenched.

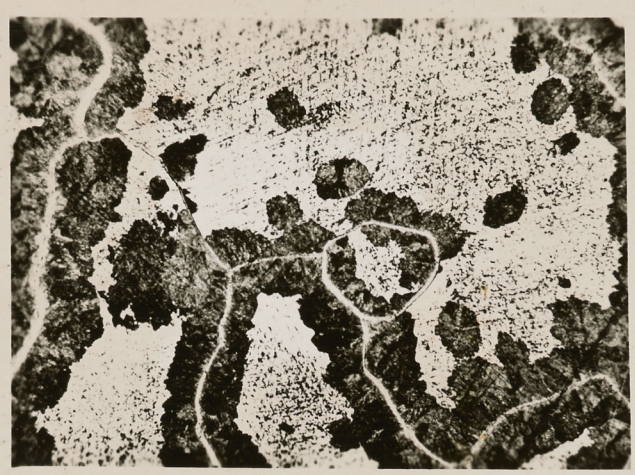


Fig.4 Sample No E5-4 200X
Cast, homogenized at 1100°F 1 hr., water quenched, transformed at 500°F 1 hr., water quenched.



Fig.5 Sample No E5-5 200X
Cast, homogenized at 1100°F 1 hr., water quenched, transformed at 500°F 3 hrs., water quenched.

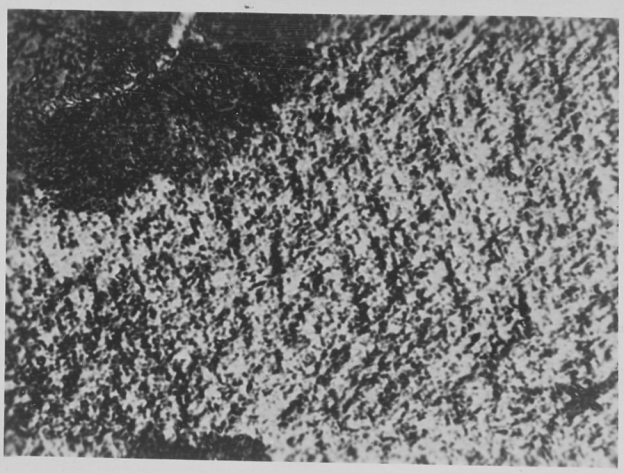


Fig.6 Sample No E5-4 800X
Cast, homogenized at 1100°F 1 hr., water quenched, transformed at 500°F 1 hr., water quenched.

Figure 2 thru 5 show the process of the transformation of the β eutectoid after quenching to room temperature and reheating to 500°F. It will be noted that the five minute sample showed the very beginning of the reaction. A light etching structure of α has been precipitated in the grain boundaries and the $\alpha + \epsilon$ product (black etching) is being nucleated at the edges of the α. The light etching structure of the whole grains are untransformed β. These series of photographs indicate that the transformation reaction at 500°F is not completed until the β structure has been heat treated from between one to three hours.

Of special interest is the fine precipitation of a constituent which appears throughout the grains of the untransformed β as the reaction continues. This precipitate may readily be observed in Figure 4. Figure 6 is a picture of this precipitation taken at a higher magnification in an attempt to bring it out more clearly.

The photographs would indicate that two separate transformations are taking place at the same time. One of these reactions is the nucleation and growth of $\delta+\epsilon$ product from the grain boundaries alone. The other is the nucleation and growth of a phase completely within the individual grains. It is almost impossible at present to predict which of these two reactions is most responsible for the final complete transformation. However, close observation of the completely reacted sample (Figure5) will show that the original decomposition reactions starting from the grain boundaries is still visible, for it etches darker than the other reaction products. It also will show that this darker etching grain boundary reaction appears to have progressed no farther than it had when shown in Figure 4 after one hour of heat treatment. This evidence would indicate that the precipitation reaction in the grains prevents the continuation of the reaction taking place from the grain boundaries, and hence was responsible for determining the time necessary for complete transformation to occur.



Fig.7 Sample No. E6-1 200X
Cast, homogenized at 1100°F hr., water quenched, transformed at 600°F 2 min. water quenched.



Fig.8 Sample No. E6-3 200X
Cast, homogenized at 1100°F 1 hr., water quenched, transformed at 600°F 6 min., water quenched.



Fig.9 Sample No. E6-4 200X
Cast, homogenized at 1100°F 1 hr., water quenched, transformed at 600°F 9 min., water quenched.

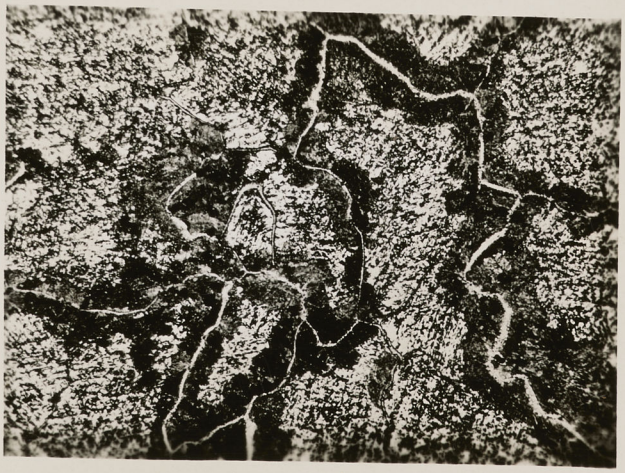


Fig.10 Sample No. E6-5 200X
Cast, homogenized at 1100°F 1 hr., water quenched, transformed at 600°F 12 min, water quenched.



Fig.11 Sample no. E6-6 200X
Cast, homogenized at 1100°F 1 hr., water quenched, transformed at 600°F 15 min., water quenched.



Fig.12 Sample No. E6-3 800X
Cast, homogenized at 1100°F 1 hr., water quenched, transformed at 600°F 6 min., water quenched.

Figures 7 thru 11 show the process of the transformation as it takes place after quenching to room temperature and reheating to 600°F. However, in this series the complete decomposition of β is obtained between times of twelve and fifteen minutes, as compared to one to three hours at 500°F. Again, at the beginning of the transformation two distinctly different reactions are observed to be going on simultaneously. However, in this case the pricipitate within the grains of untransformed β appears to be much heavier and of a more coarse nature. This fact is evident after close examination of Figure 12, which was another high magnification picture taken in an attempt to clearify the precipitate. Figure 10 would indicate that again the transformation in the grains stopped the reaction in the grain boundaries about midway through the process, and that the former reaction was responsible for the final complete transformation taking place in the given length of time. In fact, this series of photographs prove that the reactions within the grains starts much more rapidly and is more widespread at 600°F than it was in the samples transformed at 500°F.

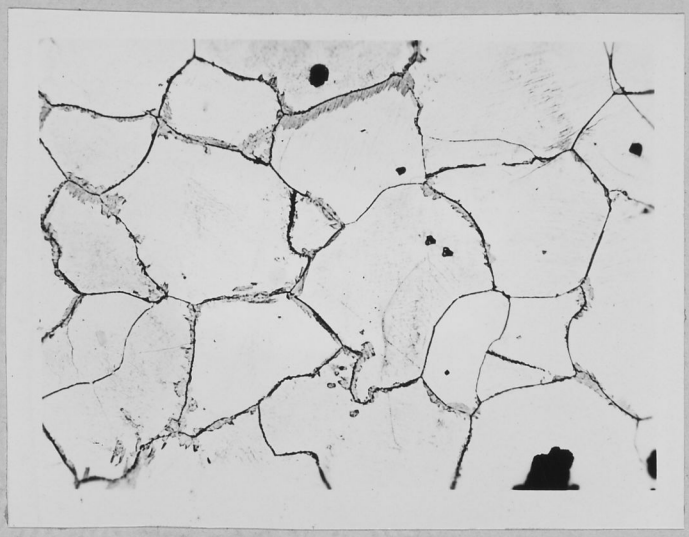


Fig.13 Sample No E7-1 200X
Cast, homogenized at 1100°F 1 hr., water quenched,
transformed at 700°F 5 Sec., water quenched.

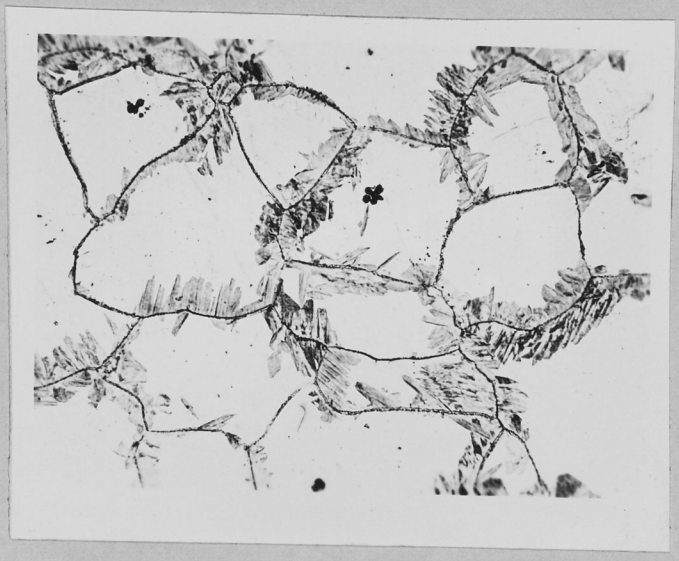


Fig.14 Sample No E7-2 200X
Cast, homogenized at 1100°F 1 hr., water quenched,
transformed at 700°F 15 sec., water quenched.



Fig.15 Sample No. E7-3 200X
Cast, homogenized at 1100°F 1 hr., water quenched, transformed at 700°F 30 sec., water quenched.



Fig.16 Sample No. E7-4 200X
Cast, homogenized at 1100°F 1 hr., water quenched, transformed at 700°F 45 sec., watrer quenched.



Fig.17 Sample No. E7-5 200X
Cast, homogenized at 1100°F 1 hr., water quenched,
transformed at 700°F 1 min., water quenched.



Fig.18 Sample No. E7-7 200X
Cast, homogenized at 1100°F 1 hr., water quenched,
transformed at 700°F 6 min., water quenched.



Fig.19 Sample No. E7-11 200X
Cast, homogenized at 1100°F 1 hr., water quenched, transformed at 700°F 1 week, water quenched.



Fig.20 Sample No E7-3 800X
Cast, homogenized at 1100°F 1 hr., water quenched, transformed at 700°F 30 sec., water quenched.

Figures 13 thur 17 show the process of the transformation as it takes place after quenching to room temperature and reheating to 700°F. As illustrated by the pictures, the β eutectoid had completely reacted between a time of 45 seconds and one minute. The two separate transformation mechanisms outlined in previous discussions are evident in the series also. However, now the reaction in the grains themselves seems to have no effect on the reaction in the grain boundaries. It will be noted that the precipitation in the grains is somewhat slower in appearing, and, after a slight growing period it stops completely and allows itself to be overtaken and passed by the decomposition products originally nucleated in the given boundary. This point is well illustrated upon careful study of Figures 14 and 15 successively. Therefore, the transformation reaction originally nucleated in the grain boundary is definitely the one responsible for determining the final transformation time at 700°F. Of some interest also is the etching characteristics of the $\alpha+\epsilon$ which is formed at 700°F. It has a tendency to be much lighter and of a finer nature than that observed at lower temperatures.

Figures 18 and 19 were included in the series to illustrate the process by which α spheroidizes in a matrix of ϵ after the transformation reaction has been completed.

Figure 20 is a picture of the same sample as figure 15; however a much higher magnification was used. The fine decomposition products in the grains are clearly seen to be of a α composition and to possess a definite Widmanstatten structure. A Widmanstatten structure is characterized by a general pattern resulting from the formation of a new phase along certain crystallographic planes of the present solid solution.. The orientation of the lattice in the new phase is related crystallographically to the orientation of the lattice in the present phase. This type of structure is familiarly seen in cast steels and in overheated wrought steel that has been cooled rather rapidly, and in age hardenable systems.

Several different conditions could have been responsible for the above mentioned structure. It is possible that the composition of the observed samples were not quite at the eutectoid point. Also, it may have resulted from a suppression of the eutectoid point, thus actually causing a continuation of the solid solution curves of the phase diagram. These possibilities will be discussed more fully later in the report.

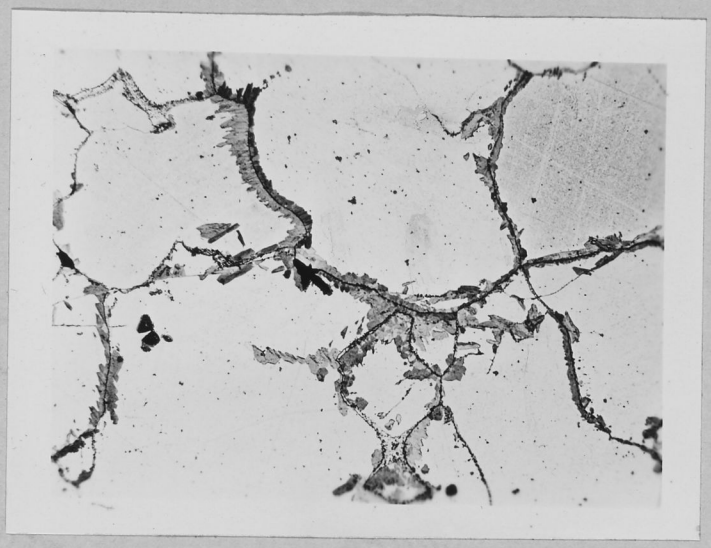


Fig. 21 Sample No E7.5-1 200X
Cast, homogenized at 1100°F 1 hr., water quenched, transformed at 750°F 15 sec., water quenched.



Fig. 22 Sample No E7.5-2 200X
Cast, homogenized at 1100°F 1 hr., water quenched, transformed at 750°F 30 sec., water quenched.



Fig. 23 Sample No E7.5-3 200X
Cast, homogenized at 1100°F 1 hr., water quenched, transformed at 750°F 1 min., water quenched.



Fig. 24 Sample No. E7.5-4 200X
Cast, homogenized at 1100°F 1 hr., water quenched, transformed at 750°F 1½ min., water quenched.



Fig. 25 Sample No. E7.5-5 200X
Cast, homogenized at 1100°F 1 hr., water quenched, transformed at 750°F 2 min., water quenched.



Fig. 26 Sample No. E7.5-6 800X
Cast, homogenized at 1100°F 1 hr., water quenched, transformed at 750°F 1½ min., water quenched.

Figures 21 thru 25 illustrate the process of the transformation as it occurs after quenching to room temperature and reheating to 750°F. The time required for complete reaction lies between $1\frac{1}{2}$ and 2 minutes. This is indicated by Figure 24 which shows small light areas of untransformed β still existing in the upper right hand corner of the picture. The transformation mechanism of this series resembles very closely that of 700°F. The reaction in the grains produces a precipitate of α with a Widmanstatten structure. However, this reaction stops completely after a short growing period, and the transformation reaction nucleated in the grain boundaries is the one responsible for final complete decomposition of the β eutectoid. Figure 26 not only shows the Widmanstatten structure clearly, but it also portrays the mechanism of the growth of the decomposition product. Its paths stretch across the white, untransformed β in an irregular pattern, presenting a typical illustration of the way it crosses and recrosses each grain until the entire area is completely transformed.

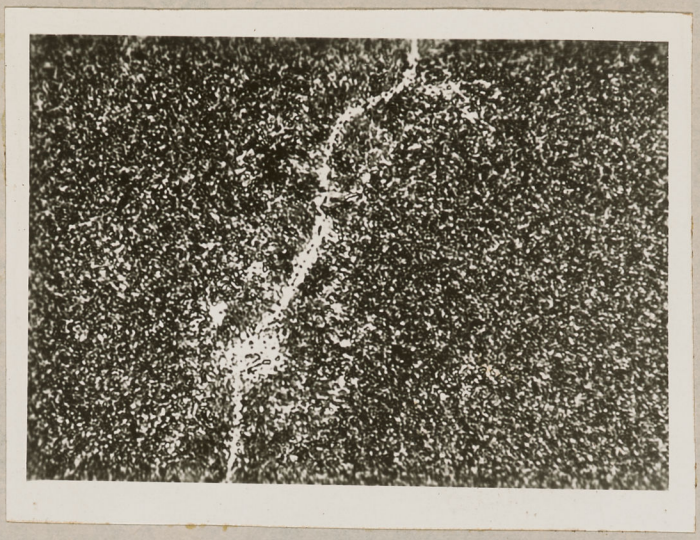


Fig. 27 Sample No. E5-8 500X
Cast, homogenized at 1100°F 1 hr., water quenched, transformed at 500°F 2 weeks, water quenched.

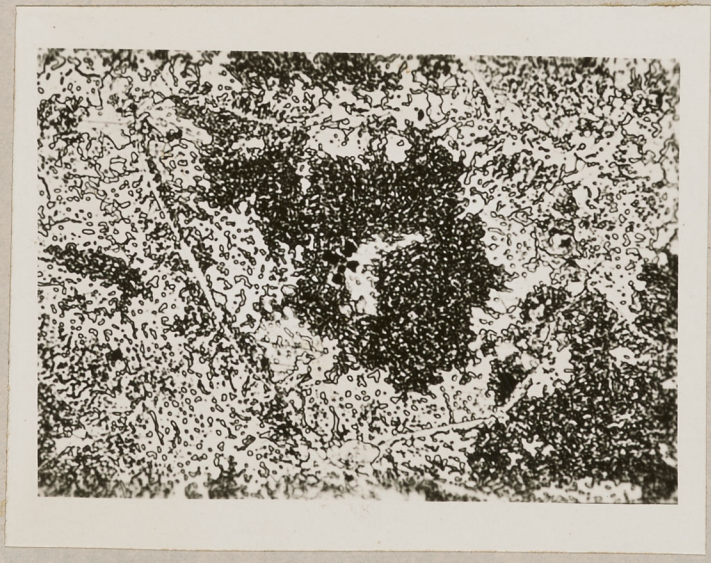


Fig. 28 Sample No. E6-9 500X
Cast, homogenized at 1100°F 1 hr., water quenched, transformed at 600°F 2 weeks, water quenched.

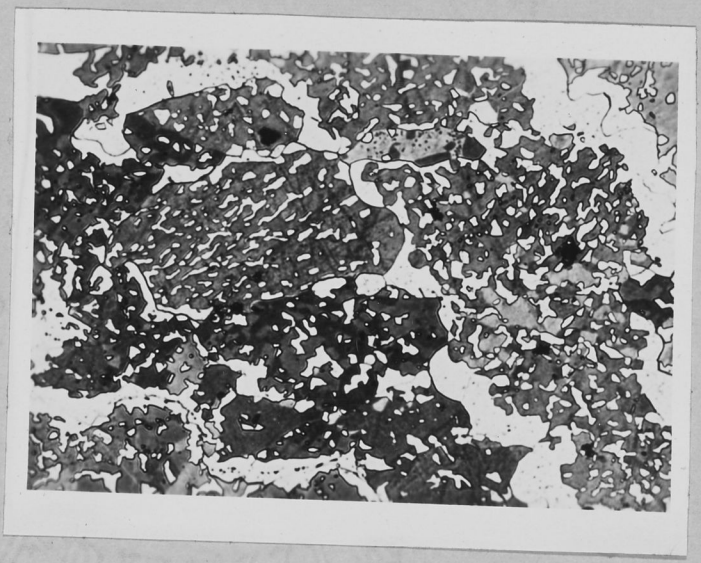


Fig. 29 Sample No. E7-14 500X
Cast, homogenized at 1100°F 1 hr., water quenched, transformed at 700°F 2 weeks, water quenched.

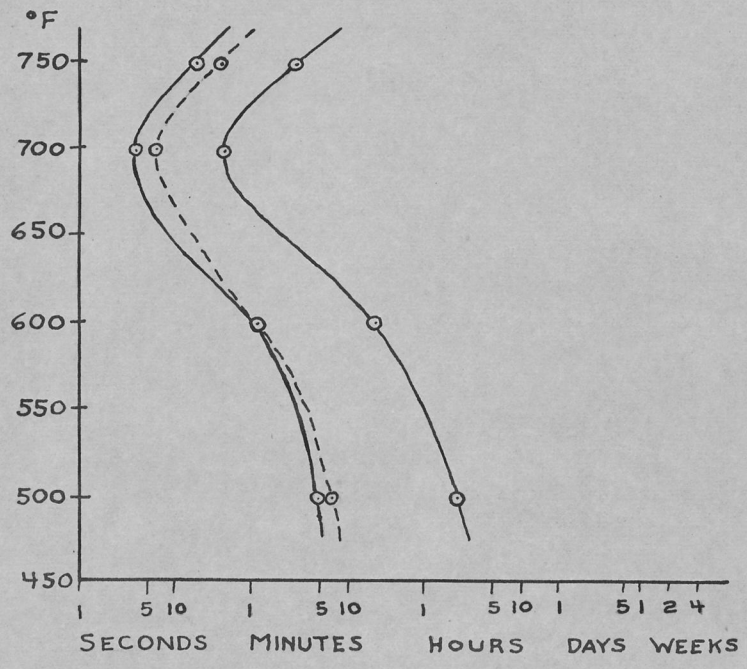
Figures 27 thru 29 were included in the series of photographs to illustrate the different amounts of spheroidization which occurred at different transformation temperatures. As would be expected, the individual areas of δ in the ϵ matrix become increasingly larger as the temperature is increased.

RESULTS

This investigation inculued the quenching of samples of the β phase of approximately eutectoid composition to room temperature and the re-heating to 500°F, 600°F, 700°F and 750°F to observe the rates of trans-formation. The results secured from a study of photographs of the trans-forming samples are is follows:

TRANSFORMATION TEMPERATURE	BEGINNING OF TRANSFORMATION	TRANSFORMATION COMPLETED
500°F	Less than 5 min.	1-3 hours
600°F	Less than 2 min.	12-15 minutes
700°F	Less than 5 sec.	45-60 seconds
750°F	Less than 15 sec.	1½-2 minutes

While these results do not permit the time-temperature curve of the eutectoid to be drawn exactly to scale, they do permit the general shape of the curve to be sketched. This has been done in the figure below. The dotted line indicates the beginning of the precipitation reactions with-in the grains.



The transformation of the β phase of approximately eutectoid composition of the copper-antimony system was observed to proceed by the following steps.

(1) The nucleation of primary δ in the grain boundaries followed by

(2) The nucleation and growth of the $\delta+\epsilon$ eutectoid product in the grain boundaries. The growth of the local primary δ stops when the $\delta+\epsilon$ product is first formed.

(3) The precipitation of a fine pattern believed to be of a δ composition within the grains.

(4) The $\delta+\epsilon$ product coarsens to δ in lamellar form in a matrix ϵ. The lamellar δ grows until it breaks into a rodlike form and starts spheroidization.

(5) Previous investigations by Pichlesimer and also by Osawa and Shibata outline a phase change whereby β goes to β' on quenching. This β' phase is reported to be self-tempering and tempered β' is reported to show a acicular structure very similiar to the tempered martensite structure in steels. However, no positive evidence could be found to substaniate these reports. While it was noted that untransformed β tempered for several months at room temperature etched slightly darker than freshly quenched β, the microhardness of both structures were found to be identical. (400 Knoop or Rockwell-47c.)

As was outlined in the "Introduction" section of this report, it was orginally proposed that a β structure, upon being quenched to sub-critical temperatures, could transform to a structure comparable to martensite in low-carbon steels. This possibility was investigated by inserting into liquid nitrogen a sample of β which had orginally been homogenized at 1100°F for 1 hour before being quenched to room temperature. The sample was left in the liquid nitrogen long enough to ensure its having reached the temper-

ature of the bath. It was then withdrawn and allowed to reheat to room temperature. Examination of this sample under the microscope failed to reveal an observable change in structure. A micro hardness test was also run on the liquid nitrogen quenched sample to compare it with other samples of β previously quenched only to room temperature. The hardnesses of both samples was found to be 400 Knoop(equivalent to Rockwell hardness of 47C). In view of this evidence, it may be assumed that the β eutectoid fails to undergo any definite phase change when quenched to temperatures as low as that of liquid nitrogen(-198°C).

A considerable difference was observed in the mechanism of the decomposition of the β eutectoid as it took place at various temperatures. For heat treatments of 500°F and 600°F, initially two separate transformation reactions were found to be taking place simultaneously. One of these was nucleated and grew into the grains only from the grain boundaries. The other was apparently nucleated at random in the grains themselves and appeared there in a lace-like pattern. About midway to completion of the transformation, the reaction within the grains seems to have produced large enough quantities of precipitation to completely halt the transformation reaction which had nucleated and begun growing in the grain boundaries. Hence, the final portion of the decomposition process was wholly enacted by the precipitation reaction taking place within the grains.

However, an entirely different situation existed for transformation temperatures of 700°F and 750°F. While the two separate above-outlined reactions were again taking place simultaneously at the beginning of the transformation, the one in the grains stopped growing very shortly after it had started. Pictures taken of the precipitate at high magnification show it to have a Widmanstatten structure. Meanwhile, the reaction which had stsrted from the grain boundaries continues until it has completely transformed the entire sample.

DISCUSSION OF RESULTS

The consistancy of the experimental results obtained in this investigation may be primarily attributed to the precautions taken in producing the original cast alloy of the β eutectoid. The portions of copper and antimony used to form the alloy were weighed on an analytical balance to ensure a cast of the correct composition. The use of a crucible equipped with a screw fitting lid to melt and thoroughly mix the molten metal greatly reduced the loss of antimony which ordinarily would have occurred through oxidation. The remelting and remixing by complete inversion of the entire crucible aided in providing an alloy of homogenous composition and completely free of segregation.

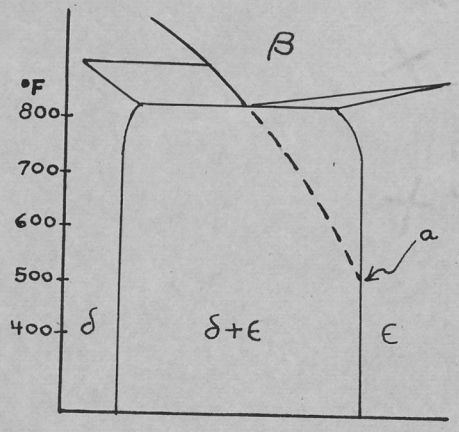
The accurary of the time-temperature-transformation results is substantiated by the series of photographs secured at each of the heat treatment temperatures. Not one of the samples prepared showed a quantity of decomposition products which were not in line with all of the other samples of that run. Also, the grains of all the samples prepared were of the same general size and shape. Nor was there a single evidence of segregation in the cast alloy at any step through out the investigation.

However, the absolute explanation of certain features of the transformation mechanisms which occur at each of the different temperatures is not possible at present, and only plausible suggestion can be offered. Such an example of this is the transformation reaction which seems to nucleate and grow independently within the grains at temperatures of 500°F, 600°F, 700°F, and 750°F. At the two lower temperatures its precipitation products seem to be in quantities large enough to completely stop the other transformation reaction which has started from the grain boundaries. In doing so, it becomes the reaction finally responsible for the complete transformation of the grains. However, at 700°F and 750°F, just the opposite is true.

The precipitation in the grains stops very shortly after it has started growth, and the grain boundary reaction is the one responsible for complete transformation.

One explanation of this phenomena, and the simplest one, is that the original cast alloy was not exactly of a β eutectoid composition. Then these precipitations of δ is the result of the β rejecting its richer phase in an attempt to reach the eutectic point. At temperatures of 500°F and 600°F this precipitation was fine enough and wide spread enough to completely halt the original transformation which had begun from the grain boundaries. However, at 700°F and 750°F the rejected δ was of a coaser nature, and did not affect the grain boundary transformation reaction.

Another possibility, though slighty more extreme, is that quenching a β phase from 1100°F to room temperature causes an extension of the solid solution curve as shown by the dotted line in the sketch. This possibility would also include the stipulation that only δ can nucleate within the grains whereas $\delta + \epsilon$ is nucleated at the grain boundaries. This explantion would then answer the question of why the grain boundary transformation reaction stopped at 500°F and 600°F but was uneffected at 700°F and 750°F. At the lower temperatures the extended solid solubility line is very near its intersection with the curve separating the ϵ and $\delta + \epsilon$ phase. Therefore, the precipitate which would take place is mostly δ, shifting the composition of β to point "a" where it transforms to ϵ by a diffusionless process. However, at high temperatures the extended solubility curve of δ indicates that β cannot reach the δ composition. Hence, less precipitates in the grains and the grain boundary reaction of $\delta + \epsilon$ is allowed to proceed completion.



While both of the above explantions are quite rational, it is impossible to decide which is correct, if either, due to the lack of more concrete evidence.

CONSLUSIONS

The following conclusions may be drawn concerning the heat treatment of the β eutectoid of the copper-antimony system.

(1) A uniform, segregation-free cast of the β eutectoid is obtainable if the original sample is prepared in a closed crucible which allows thorough mixing by continuous inversion.

(2) A definite time-temperature-tranformation curve, similiar to that of steels, exists for the β eutectoid of the copper-antimony system.

(3) However, no strusture comparable to that of martensite in steels was observed in samples of β quenched to sub-critical temperatures in liquid nitrogen. Also, the microhardness of such a quenched sample was the same as the microhardness of a sample of β quenched only to room temperature.

(4) The minimum length of heat treatment time necessary to secure complete transformation of a sample of β which has been quenched to room temperature and reheated occurs either at or very near 700°F.

(5) The transformation of the β eutectoid was found to follow the following process. The rejection of primary δ in the grain boundaries followed by the nucleation and growth of the $\delta + \epsilon$ product in the grain boundaries. The growth of the local primary δ stops when the $\delta + \epsilon$ is first formed. A fine precipitation believed to be δ is nucleated and grows in the grains about midway through the transformation process. The $\delta + \epsilon$ product precipitates δ in lameller form in a matrix of ϵ. The lamellar δ grows until it breaks into rodlike forms and starts spheroidization.

(6) It is possible that the reaction $\beta \rightarrow \beta' \rightarrow \delta + \epsilon$ which has been reported by eariler investigations also took place in the transforming samples. No concrete evidence could be obtained either to substaniate or disprove

the presence of such a reaction.

(7) At heat treating temperatures of 500°F and 600°F these are initally two separate transformation reactions occuring simultaneously. One is nucleated and grows only from the grain boundaries. The other is nucleated within the grains themselves and appears as a fine precipitate there. About midway through the transformation, this precipitate has been produced in quantities large enough to halt the grain boundary reaction completely.

(8) At transformation temperatures of 700°F and 750°F the same two reactions are present. However, in this case the precipitate in the grains stops growing shortly after it started, and complete transformation of the grains is caused by the reaction which originally began in the grain boundaries.

RECOMMENDATIONS

Before any futher investigation of the system is carried out, it is recommended that the portion of the phase diagram containing the β eutectoid be throughly checked to obtain the exact composition of that point.

Since the entire results of this investigation were secured by quenching β to room temperature before heat treating the structure, it is proposed that an isothermal transformation study be conducted employing the same temperatures as were used in this study.

For futher investigation of the system it is recommended that the following determinations be made:

(1) The development of an electrolytic polishing technigue which would enable more respresentative samples to be prepared.

(2) A determination of the accuracy of the reports of earlier investigators concerning the existance of a tempered β phase, commonly known as β'.

(3) The microhardness of the primary phases and changes of microhardness with the decomposition reaction.

(4) Analytical determinations be made of the exact composition of all samples of β eutectoid cast for study of the alloy.

APPROVAL

The foregoing thesis is hereby approved as a creditable study of an engineering subject, carried out and presented in a manner sufficiently satisfactory to warrant its acceptance as a prerequisite to the degree for which it has been submitted. It is to be understood that by this approval the undersigned does not necessarily endorse or approve any statement made, opinions expressed, or conclusions drawn therein but approves the thesis only for the purpose for which it is submitted.

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