1965

The effect of copper upon the eutectoid reaction in the zinc-aluminum system

Paul Theodore Corcoran

Recommended Citation

Corcoran, Paul Theodore, "The effect of copper upon the eutectoid reaction in the zinc-aluminum system" (1965). *Masters Theses*. 6958.
https://scholarsmine.mst.edu/masters_theses/6958

THE EFFECT OF COPPER UPON THE EUTECTOID REACTION IN THE ZINC-ALUMINUM SYSTEM

BY

PAUL THEODORE CORCORAN

A

THESIS

submitted to the faculty of the

UNIVERSITY OF MISSOURI AT ROLLA

in partial fulfillment of the requirements for the

Degree of

MASTER OF SCIENCE IN METALLURGICAL ENGINEERING

Rolla, Missouri

1965

Approved by

(advisor) H. O. McDonald

William A. Frad

ABSTRACT

A Leitz dilatometer was used to study the kinetics of the eutectoid reaction in the zinc-aluminum system and the effect of small additions of copper upon this reaction. Three alloys were investigated: a pure 78% zinc - 22% aluminum alloy; a 78% zinc - 21.9% aluminum - 0.1% copper alloy; a 78% zinc - 21% aluminum -1.0% copper alloy.

It was found that this reaction was similar to the pearlite reaction in the iron-carbon system. The reaction occurred by diffusion processes and the products of the reaction looked similar to pearlite when examined under the microscope.

Copper was found to impede the reaction by interfering with the diffusion of zinc and aluminum atoms. This effect was most pronounced at temperatures below 80° C. At higher temperatures, the copper atoms caused relatively little difference in the kinetics of the eutectoid reaction.

ACKNOWLEDGMENTS

The author wishes to express his gratitude and sincere appreciation to Dr. Daniel S. Eppelsheimer and Dr. William A. Frad of the University of Missouri at Rolla for the training, valuable suggestions, and assistance they have given him through their lectures and personal guidance.

The author is also indebted to the New Jersey Zinc Co. for the high purity zinc, to the Alcoa Aluminum Company for aluminum, and to the Sinclair Refining Company for the Marquench oil used as a high temperature quenching medium.

TABLE OF CONTENTS

LIST OF ILLUSTRATIONS

---

* TTT will be used to denote Time-Temperature-Transformation in relation to curves.

Figures Page

LIST OF TABLES

I. INTRODUCTION

Importance

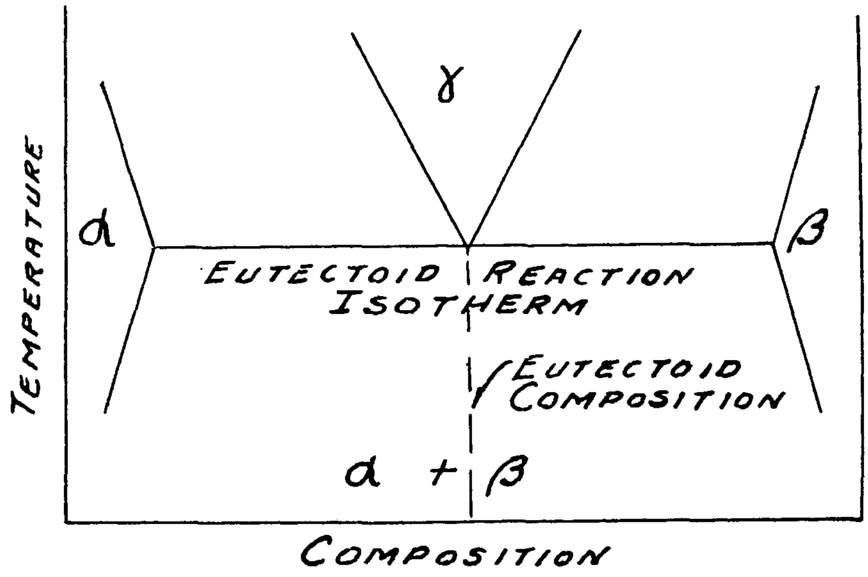
The kinetics and mechanism of the eutectoid reaction have been subjected to a great deal of study in the iron-carbon system. The decomposition of austenite in steel has interested physical metallurgists for so long that it can even be considered a field of study in itself. Out of these investigations have come great strides in the alloying and heat treatment of steels in order to get the physical properties desired--such as, strength or ductility. By dissimilar heat treatments, it was found that two steels of the same chemical composition could be made to have widely different mechanical properties. It can be truthfully said that much of the progress in the field of ferrous physical metallurgy can be traced to the study of the austenitic eutectoid decomposition.

Although the eutectoid reaction has been extensively studied in the iron carbon system, in nonferrous systems (with the possible exception of copper-aluminum) it has been largely ignored. The author believes that a study of these reactions would greatly benefit non-ferrous metallurgy in the same way that a study of the austenitic decomposition has benefited ferrous metallurgy. The effects of such studies would shed even more light upon the decomposition of austenite, and might lead to the development of improved alloying procedures by which the speed of the austenite decomposition, along with the decomposition products, could be more closely controlled in ferrous base alloys. In nonferrous alloys, such investigations could pay the same type of dividends that understanding the austenitic decomposition brought to ferrous metallurgy.

The author chose the eutectoid reaction in the zinc-aluminum system as a basis for this study because of the commercial as well as the academic importance of zinc-aluminum alloys--especially the die-casting alloys. The effects of copper upon this eutectoid reaction were studied because copper is a common alloying agent in zinc-aluminum alloys and is known to slow down the eutectoid decomposition. The understanding of this reaction could lead to such practical results as controlling the dimensional change of zinc die-castings or developing heat treatable die-castings.

Explication

The eutectoid reaction is a solid state reaction in which a solid phase, stable at high temperature, becomes unstable and decomposes into two or more phases upon being subjected to slow cooling. In a binary or two component system, the phase diagram of a typical eutectoid reaction is similar to the partial diagram shown in figure 1.



In this figure, pressure is considered constant and the phases of alloys of varying compositions are plotted versus temperature. The eutectoid point is the point on the temperature-composition co-ordinates where the γ field makes contact with the three-phase horizontal, labeled the eutectoid reaction isotherm in figure 1. Although this diagram represents the phases only under equilibrium conditions, by understanding the information it contains, a metallurgist can partially predict the structure of any alloy (whose composition could be represented on the diagram) under non-equilibrium conditions.

Under equilibrium conditions, the γ phase does not exist below the eutectoid reaction isotherm, shown in figure 1; under non-equilibrium conditions the γ phase may exist in an unstable or metastable condition for considerable periods of time. This is caused because the reaction $\gamma \rightarrow \alpha + \beta$ does not occur instantaneously. Therefore, if the alloy is cooled rapidly from the γ phase field, this reaction may not have time to go to completion. Under non-equilibrium conditions it is possible to have γ at a temperature below the eutectoid reaction isotherm, but the γ phase would not be in equilibrium and would tend to decompose to form the stable phases shown in the equilibrium diagram at the temperature considered.

This study is concerned with the eutectoid decomposition of the high temperature phase in the aluminum-zinc system and the kinetics with which it occurs. The effect of copper upon the reaction was studied also, and it was found that copper greatly slows down this reaction especially at low temperatures.

Types of Eutectoid Reactions

Eutectoid reactions may occur because of allotropic changes in the base constituent as in the iron-carbon system, or through the decomposition of an intermediate phase as in the aluminum-zinc diagram. Spencer and Mack[1] divide the possible methods in which the eutectoid reaction can occur into four basic mechanisms.

The first type of reaction is the pearlite reaction, named for the austenite-pearlite reaction in iron-carbon alloys. In this type of reaction, the two low-temperature phases precipitate practically simultaneously from the parent phase without an over-all composition change taking place as the reaction interface proceeds through the high-temperature phase.

The next major type of reaction is the massive reaction in which the high temperature phase transforms into a low-temperature phase of essentially the same composition. This low-temperature phase is supersaturated or a metastable form of one of the stable low-temperature phases and precipitates the second low-temperature phase, thereby changing into one of the stable low-temperature phases. This type of eutectoid reaction occurs in the silver-cadmium and copper-gallium systems.

The third major type of eutectoid reaction is the monophase or proeutectoid precipitation reaction. In this type

---

[1] C. W. Spencer and D. J. Mack, "Eutectoid Transformations in Nonferrous and Ferrous Alloy Systems," Decomposition of Austenite by Diffusional Processes, AIME, (1962), pp. 549-603.

of reaction, a single phase (usually one of the low-temperature phases) precipitates directly from the high temperature phase while the latter undergoes a change in composition. After a certain amount of precipitation has occurred, the composition of the high-temperature phase remains constant until it decomposes by another reaction mechanism. This type of reaction is the one by which the aluminum-zinc eutectoid decomposes according to Spencer and Mack (reference already cited).

The final type of possible reaction is the bainite reaction. At this time, bainite type reactions have definitely been observed only in ferrous eutectoidal systems, although structures which resemble high-temperature bainite in steel have been observed in nonferrous systems, such as copper-aluminum and copper-tin. Bainite is considered to be a product of diffusional growth below the "nose" of the TTT* curve.

---

*TTT will be used to denote Time-Temperature-Transformation in relation to curves.

II. REVIEW OF THE LITERATURE

The Eutectoid Transformation

Davenport and Bain[2] opened the field of scientific investigation of the eutectoid type reactions when they devised the concept of a Time-Temperature-Transformation diagram representing the occurrence of the eutectoid change. Their method utilized the well-known fact that, if an iron-carbon alloy is cooled in excess of a particular critical cooling rate, an easily identifiable microconstituent (Martensite) will form. Their method consisted of quenching from the austenitic state into an isothermally controlled bath, of holding a predetermined interval in this bath, and then of requenching into a second bath to transform any remaining austenite to martensite. The specimens were then viewed under a microscope so that the progress of the reaction that had occurred before the second quench could be determined.

Smith and Lindlief,[3] in a prize-winning paper, enlarged this basic method in their study of the more complex copper-

---

[2] E. E. Davenport and E. C. Bain, "Transformation of Austenite at Constant Subcritical Temperatures," Trans. AIME. Vol. 90, (1930) p. 117.

[3] C. S. Smith and W. E. Lindlief, "A Micrographic Study of the Decomposition of the B Phase in the Copper-Aluminum System," Trans. AIME, Vol. 104, (1933) p. 69.

aluminum eutectoid. In addition to Bain's techniques, Smith and Lindlief utilized the changes in length and electrical conductivity of the specimen as it transformed from the high temperature state to the stable low temperature phases. Preceding the Smith and Lindlief work, Matsuda [4] and Obinata [5] had demonstrated that the electrical conductivity curves for copper-aluminum alloys showed two decided breaks in slope at the eutectoid temperature. Obinata interpreted this as meaning that the eutectoid change took place in two stages with an intermediate phase occurring between the disappearance of the high-temperature phase and the growth of the two low-temperature phases. Smith and Lindlief proved that the eutectoid definitely decomposes with an intermediate reaction product.

Mack [6] reinvestigated the copper-aluminum system and concluded that the work of Smith and Lindlief was correct in all essential details. This copper-aluminum system

---

[4] M. Matsuda, Jnl. Inst. Metals, Vol. 39, (1928) p. 67.

[5] I. Obinata, Mem., Ryojum Coll. Eng., Vol. 2, (1928-1930) p. 205.

[6] D. J. Mack, "The Isothermal Transformation of a Eutectoid Aluminum Bronze," Trans. AIME, (1948) Vol. 175, p. 240.

eutectoid reaction has been studied in more detail than any other non-ferrous system. It was found that this reaction was more intricate than those in the ferrous systems.

Since 1948, the methods of Smith and Lindlief have been applied to the study of eutectoid transformations in the copper-aluminum,[7,8] iron nitrogen,[9] copper-silicon,[10] copper-baryllium systems,[11] and many others.

---

[7] R. Haynes, <u>Journal Institute Metals</u>, (1954) Vol.83, p. 105.

[8] E. P. Klier and S. M. Grymko, <u>Trans</u>. AIME, (1949) Vol. 185, p. 611.

[9] B. N. Bose and M. F. Hawkes, <u>Trans</u>. AIME,(1950) Vol.188, p. 307.

[10] W. R. Hibbard, Jr., G. H. Eichelman,Jr., and W. P. Saunders, <u>Trans</u>. AIME, (1949) Vol. 180, p.92.

[11] R. H. Fillnow and D. J. Mack, <u>Trans</u>. AIME,(1950) Vol. 188, p. 1229.

The Aluminum-Zinc Phase Diagram

In years past, the aluminum-zinc phase diagram has been studied by many investigators. This scientific effort has been due both to the commercial importance of some aluminum-zinc alloys and to the scientific interest in their alloying behavior. The main reason for the abundance of study of this system was the conflict whether or not a peritectic reaction occurred at approximately 440° C. Early investigators, such as Rosenhain and Archbutt,[12] Bauer and Vogel,[13] Hanson and Gayler,[14] Tanabe,[15] and Isihara[16] presented evidence that there was a peritectic reaction at 443° C. Later writers, Owen and Pickup,[17] Fink and Willey,[18] Gayler and Sutherland[19] concluded that the peritectic reaction was non-

---

[12] W. Rosenhain and S. L. Archbutt, Phil. Trans., Roy. Soc., (1911) A, Vol. 211, p. 315.

[13] O. Bauer and R. Vogel, Internat. Z. Metallographie, (1916) No. 8, p. 101.

[14] D. Hanson and M. L. V. Gayler, J. Inst. Metals, (1922) No. 27, p. 267.

[15] T. Tanabe, J. Insti. Metals, (1924) No. 32, p. 415.

[16] T. Isihara, J. Insti. Metals, (1925) No. 33, p. 73.

[17] E. A. Owen and L. Pickup, Phil. Mag., (1935) No. 20, p. 761.

[18] W. L. Fink and L.A. Willey, Trans. AIME, (1936) No. 122, p.244.

[19] M. L. V. Gayler and E. G. Sutherland, J. Inst. Metals, (1938) Vol. 63, p. 123.

existent on the basis of thermal, microscopic, and dilatometric evidence. The phase diagram generally accepted until recently was that published by Hanson and Gayler (figure 2). However, recent research by Presnyakov, Gorban, and Chervyakova,[20] E. C. Ellwood,[21, 22] and the new corroborative evidence presented by G. R. Goldak and J. G. Parr[23] has resulted in the revised phase diagram (figure 3).

This report is based on the phase diagram of Presnyakov, Gorban, and Chervyakova. According to this phase diagram, the eutectoid reaction which occurs at 78 wt. % zinc is:

$$\gamma \rightarrow \alpha + \beta$$

---

[20] A. A. Presnyakov, Yu. A. Gorban, and V. V. Chervyakova, Trudy Institute Yadernoi Fiziki, Akademii Nauk Kazakhakoi S.S.R., (1961) Vol. 4, P. 85.

[21] E. C. Ellwood, J. Inst. Metals, (1940) Vol. 66, p. 87.

[22] E. C. Ellwood, J. Inst. Metals, (1952) Vol. 80, p. 1345.

23

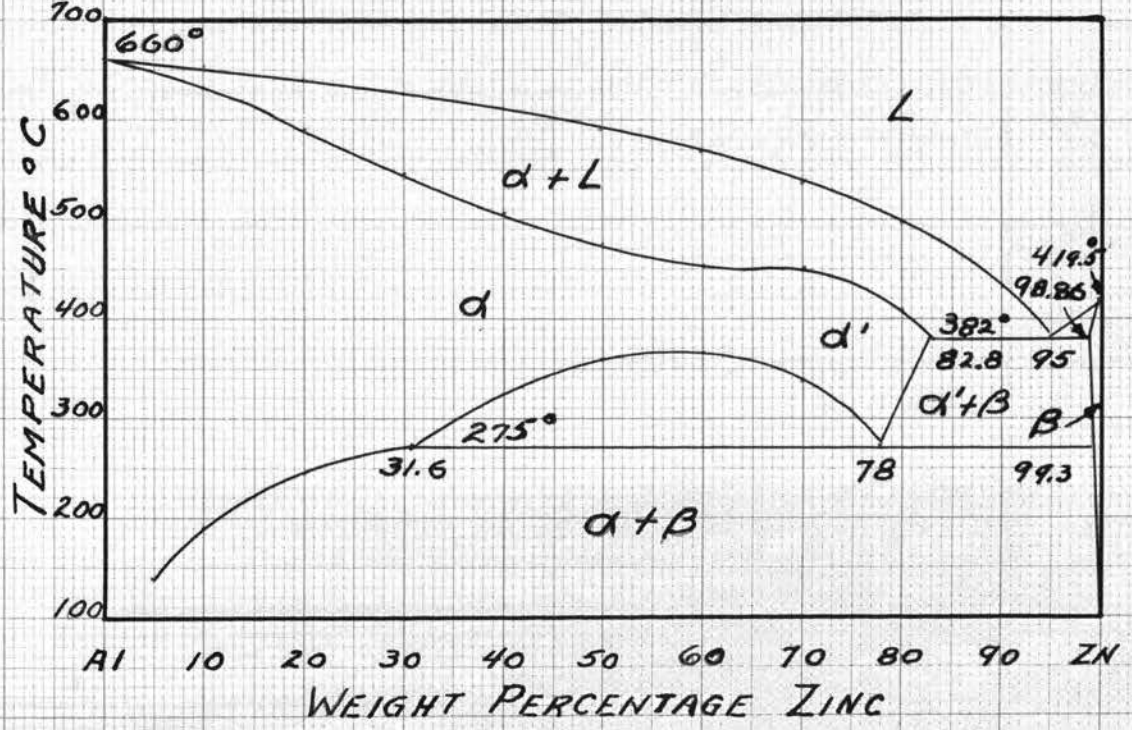


Figure 2

Aluminum-Zinc Phase Diagram

From Hansen's <u>Constitution of Binary Alloys</u>

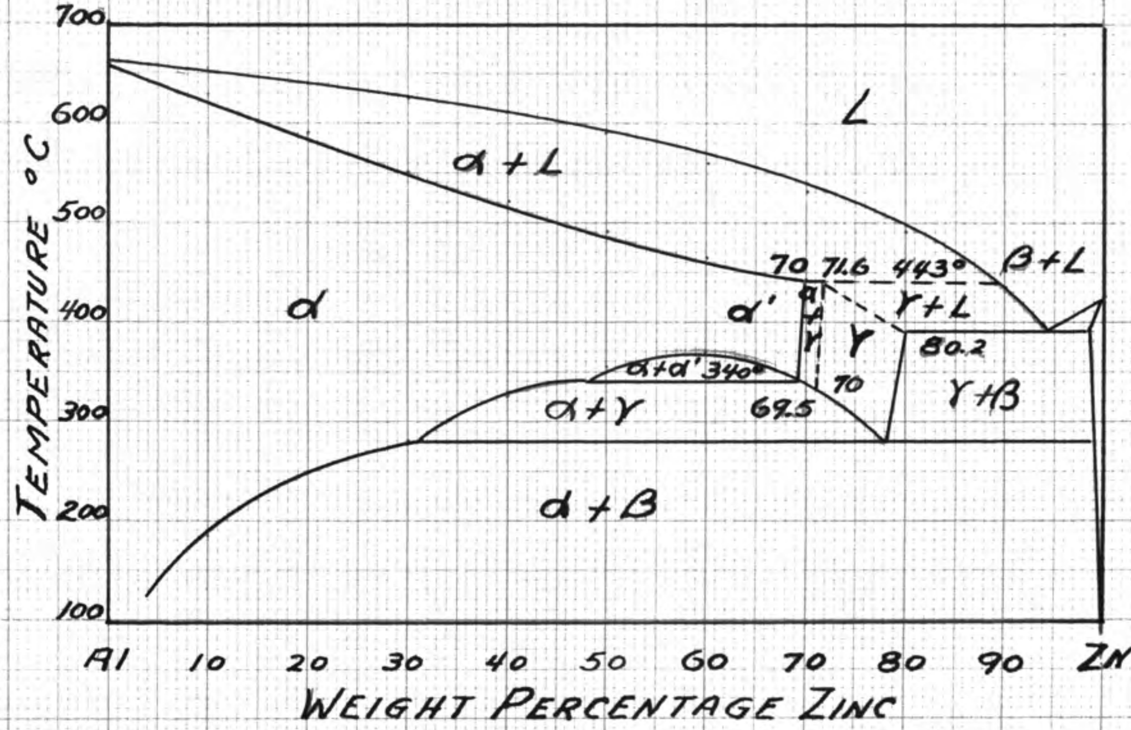


Figure 3

Aluminum-Zinc Phase Diagram

By Presnyakov, Gorban, and Chervyakova

The Aluminum-Zinc Eutectoid Reaction

Much of the literature on the eutectoid reaction in the aluminum-zinc system is based on the phase diagram by Anderson that appears in the 1948 edition of the Metals Handbook. The eutectoid reaction is represented as: $\alpha' \rightarrow \alpha + \beta$. Recently, the phase diagram by Presnyakov, Gorban, and Chervyakova[24] has changed the phase designation so that the reaction appears: $\gamma \rightarrow \alpha + \beta$. In this review of the literature published on the aluminum-zinc eutectoid, the newer terminology will be used.

Raynor[25] has shown that the reaction is the decomposition of a face-centered cubic phase (γ) which contains 78% zinc into a face-centered cubic, aluminum-rich α solid solution and a close-packed hexagonal, zinc-rich β solid solution.

The earliest studies of this reaction in the aluminum-zinc system have been based on the fact that the alloy gives off considerable heat when it transforms. Hanson and Gayler[26] have studied the eutectoid reaction in alloys ranging from

---

[24] A. A. Presnyakov, Yu. A. Gorban, and V. V. Chervyakova, Trudy Institute Yadernoi Fiziki, Akademii Mauk Kazakjskoi S.S.R. (1961) Vol.4, p.85.

[25] G. V. Raynor, J. Inst. Metals, Annotated Equilib. Diagr. Series, No.1, (1943).

[26] H.D. Hanson and M. L. V. Gayler, J. Inst. Metals, (1922) Vol. 27, p. 267.

40% to 80% zinc and have found that the temperature would rise as much as 50° C. as the eutectoid reaction occurred. Burke[27] has used the same method to study the reaction in a pure aluminum-zinc eutectoid alloy. Anderson[28] has studied the effect of various alloying elements on the reaction by the same thermal method.

Later investigations point out that the eutectoid transformation in the aluminum-zinc system is accompanied by a contraction in volume of 0.28% [29,30,31]. Garwood and Hopkins[32] employ this in making a dilatometric investigation of the transformation. Microscopic evidence demonstrates that the transformation ends before the volume change is complete on specimens that transformed at low temperatures.

---

[27] T. J. Burke, "The Transformation of the Aluminum-Zinc Eutectoid Alloy at Subcritical Temperatures," Thesis, M.S.M.

[28] C. R. Anderson, "The Action of Impurities Upon the Low Temperature Transformation in Zinc-Aluminum Alloys," Master's Thesis, Yale (1931)

[29] T. Isihara, Sci. Rep., Tohoku Imp. Univ., (1926),(1), Vol.15, p. 209.

[30] T. Tanabe, J. Inst. Metals, (1924) Vol. 32, p. 415.

[31] W. Fraenkel and E. Wachsmuth, Z. Metallkunde, (1930) Vol. 22, p. 162.

[32] R. D. Garwood and A. D. Hopkins, J. Inst. Metals, (1952) Vol. 81, p. 407.

The same investigators have found that there is no evidence of an intermediate structure forming during the progress of the transformation[33] and that final products of the transformation are produced in equilibrium concentrations[34]. Cahn[35] has disclosed that during such reactions the equilibrium compositions of the low-temperature phases are not obtained for any nonzero growth rate. Garwood, Davies, and Richards[36] have detected a face-centered transition phase in the isothermal transformation of an aluminum-25% zinc alloy.

---

[33] E. Geghardt, Z. Metallkunde, (1941) Vol. 33, p. 328.

[34] I. Obinata, M. Hagiya, and S. Itimura, Tetsu to Hagane, (1936) Vol. 22, p. 622.

[35] J. W. Cahn, Acta Met., (1959) Vol. 7, p. 18.

[36] R. D. Garwood, A. L. Davies, and G. L. Richards, J. Inst. Metals, (1959) Vol. 88, p. 375.

III. DISCUSSION

Preparation of the alloys

Three alloys were used in this investigation. Each of these alloys contained 78% zinc with aluminum and copper making up the rest of the alloy. The amount of copper in this set of alloys was respectively: 0.0%, 0.1%, and 1.0%.

The zinc used in the preparation of these alloys was supplied by the New Jersey Zinc Company. Their analysis of this material, designated by lot code N1948, was: 0.002% lead, 0.002% iron, and 0.0005% cadmium; balance zinc.

The aluminum was supplied by Alcoa Aluminum Company. This material was covered by their analysis sample #268041 which read: 0.002% copper, 0.001% iron, and 0.001% silicon; balance aluminum.

Sargent Reagent grade copper with a purity at least 99.99% was employed for the copper additions.

By induction melting, these alloys were prepared in graphite crucibles and poured into graphite molds. The aim composition of each melt was 78% zinc, but, under the melting conditions prevailing, it was found that between 1.5% and 2.0% zinc was lost during the melting operation.

The first step was the preparation of a copper-aluminum master alloy of near-eutectic composition. Fifty grams of copper were melted in a graphite crucible by induction melting and 150 grams of aluminum were added slowly to the melt. The resultant, brittle, near-eutectic alloy was poured into graphite molds and, subsequently, broken into small pieces for use in making the zinc-aluminum-copper alloys to be studied.

The manufacture of the actual alloys for this experiment was then initiated. The proper amount of aluminum was weighed out into a clean graphite crucible and melted. When this was in a molten state, the proper amount of a eutectic copper-aluminum (25% copper) alloy was added to give the essential amount of copper to the finished alloy. After this addition, the zinc was slowly and carefully added to the melt so that no part of the melt was ever cooled enough to freeze during the alloy additions.

During the first attempts at making this alloy, the melt was stirred with a graphite rod for two or three minutes prior to pouring. The result was that the ingots varied greatly in composition--the zinc content would vary in some cases from 65% to 95% zinc in the same ingot. This problem was solved by using a nitrogen lance and bubbling nitrogen gas through the melt just prior to pouring. It was necessary to make the gas stir the melt very vigorously in order to avoid inhomogeneous ingots from the cast alloy. Green flames during this mixing step showed that the greatest zinc loss occurred here.

After casting into the graphite crucibles, each ingot was clearly stamped with melt number and ingot number for future identification. Each ingot was then cold swaged to a diameter of 0.450 inches from its original diameter of 0.625 inches, a reduction of 48%. Each ingot was then annealed at 350° Centigrade for a minimum time of 36 hours. Following this, each ingot was quenched into room temperature water. A metallographic sample was then cut from both the bottom and the top of each ingot. These were cold mounted and viewed under a microscope at 600x to determine whether the eutectoid composition was obtained or whether the bar showed evidences of primary material on a eutectoid background. All the samples examined showed no detectible primary constituents even when viewed at magnifications approaching 1500x.

This metallographic examination was used in place of an analysis of the material because previous experience showed that large samples wanted for commercial wet chemical analysis (1 ounce) would not satisfactorily reveal the type of segregation that was being encountered.

Figure 4

Cold Swaging Machine

Cold swaging machine used in cold working cast alloy ingots to refine the structure.

Investigation with a Dilatometer

The Time=Temperature-Transformation curves of the three alloys were determined by making use of the change in dimensions as the alloy transformed from the high temperature phase to the two low temperature phases. This was accomplished in a Leitz Quenching type Dilatometer (Model HTV) which was equipped with an isothermal quenching bath made especially for this experiment by the author. The principal problem in constructing this quenching bath was installing all the necessary elements--heaters, stirrer, temperature controlling device, etc.--into the small space available in the instrument.

The isothermal quenching bath was heated by four 300 watt Japanese coffee cup immersion heaters and regulated with a stepless input timer. This provided the necessary heating capacity within the small space limitations. The quenching medium was water from 25° C. to 100° C., ethylene glycol from 100° C. to 150° C., and Sinclair Marquench Oil from 150° C. to 260 ° C.

In operation,the quartz tube (1 in Figure 5) was loaded with a small hemispherical quartz body (2 in Figure 5), with the specimen to be examined (3 in Figure 5), and with a small pointed quartz body and a thin quartz rod (4 and 5 in Figure 5 in the order named). The filled quartz tube was then inserted into the dilatometer.

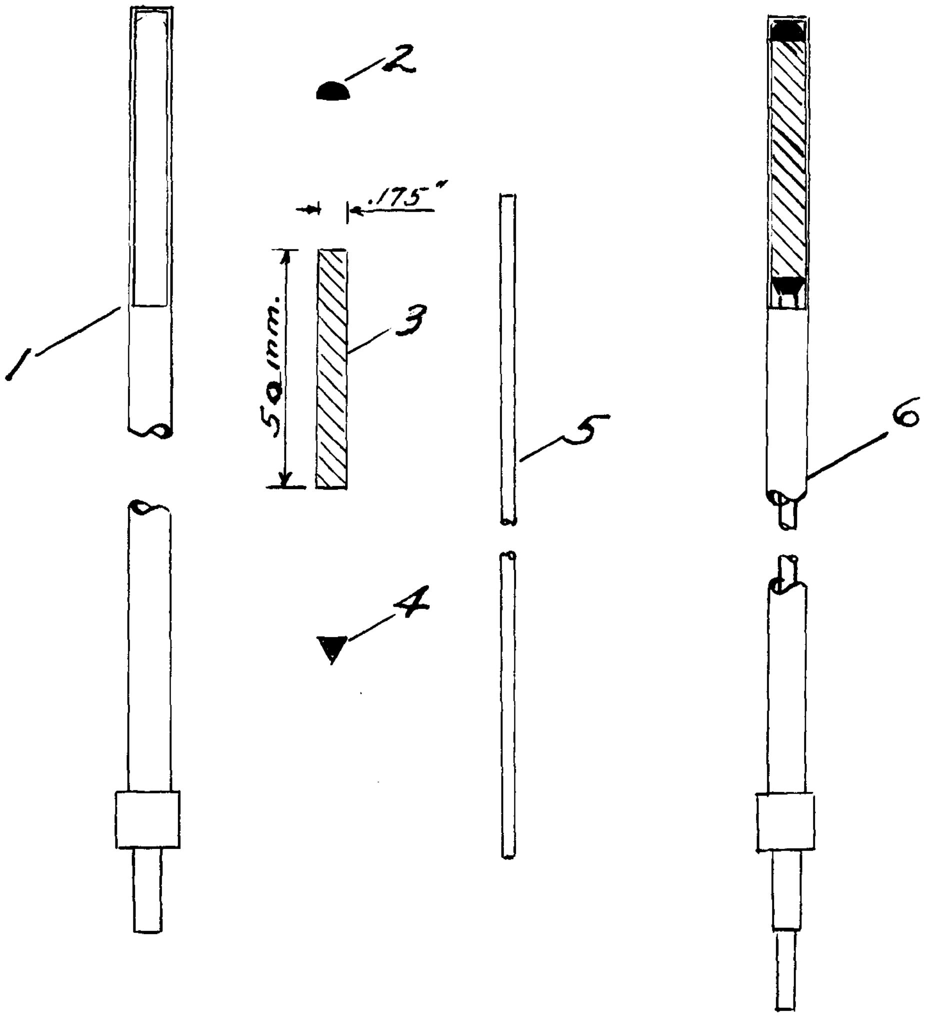


Figure 5.

Dilatometer Specimen Sub-Assembly

1. Quartz tube to hold the specimen
2. Hemispherical quartz body
3. Specimen
4. Cone-shaped quartz body
5. Quartz rod
6. Completed assembly ready for insertion in the dilatometer

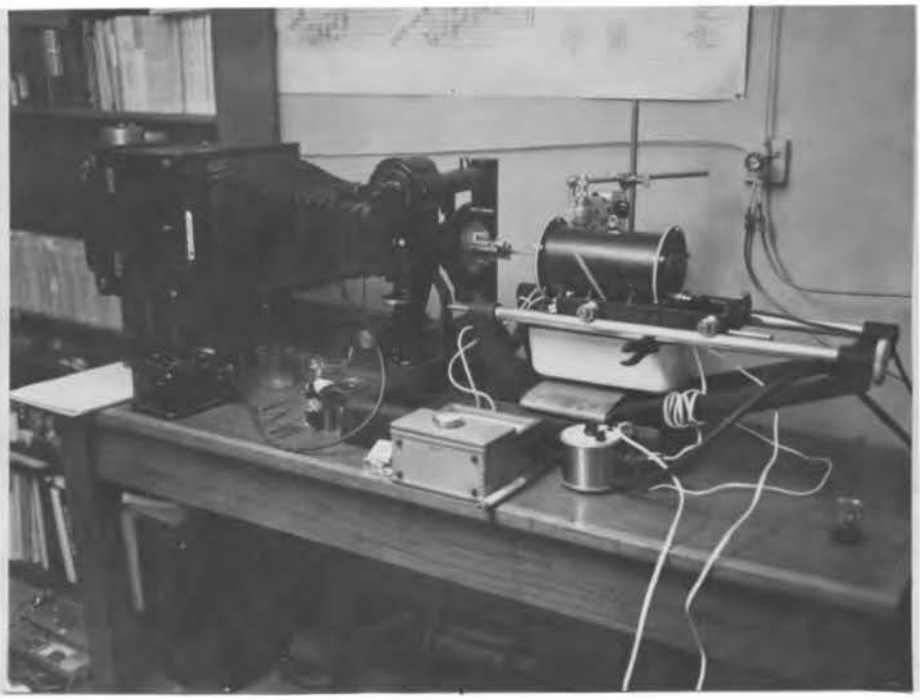


Figure 6

Dilatometer During the Heating Operation

Dilatometer with furnace in position to heat specimen into the high temperature phase region for 30 minutes.

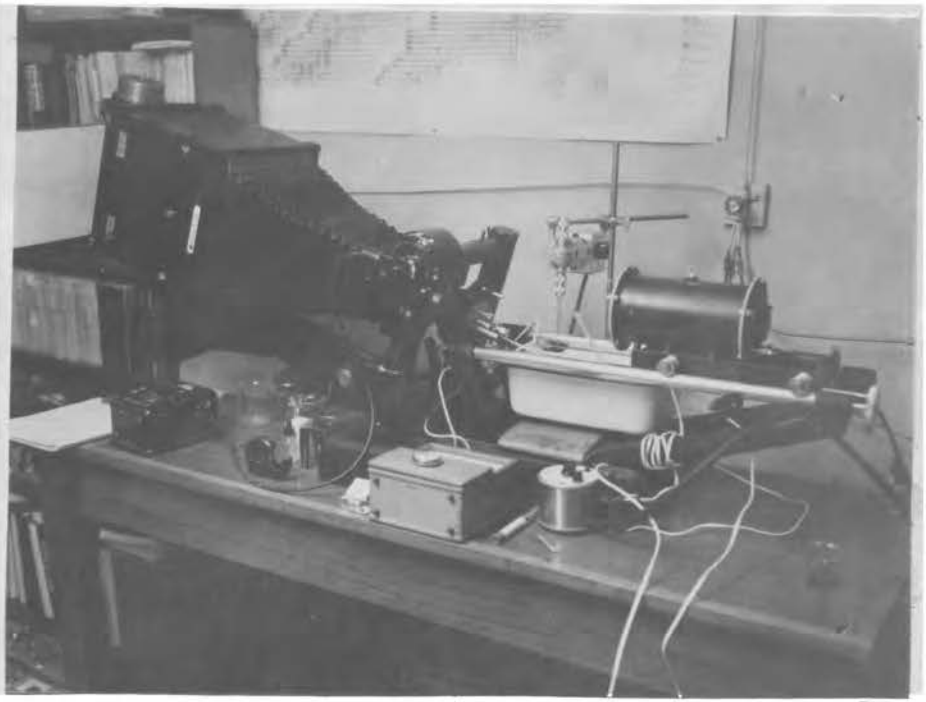


Figure 7

Dilatometer During the Quench

Dilatometer tilted in quench cycle so that the specimen is thrust into the quenching medium.

In operation, the expansion or contraction of the specimen caused the quartz rod to move in relation to the quartz tube and push against a prism. A light source which was incident upon this prism was then deflected and the resulting movement optically enlarged. Enlargements of 200x (standard), 400x, and 800x could be selected at the discretion of the operator. This spot of light could then be recorded on photographic paper mounted on a spring-driven drum capable of speeds of 50 mm., 100 mm., 150 mm. per hour respectively, or it could be visually observed. It was necessary to observe the light spot visually for some of the transformations because they occurred too fast for accurate measurement of time from the drum speed available.

In a typical run, the specimen was loaded into the dilatometer, as previously described. Next, the dilatometer furnace was guided into position so that the specimen could be heated (Figure 6). It was found advantageous to leave the furnace at its 305° Centigrade $\pm 1^{\circ}$ operating temperature throughout the entire length of the experiment. At this temperature, the furnace operated in steady state conditions; heat input balanced heat loss. Under these conditions, the specimen reached a temperature of 295° C. within 5 minutes 30 seconds after insertion into the furnace. Under normal operating conditions, the specimen was in the furnace for 30 minutes at operating temperature, making the total time the specimen was in the furnace prior to the quench 35 minutes, 30 seconds. The furnace was quickly moved out of the way and the unit tilted (Figure 7) so that the specimen was thrust into the quenching tank. It was possible to quench a specimen from the 305° C. furnace temperature to within 5° C. of the bath temperature of 25° C. consistently within 11 seconds when using water as the quenching medium. When Marquench Oil was used for the high temperature runs, 25 seconds were required for the specimen to reach bath temperature.

Originally it was intended that the whole heating to temperature, holding at temperature, and the quenching cycle would be recorded on photographic paper for a permanent record. It was soon found that the pure zinc-aluminum eutectoid alloy was extremely plastic, and small amounts of pressure would cause permanent creep deformation. In order for a dilatometer to record changes in specimen length, it was necessary for a small amount of pressure to be applied to the speciman by the return spring on the quartz rod (5 in Figure 5). This problem was eliminated by applying the pressure no more than 3 minutes before quenching the specimen. Unfortunately this prevented recording the original specimen length on the photographic paper or changes in the specimen length until just before the quenching operation.

The small hole in the standard sample[37] was eliminated from the specimens used in this investigation in order to strengthen the sample and avoid creep deformation. However, in the preliminary work, the thermocouple was inserted into a small hole in the sample for accurate determinations of the exact specimen temperature and cooling rate, etc.;but, thereafter, the thermocouple was placed just touching the sample, and the hole in the specimen was eliminated. This gave the temperature of the specimen surface, and, from the previous data, the temperature of the specimen center was known under the various conditions, occurring in this investigation.

Typical dilatometer recorded curves resulting from this procedure are given on the following pages.

---

[37] Pamphlet, Dilatometer for the Thermal Analysis of Metals and other Materials,(Ernest Leitz Wetzler, Germany,VI/58/AX/L.)

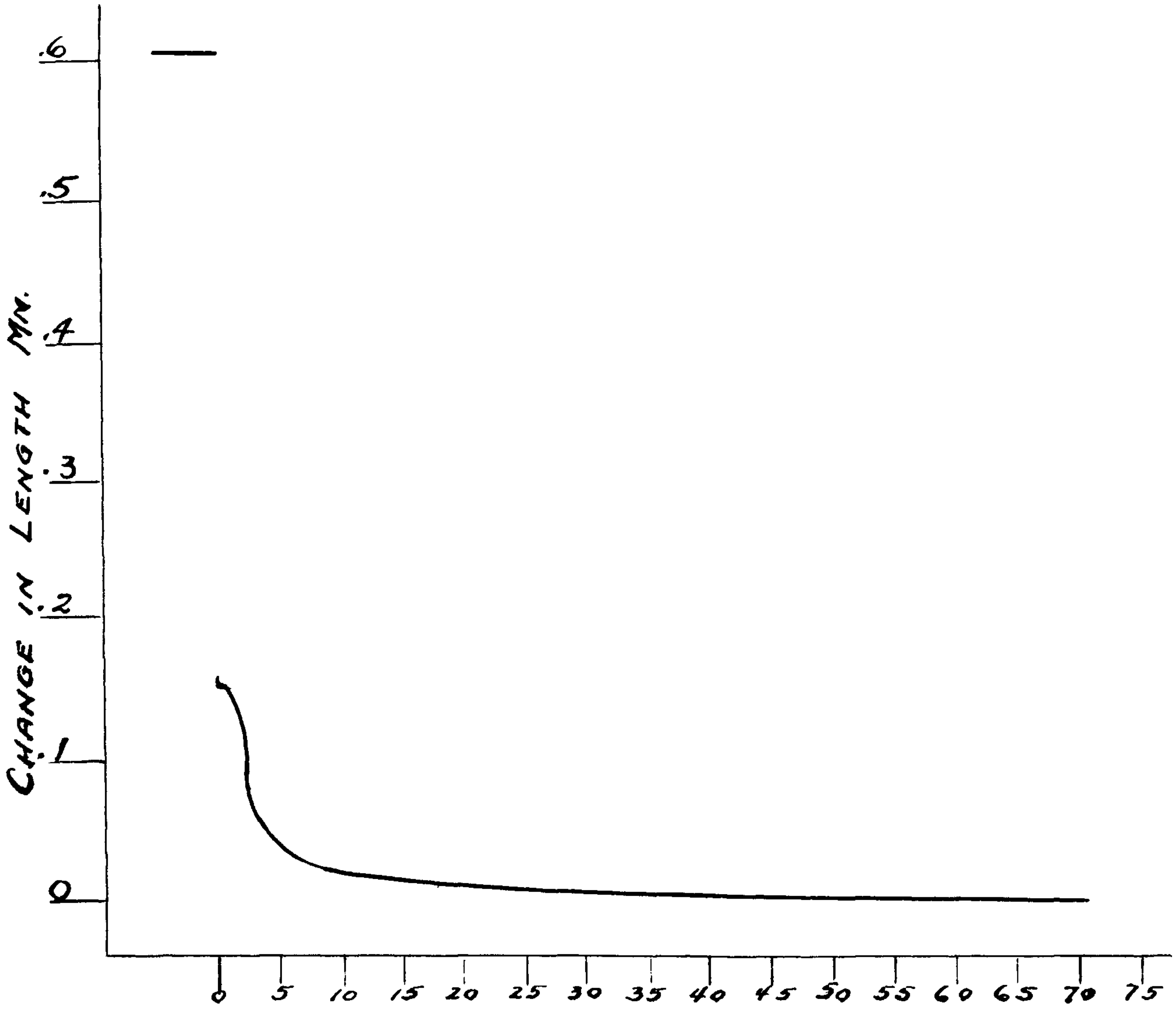


Figure 8

Dilatometer tracing of a 78% zinc-22% aluminum alloy quenched from 305° C. into water at 25° C. The specimen was heated 30 minutes at 305° C. before quenching.

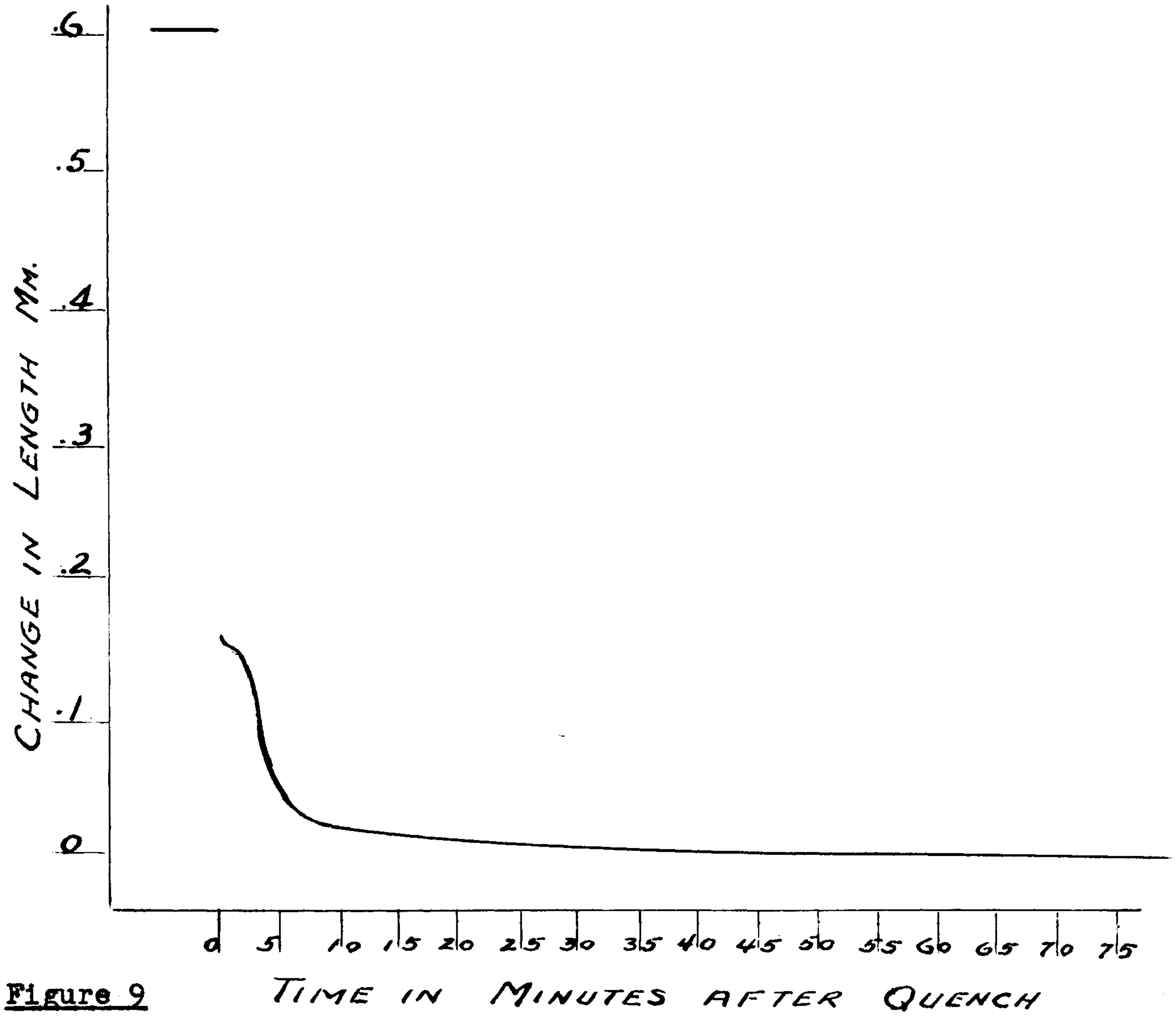


Figure 9

Dilatometer tracing of a 78% Zn-21.9% Al-0.1% Cu alloy quenched from 305° C. into water at 25° C. The specimen was heated 30 minutes at 305° C. before quenching.

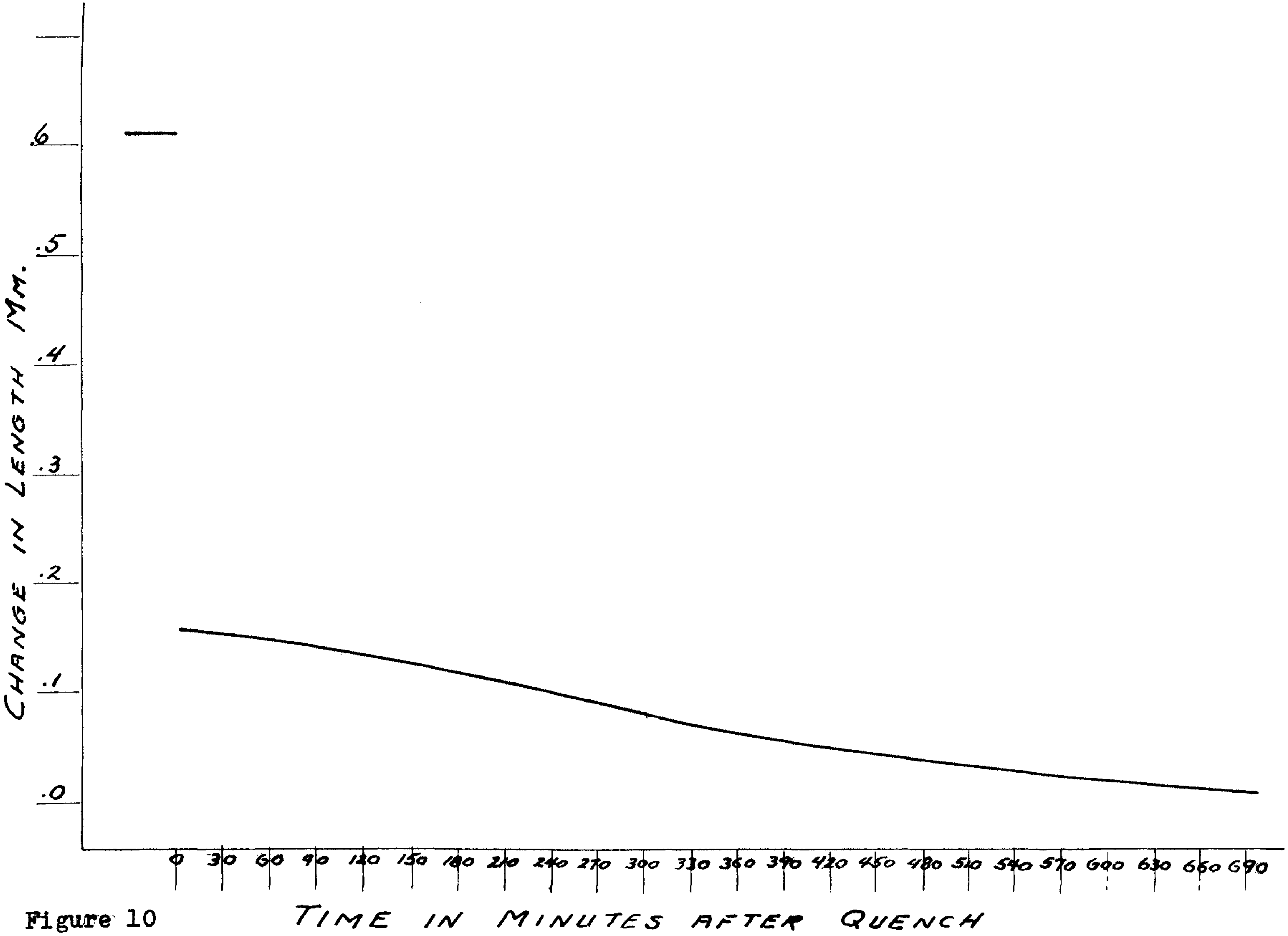


Figure 10

Dilatometer tracing of a 78% Zn.-21.0% Al.-1.0% Cu. alloy quenched from 305° C. into water at 25° C. The specimen was heated 30 minutes at 305° C. before quenching.

Microstructures

Specimens of each of the three alloys were metallographically polished and then given a high-temperature soak at 320° C. for two hours. The specimens were then removed from the furnace and quenched into water at room temperature. After various lengths of time in the quench bath, the specimens were removed and etched with a 5% solution of nital, (5% solution of concentrated nitric acid and alcohol), washed with alcohol, and dried.

The etched specimen was found to remain visibly unchanged, although the phase change proceeded normally after the surface had been etched.

Garwood and Hopkins[38] in a previous investigation showed that the first microscopically visible changes began slightly before the change in length of a dilatometric specimen indicated as the start of the reaction at temperatures below the nose of the TTT curve. It is thought that this is a surface phenomenon, associated with the fact that the specimens were already polished before being given the heat treatment cycle.

The photomicrographs obtained by this method are presented on the following pages.

---

[38] R. D. Garwood and A. D. Hopkins, "The Kinetics of the Eutectoid Transformation in Zinc-Aluminum Alloys," J. Inst. Metals, (1952) Vol. 81, p. 409.

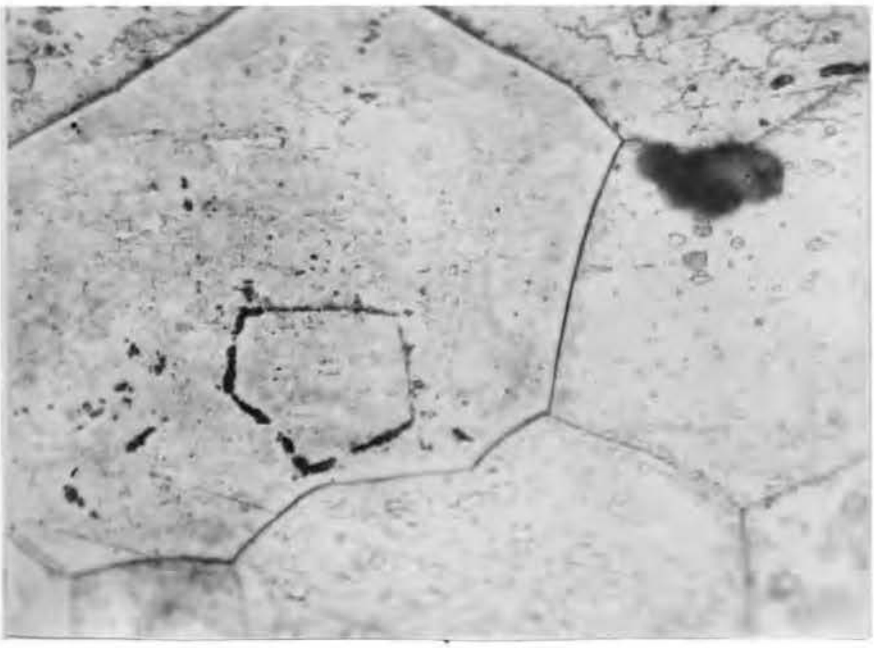


Figure 11 500x

78% zinc-22% aluminum alloy heated to 320° C. for 30 minutes and then quenched into water maintained at 25° C. Photograph shows the microstructure 18 seconds after quenching. (Etched with 5% Nital) The high-temperature phase (γ) appears light in color, while the reaction products ($\alpha + \beta$) appear dark in the photomicrograph.

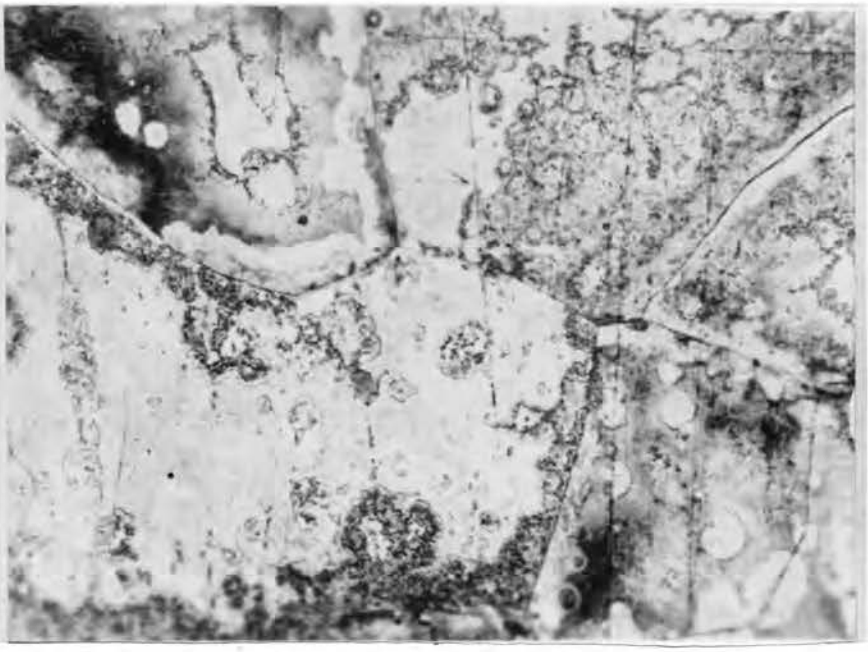


Figure 12 500x

78% zinc-22% aluminum alloy heated to 320° C. for 30 minutes and then quenched into water maintained at 25° C. Photograph shows the microstructure 65 seconds after quenching.

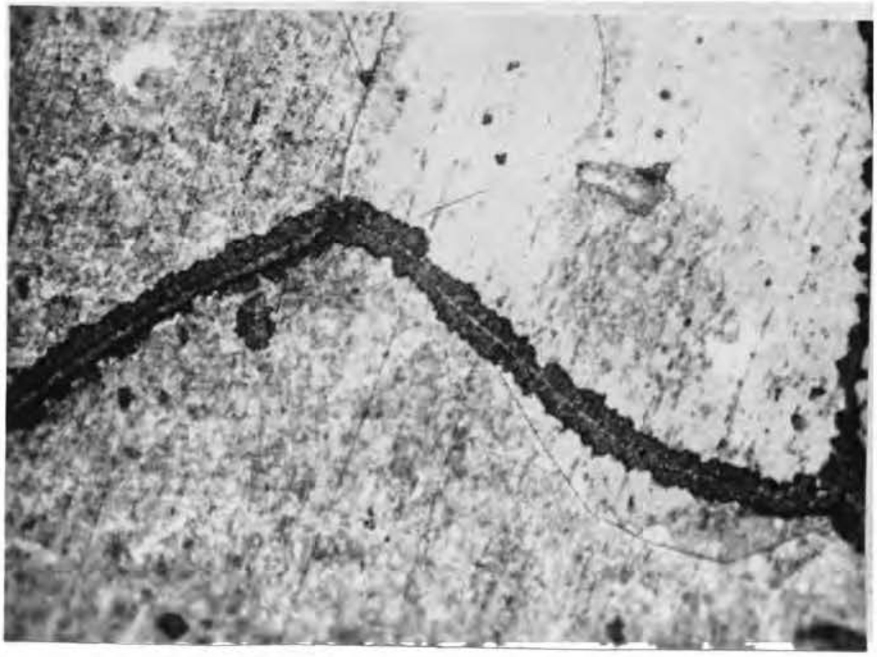


Figure 13 500x

78% zinc-22% aluminum alloy heated to 320° C. for 30 minutes and then quenched into water maintained at 25° C. Photograph shows the microstructure 5 minutes after quenching. (Etched with 5% Nital)

Figure 14 500x

78% zinc-22% aluminum alloy heated to 320° C. for 30 minutes and then quenched into water maintained at 25° C. Photograph shows the microstructure 8 minutes after quenching. (Etched with 5% Nital)

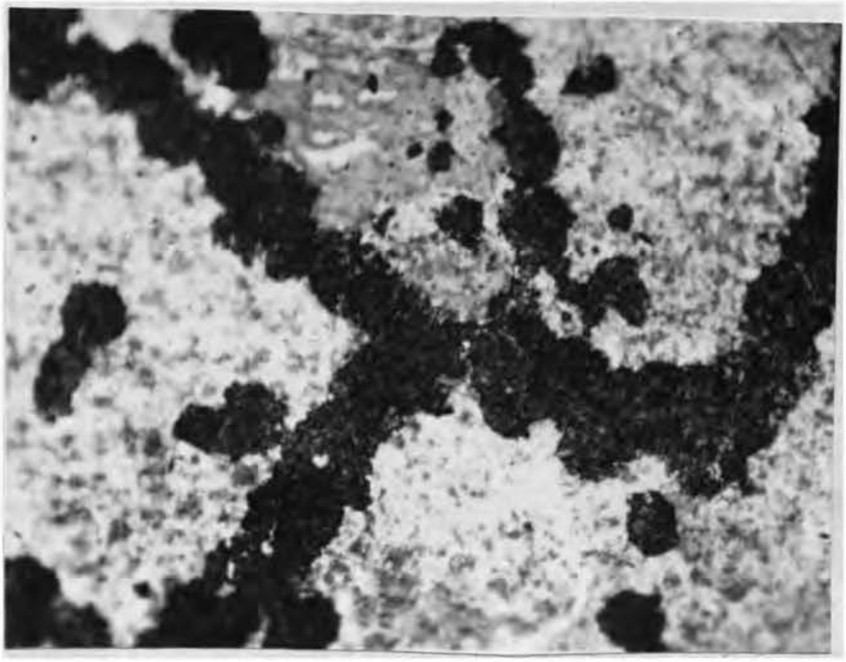


Figure 15 500x

78% zinc-22% aluminum alloy heated to 320° C. for 30 minutes and then quenched into water maintained at 25° C. Photograph shows the microstructure 10 minutes after quenching. (Etched with 5% Nital)

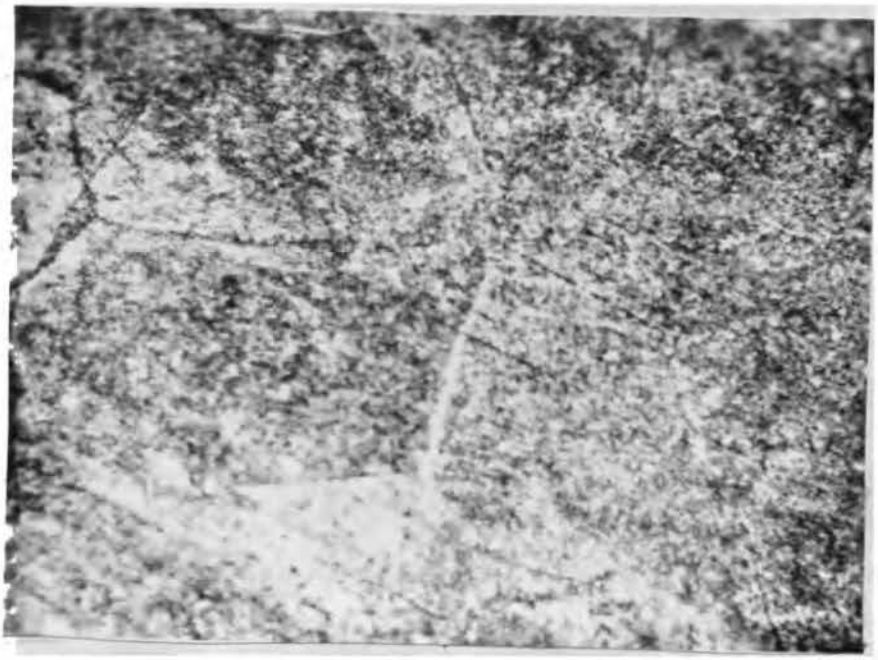


Figure 16 500x

78% zinc-22% aluminum alloy heated to 320° C. for 30 minutes and then quenched into water maintained at 25° C. Photograph shows the microstructure 15 minutes after quenching. (Etched with 5% Nital)

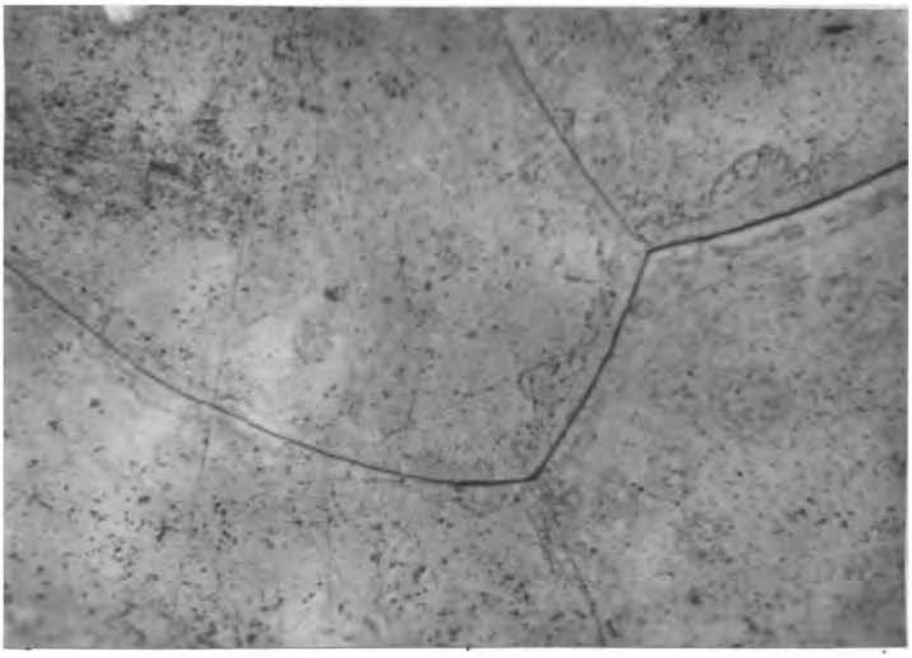


Figure 17 500x

78% Zn.-21.9% Al.-0.1% Cu. alloy heated to 320° C. for 30 minutes and then quenched into water maintained at 25° C.. Photograph shows the microstructure 10 seconds after quenching. (Etched with 5% Nital)

Figure 18 500x

78% Zn.-21.9% Al.-0.1% Cu. alloy heated to 320° C. for 30 minutes and then quenched into water maintained at 25° C. Photograph shows the microstructure 3 minutes after quenching. (Etched with 5% Nital)

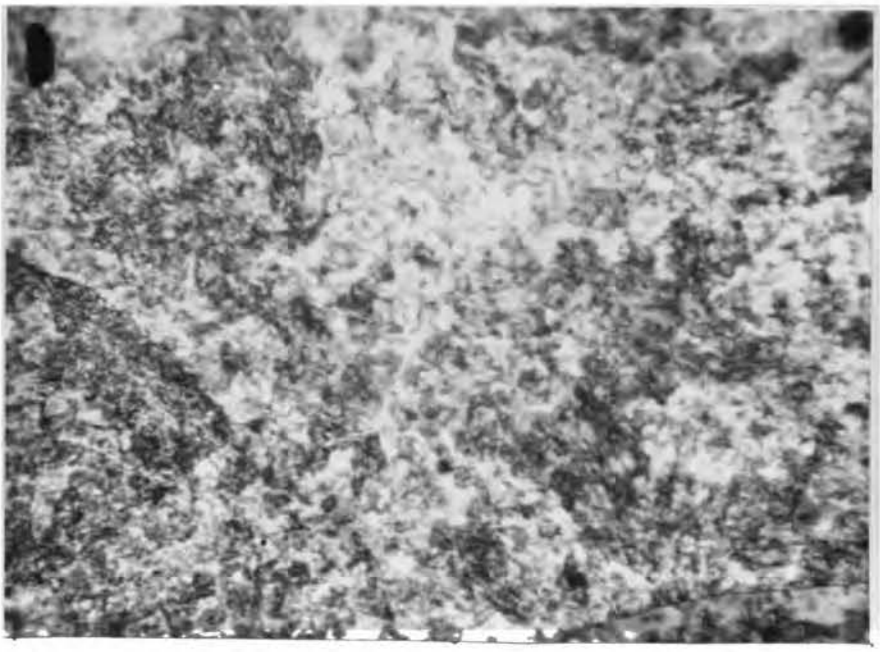


Figure 19 500x

78% Zn.-21.9% Al.-0.1% Cu. alloy heated to 320° C. for 30 minutes and then quenched into water maintained at 25° C.. Photograph shows the microstructure 5 minutes after quenching. (Etched with 5% Nital)

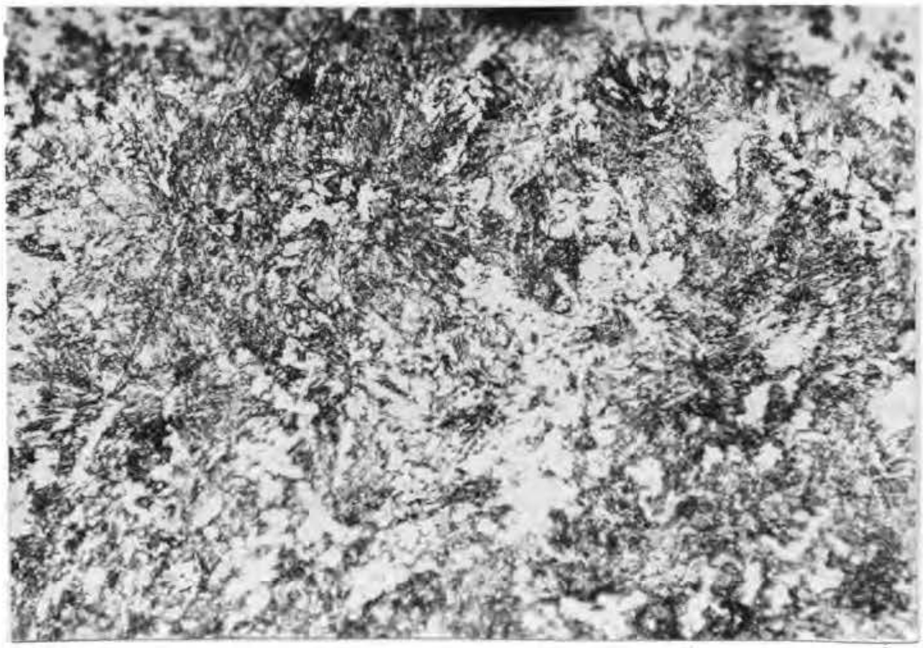


Figure 20 500x

78% Zn.-21.9% Al.-0.1% Cu. alloy heated to 320° C. for 30 minutes and then quenched into water maintained at 25° C. Photograph shows the microstructure 10 minutes after quenching. (Etched with 5% Nital)

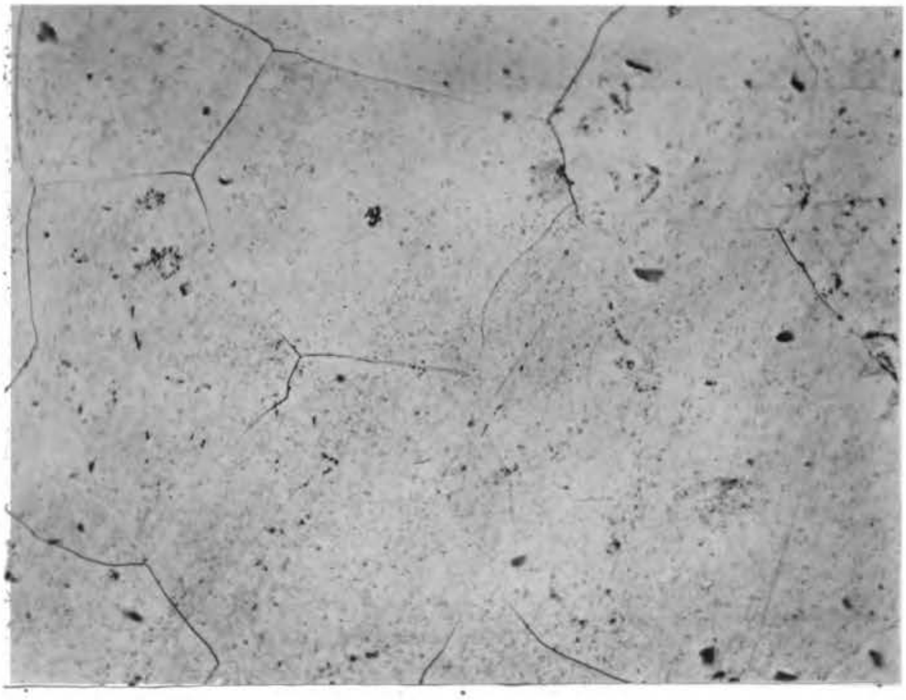


Figure 21 500x

78% Zn.-21% Al.-1.0% Cu. alloy heated to 320° C. for 30 minutes and then quenched into water maintained at 25° C. Photograph shows the microstructure 10 seconds after quenching. (Etched with 5% Nital)

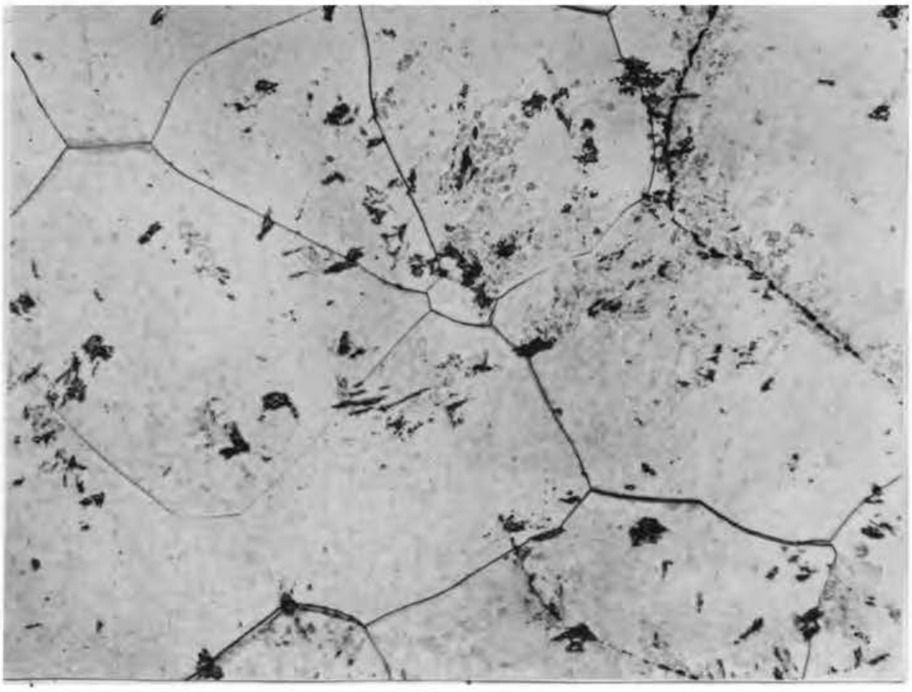


Figure 22 500x

78% Zn.-21% Al.-1.0% Cu. alloy heated to 320° C. for 30 minutes and then quenched into water maintained at 25° C. Photograph shows the microstructure 2 minutes after quenching. (Etched with 5% Nital

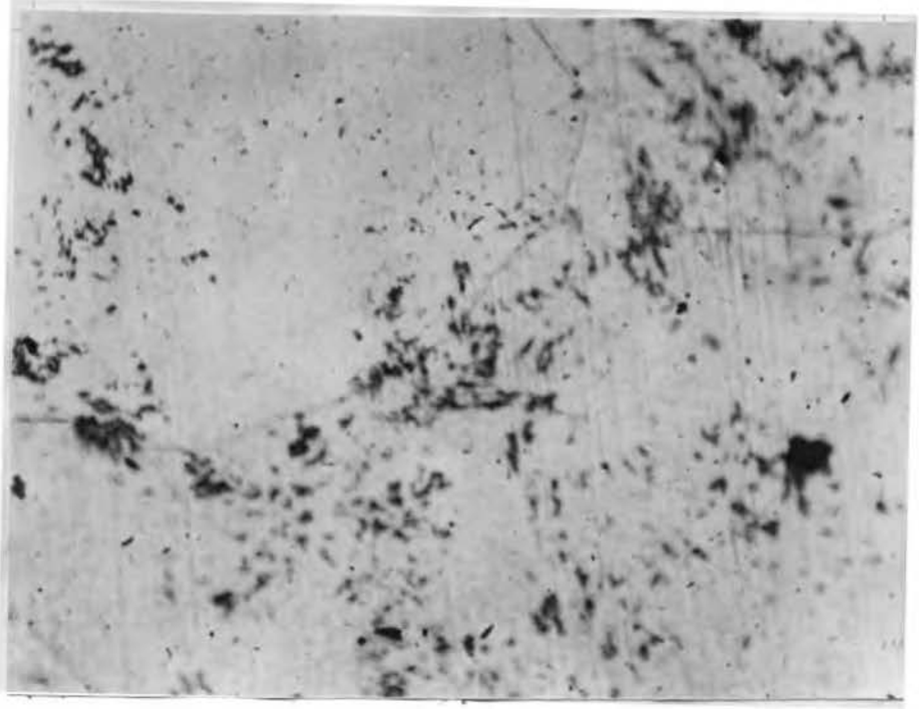


Figure 23 500x

78% Zn.-21% Al.-1.0% Cu. alloy heated to 320° C. for 30 minutes and then quenched into water maintained at 25° C. Photograph shows the microstructure 10 minutes after quenching. (Etched with 5% Nital)

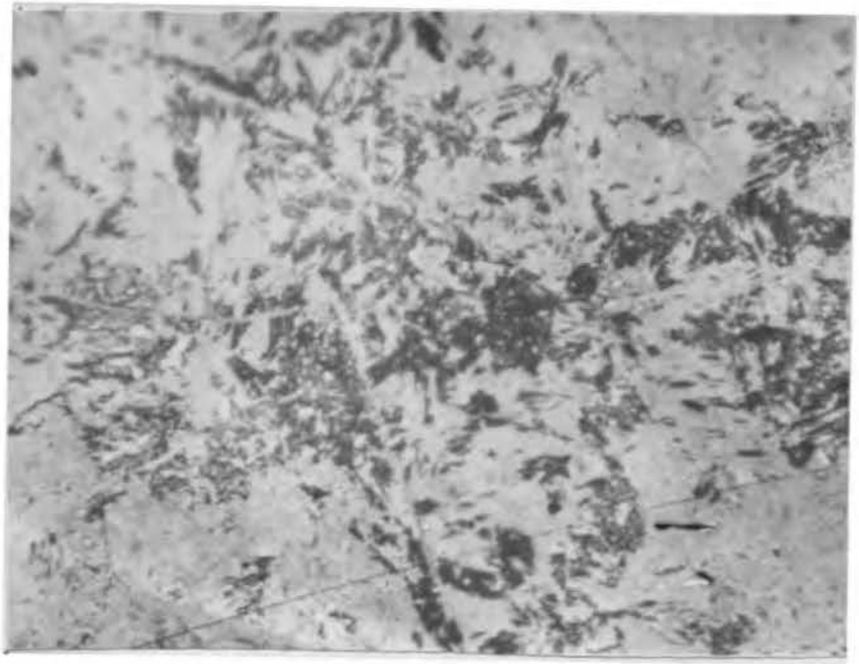


Figure 24 500x

78% Zn.-21% Al.-1.0% Cu. alloy heated to 320° C. for 30 minutes and then quenched into water maintained at 25° C. Photograph shows the microstructure 30 minutes after quenching. (Etched with 5% Nital)

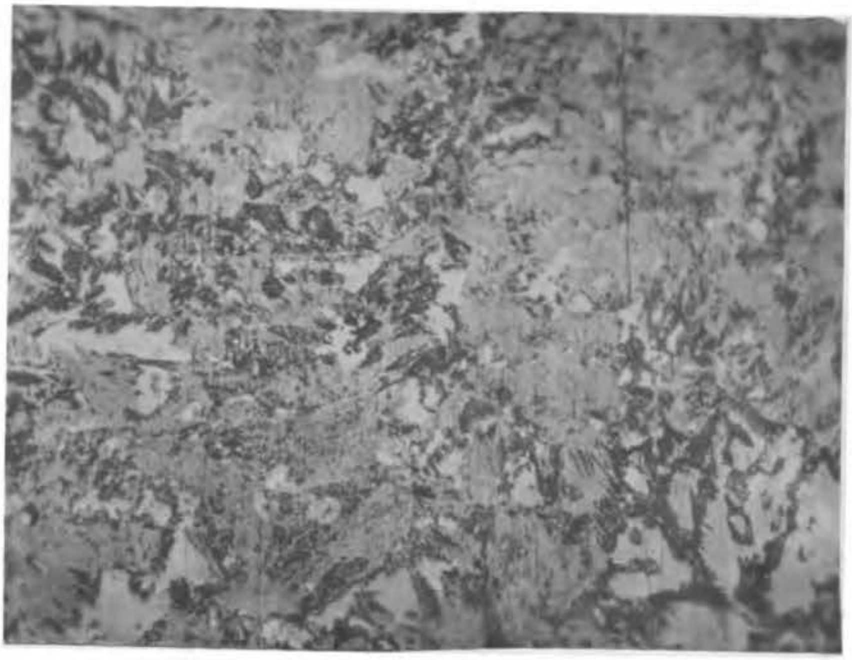


Figure 25 500x

78% Zn.-21% Al.-1.0% Cu. alloy heated to 320° C. for 30 minutes and then quenched into water maintained at 25° C. Photograph shows the microstructure 60 minutes after quenching. (Etched with 5% Nital)

IV. EXPERIMENTAL DATA AND DISCUSSION

The dilatometer was utilized in the manner previously discussed (pages 21-27) in investigating the kinetics of the eutectoid reaction for each of the three alloys. The effect of both time and temperature of the high temperature "soak" on the kinetics of the eutectoid reaction were investigated, and the Time-Temperature-Transformation (TTT) curves were determined for each of the three alloys.

It was found that the time of the high-temperature "soak" had no effect on the speed of the eutectoid reaction within the limits of the 15 minute to 60 minute soaking times employed in this investigation. The experimental data, supporting this conclusion, are shown in tables II, III, and IV.

The soaking temperature was discovered to have no detectable effect on the reaction kinetics of the pure zinc-aluminum eutectoid alloy or the alloy with 0.1% copper content. However, in the alloy containing 1.0% copper, it was found that higher soaking temperatures delayed the onset of the transformation. Nevertheless, once the reaction began, the specimens' transformations occurred at the same speed regardless of the soaking temperature employed before the specimens were quenched. In other words, the effect of the higher soaking temperatures was to move the transformation versus time curve toward the right on the time axis without changing its shape. (See figures 29 and 30.) Except for the length of time before the transformation began, the dilatometer curves are identical.

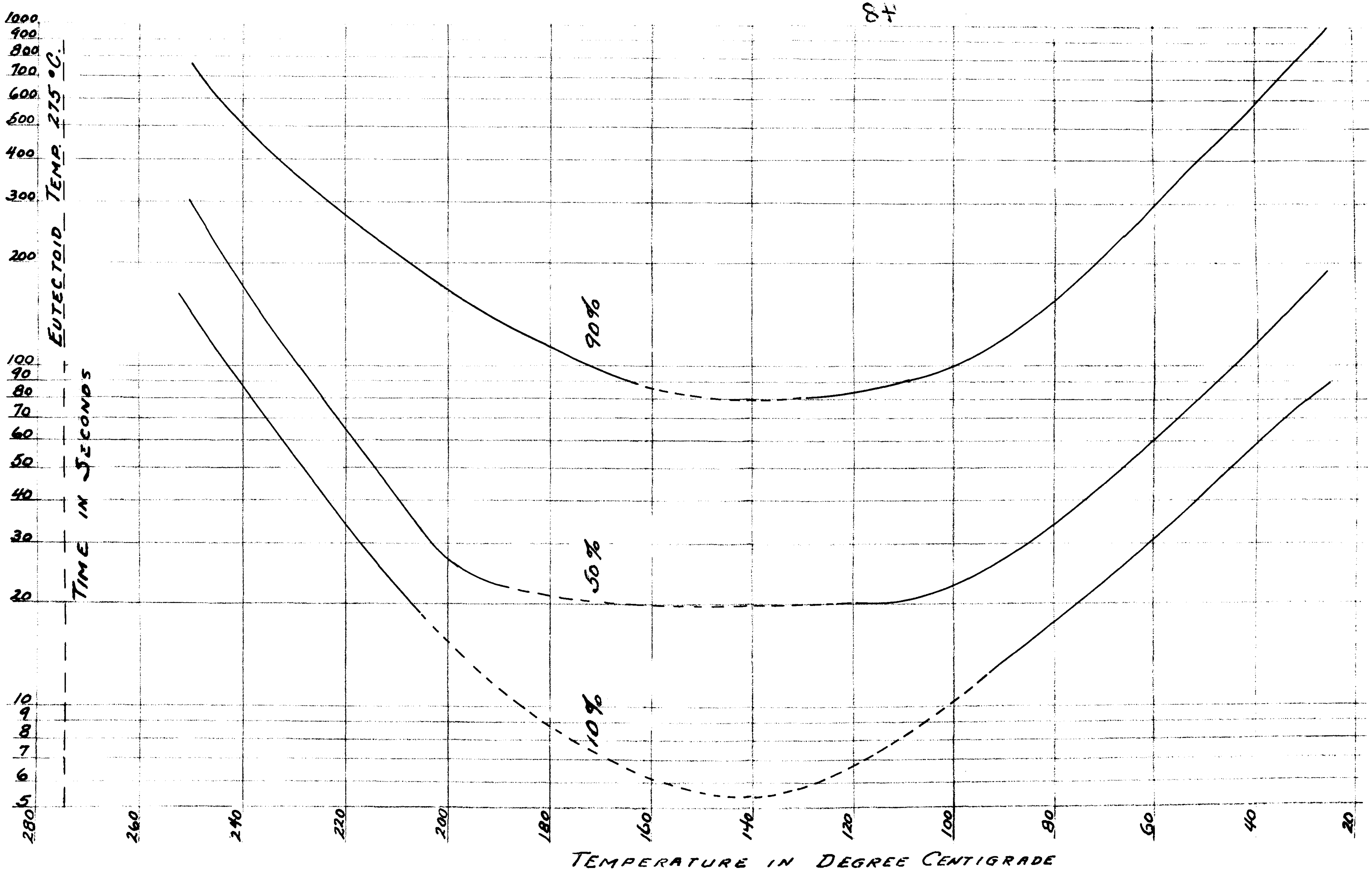


FIGURE 26 — TIME / TEMPERATURE / TRANSFORMATION (TTT) DIAGRAM FOR ZINC — 22 % ALUMINUM ALLOY, CONSTRUCTED FROM DILATOMETER CURVES.

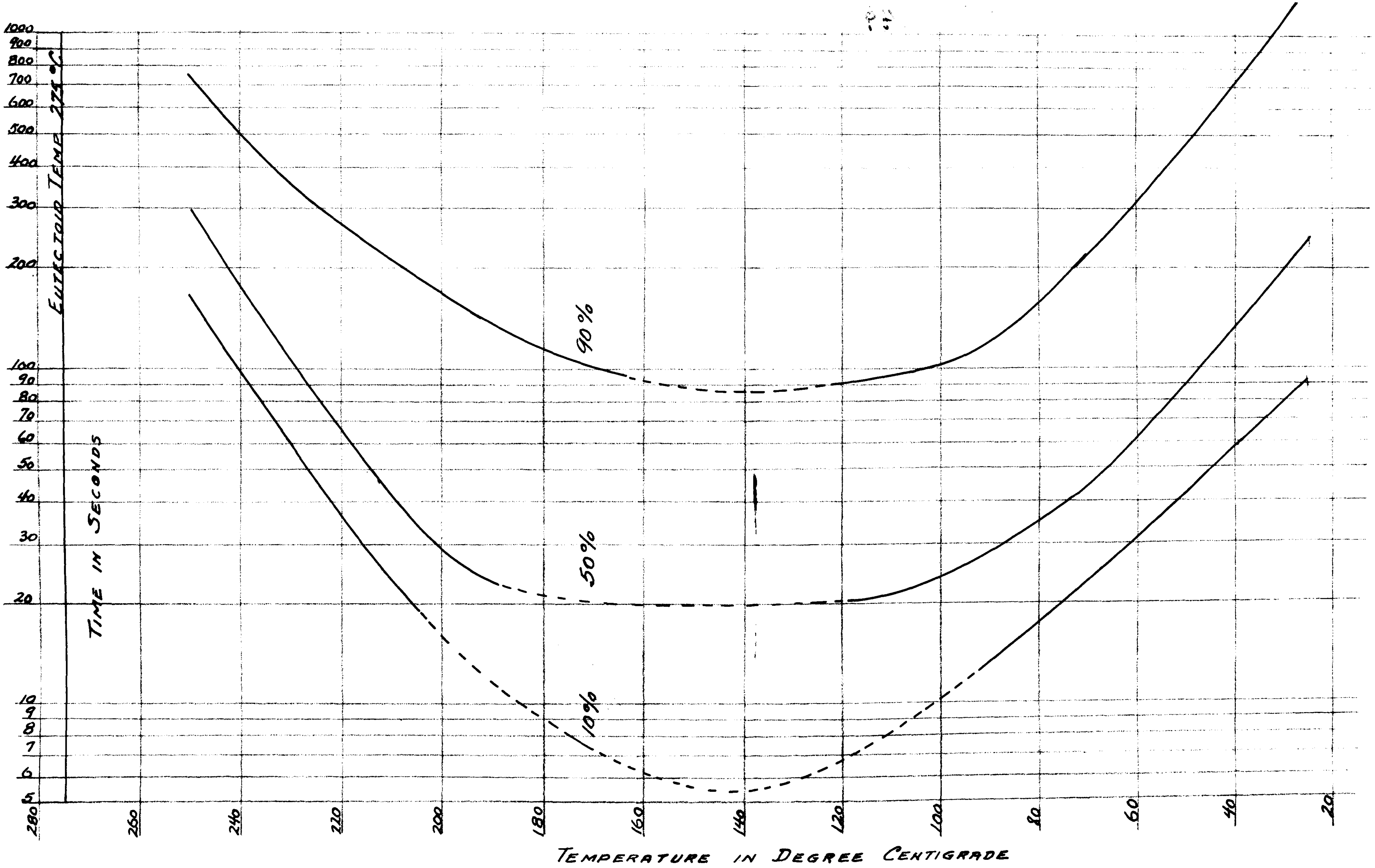


FIGURE 27 – TIME/TEMPERATURE/TRANSFORMATION (TTT) DIAGRAM FOR ZINC – 21.9% ALUMINIUM, 0.1% COPPER ALLOY, CONSTRUCTED FROM DILATOMETER CURVES.

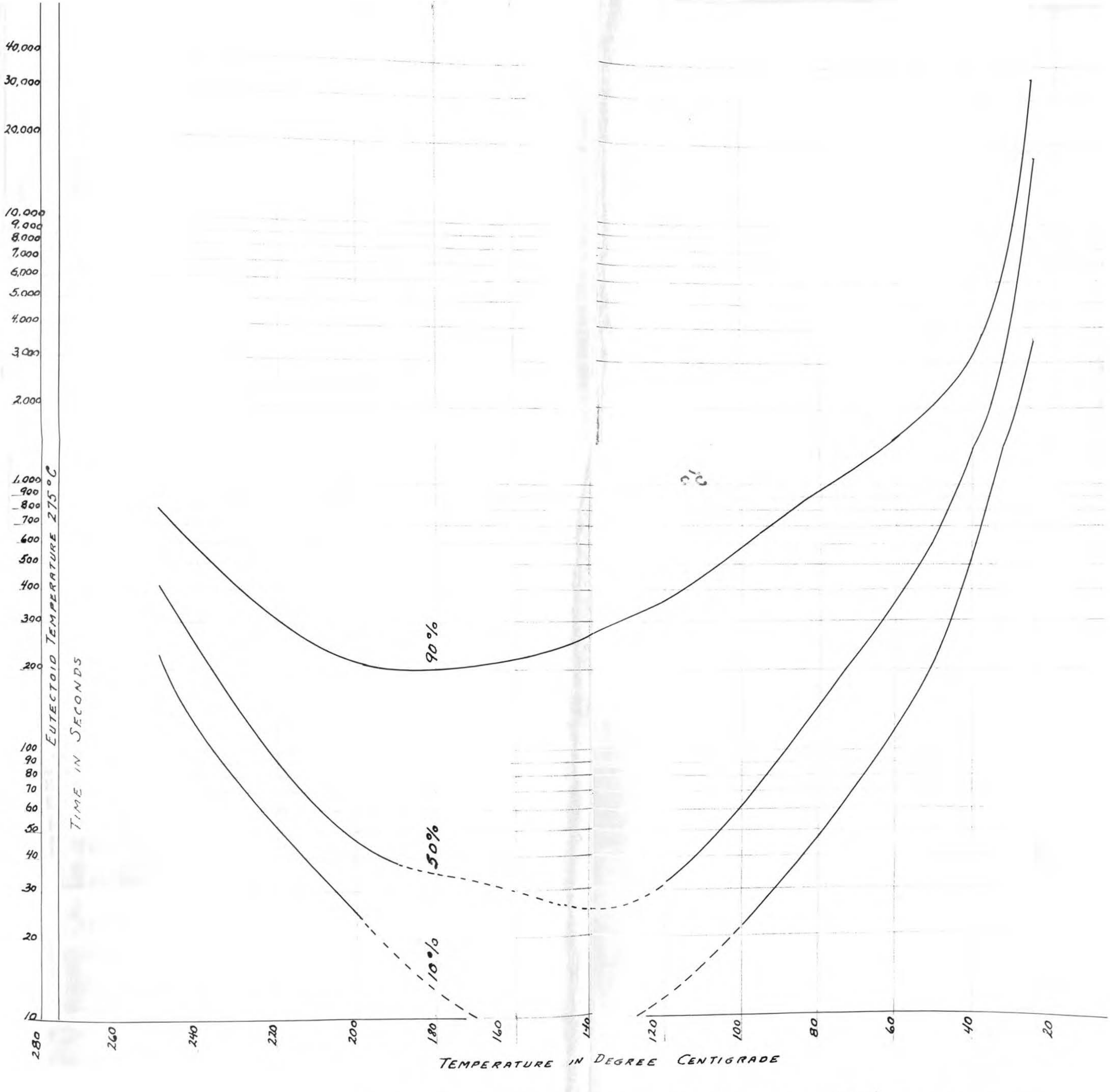


Figure 28 — Time/Temperature/Transformation (TTT) Diagram for Zinc — 21.0 % Aluminium — 1.0 % Copper Alloy, Constructed from Dilatometer Curves.

TABLE I

Effect of solution temperature on the speed of the eutectoid reaction for a 78% Zn-22% Al specimen quenched in water at 25° C. Time at temperature held constant at 30 minutes.

REACTION KINETICS IN SECONDS

Solution Temperature	Transformation Begins	Transformation 10% complete	Transformation 50% complete	Transformation 90% complete	Transformation Ends
300° C.	60	105	215	970	2075
310° C.	40	80	195	1080	2060
320° C.	65	90	195	1005	2130
330° C.	50	100	230	1140	2580
340° C.	45	80	205	1080	2040
Average	52	91	208	1055	2177

TABLE II

Effect of solution time on the speed of the eutectoid reaction for a 78% Zn-22% Al specimen quenched in water at 25° C. Temperature held constant at 310° C.

REACTION KINETICS IN SECONDS

Time at Temperature	Transformation Begins	Transformation 10% complete	Transformation 50% complete	Transformation 90% complete	Transformatio Ends
15 min.	30	60	160	1080	2130
20 min.	60	120	240	945	1950
30 min.	30	70	195	1080	2060
60 min.	45	70	165	930	1980
Average	41	80	190	1008	2030

TABLE III

Effect of solution time and temperature on the speed of the eutectoid reaction for a 78% Zn - 21.9% Al - 0.1% Cu alloy quenched in water at 25° C.

REACTION KINETICS IN SECONDS

Solution Temperature	Solution Time	Transformation 10% complete	Transformation 50% complete	Transformation 90% complete
300° C.	15 min.	88	255	1080
300° C.	30 min.	90	255	1080
300° C.	60 min.	90	250	1080
310° C.	30 min.	83	255	1075
320° C.	30 min.	91	250	1080
330° C.	30 min.	100	240	1080
340° C.	15 min.	88	245	1085
340° C.	60 min.	90	250	1075
	Average	90	250	1080

TABLE IV

Effect of solution time and temperature on the speed of the eutectoid reaction for a 78% Zn - 21.0% Al -1.0% Cu alloy quenched in water at 80° C.

REACTION KINETICS IN SECONDS

Solution Temperature	Solution Time	Transformation 10% complete	Transformation 50% complete	Transformation 90% complete
300° C.	15 min.	45	148	945
300° C.	60 min.	47	148	950
310° C.	30 min.	50	155	955
320° C.	30 min.	60	164	965
330° C.	30 min.	75	180	980
340° C.	30 min.	90	192	980
350° C.	15 min.	105	208	1005
350° C.	60 min.	105	210	1000

TABLE V

Effect of quench bath temperature on the speed of the eutectoid reaction for a 78% Zn - 22% Al alloy. Specimens were held at 305° C. for 30 minutes before quenching.

REACTION KINETICS IN SECONDS

Quench bath Temperature	Transformation 10% complete	Transformation 50% complete	Transformation 90% complete
250° C.	143	308	761
240° C.	88	270	507
230° C.	56	105	360
210° C.	23	41	210
190° C.	11	22	128
170° C.	7	20	97
160° C.	6	20	86
150° C.	5	20	78
130° C.	6	20	81

TABLE V (continued)

Quench bath Temperature	Transformation 10% complete	Transformation 50% complete	Transformation 90% complete
110° C.	8	20	88
90° C.	14	27	119
70° C.	23	45	209
50° C.	42	84	417
25° C.	80	191	1008

TABLE VI

Effect of quench bath temperature on the speed of the eutectoid reaction for a 78% Zn - 21.9% Al - 0.1% Cu alloy. Specimens were held at 305° C. for 30 minutes before quenching.

REACTION KINETICS IN SECONDS

Quench bath Temperature	Transformation 10% complete	Transformation 50% complete	Transformation 90% complete
250° C.	170	300	760
240° C.	98	180	500
230° C.	60	105	350
210° C.	23	41	208
190° C.	11	23	142
170° C.	7	21	99
160° C.	6	20	92
150° C.	6	20	87
130° C.	6	20	88

TABLE VI (continued)

Quench bath Temperature	Transformation 10% complete	Transformation 50% complete	Transformation 90% complete
110° C.	8	21	96
90° C.	13	29	103
70° C.	24	46	223
50° C.	44	91	483
25° C.	92	250	1080

TABLE VII

Effect of quench bath temperature on the speed of the eutectoid reaction for a 78% Zn - 21.0% Al - 1.0% Cu alloy. Specimens were held at 305° C. for 30 minutes before quenching.

REACTION KINETICS IN SECONDS

Quench bath Temperature	Transformation 10% complete	Transformation 50% complete	Transformation 90% complete
250° C.	263	411	816
240° C.	131	243	560
230° C.	79	148	406
210° C.	36	62	248
190° C.	17	38	200
170° C.	10	34	206
160° C.	8	29	221
150° C.	6	27	242
130° C.	10	26	308

<u>TABLE VII</u> (continued)

Quench bath Temperature	Transformation 10% complete	Transformation 50% complete	Transformation 90% complete
110° C.	15	42	440
90° C.	31	92	743
70° C.	76	248	1194
50° C.	218	670	2410
25° C.	3,600	18,000	36,000

The Time-Temperature-Transformation curves (figures 26, 27, and 28) show that copper inhibits the transformation, especially at low temperatures (80° C. and below). At temperatures near or above the nose of the TTT curve, the effect of copper additions on the eutectoid reaction kinetics is much smaller than at lower temperatures because diffusion occurs much more rapidly at higher temperatures.

The TTT curves, illustrated in figures 26, 27, and 28, have broken lines in the vicinity of the curves' "nose" because the transformation proceeds at these temperatures so quickly that it is impossible to ascertain the exact reaction kinetics with the techniques employed in this investigation.

These results indicate that copper influences the speed of the eutectoid reaction in the zinc-aluminum system by interfering with the diffusion of zinc and aluminum atoms as the high-temperature phase decomposes into two low-temperature phases. One of these low-temperature phases must contain a higher percentage of zinc atoms than the "parent" phase; the other must be richer in aluminum atoms. Copper atoms act as "roadblocks" and slow down the speed with which the necessary diffusion can proceed, thereby delaying the reaction. This process is most effective at lower temperatures where diffusion is slower anyway.

If copper slows the eutectoid reaction when the alloy changes from the one-phase field into the two-phase field, copper atoms would be expected to slow also the reverse

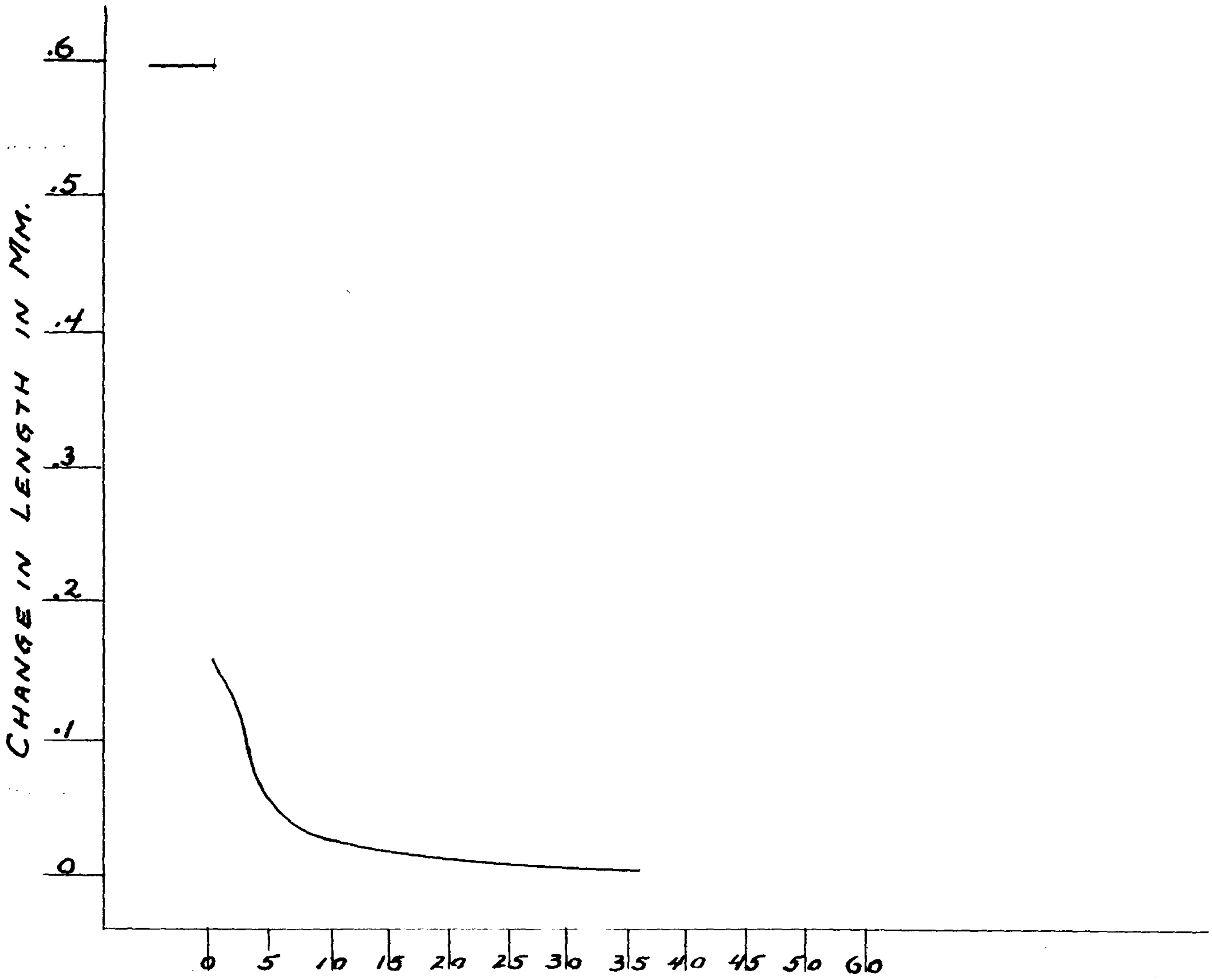


Figure 29

Dilatometer tracing of a 78% Zn-21.0% Al-1% Cu alloy quenched from 300° C. into water at 80° C. The specimen was heated 30 minutes at 300° C. before quenching.

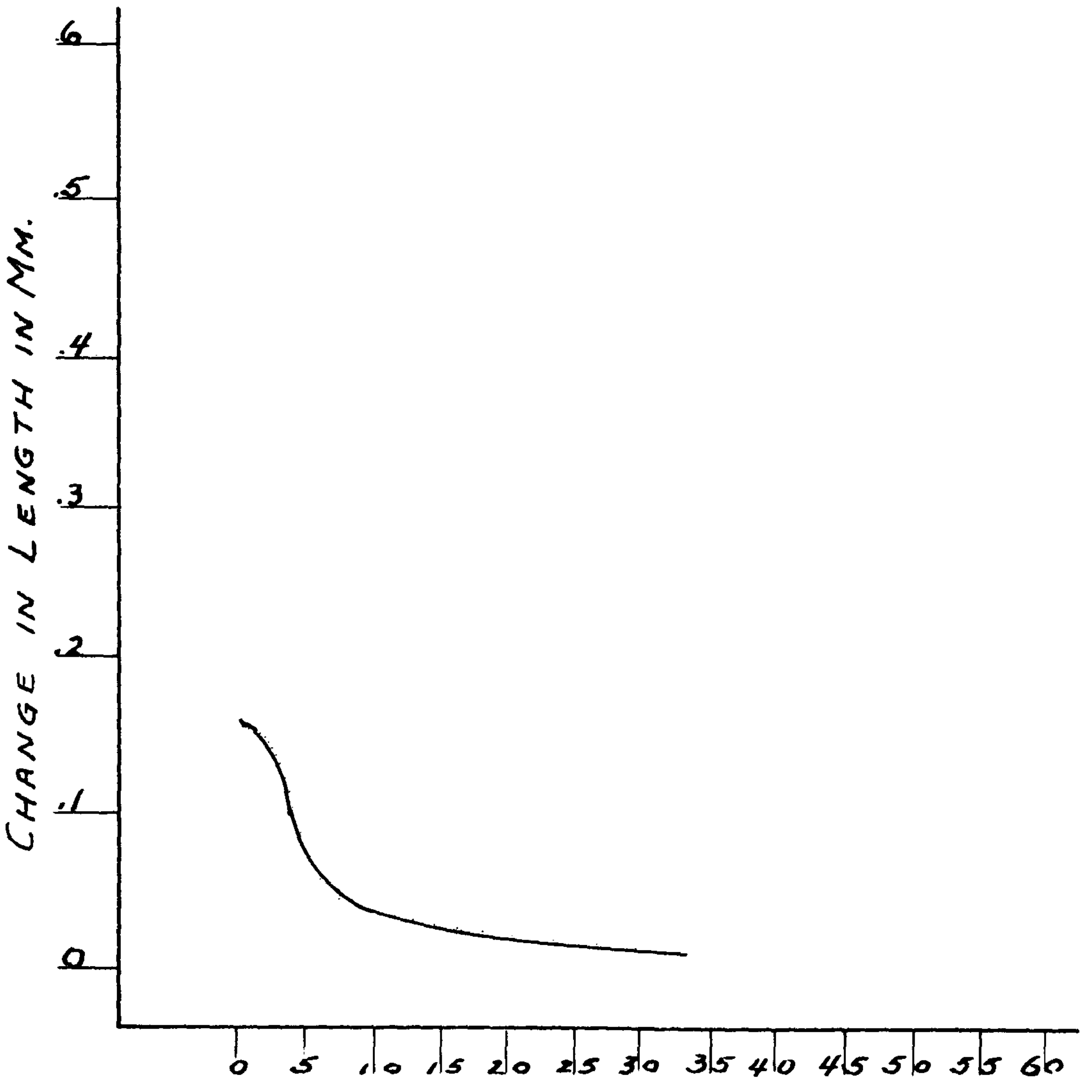


Figure 30

Dilatometer tracing of a 78% Zn-21.0% Al-1.0% Cu alloy quenched from 350° C. into water at 80° C. The specimen was heated 30 minutes at 350° C. before quenching.

reaction. Therefore, if the two-phase alloy were heated into the one-phase field, the copper atoms would tend to inhibit the zinc atoms from moving away from the zinc rich portions of the high-temperature phase and the aluminum atoms from leaving the aluminum rich areas in the same manner. This would lead to the high-temperature phase--unless the temperature to which it was heated was high enough to promote rapid diffusion, or unless sufficient time elapsed for the alloy to become homogeneous. The most effective of these two variables in promoting the necessary diffusion is temperature.

Since zinc and aluminum atoms have to move or diffuse when the high-temperature phase decomposes into two low-temperature phases, an inhomogeneous high-temperature phase (with some areas rich in zinc and other areas rich in aluminum) requires less diffusion before the necessary zinc or aluminum concentration is reached for the low-temperature phase to form. Consequently, an inhomogeneous high-temperature phase would be expected to undergo a phase change upon quenching quicker than a more homogeneous phase would. Experimental data showed that specimens containing 1.0% copper transformed slower when the "soaking temperature" was raised. (See figures 29 and 30.) This effect was not noted on either of the two other alloys employed in this experiment.

Photomicrographs showed no evidence of any intermediate phase occurring during the eutectoid reaction. The photographs revealed that the transformation products were nucleated both at the grain boundaries of the "parent" high-temperature phase and at random "centers" located within the parent grains. The transformation products are nucleated at these points and then grow by diffusion processes until the entire parent grain is consumed.

V. CONCLUSIONS

The study of the eutectoid reaction (by metallographic and dilatometric methods of both the pure zinc-aluminum eutectoid alloy and alloys containing copper) leads to the following conclusions:

1. The eutectoid reaction in this system is similar to the pearlite transformation in ferrous alloys in that it proceeds by diffusion processes. No intermediate phases can be detected as the alloy transforms from the single high-temperature phase into the two low-temperature phases.
2. Copper atoms interfere with these diffusion processes and slow down the speed of the eutectoid transformation, especially when the alloy transforms at temperatures of 80° C. and below.
3. The low-temperature products are nucleated and grow both from the grain boundaries of the "parent" high-temperature phase and from random "centers" within the parent grains.

APPENDIX

SUGGESTIONS ON EXPERIMENTAL PROCEDURE WITH A DILATOMETER

One of the first factors to be studied in making an investigation of this type is the ability of the quench bath to cool the specimen quickly. It is necessary to insure that the thermal contraction effects from the quench cease quickly so that they do not interfere with or "mask" length changes due to phase changes occurring in the specimen. This was explored in this experiment by quenching a pure aluminum standard specimen from the same temperature (305° C.) that was to be used in a later experiment on the eutectoid alloys. The results of this procedure are shown in figure 31.

When studying the kinetics of the eutectoid reaction near the nose of the TTT curve (around 150° C.), the reaction occurs so quickly that special techniques must be used in following the progress of the reaction. It was found that the best method for accomplishing this was to substitute a piece of graph paper for the photographic paper normally used with this instrument. The spot of light indicating the specimen's changes in length can then be visually observed. As the spot of light passes various points on the graph paper, the position of the light spot can be verbally reported into the microphone of a tape recorder. This will enable the investigator to follow the faster length changes in the

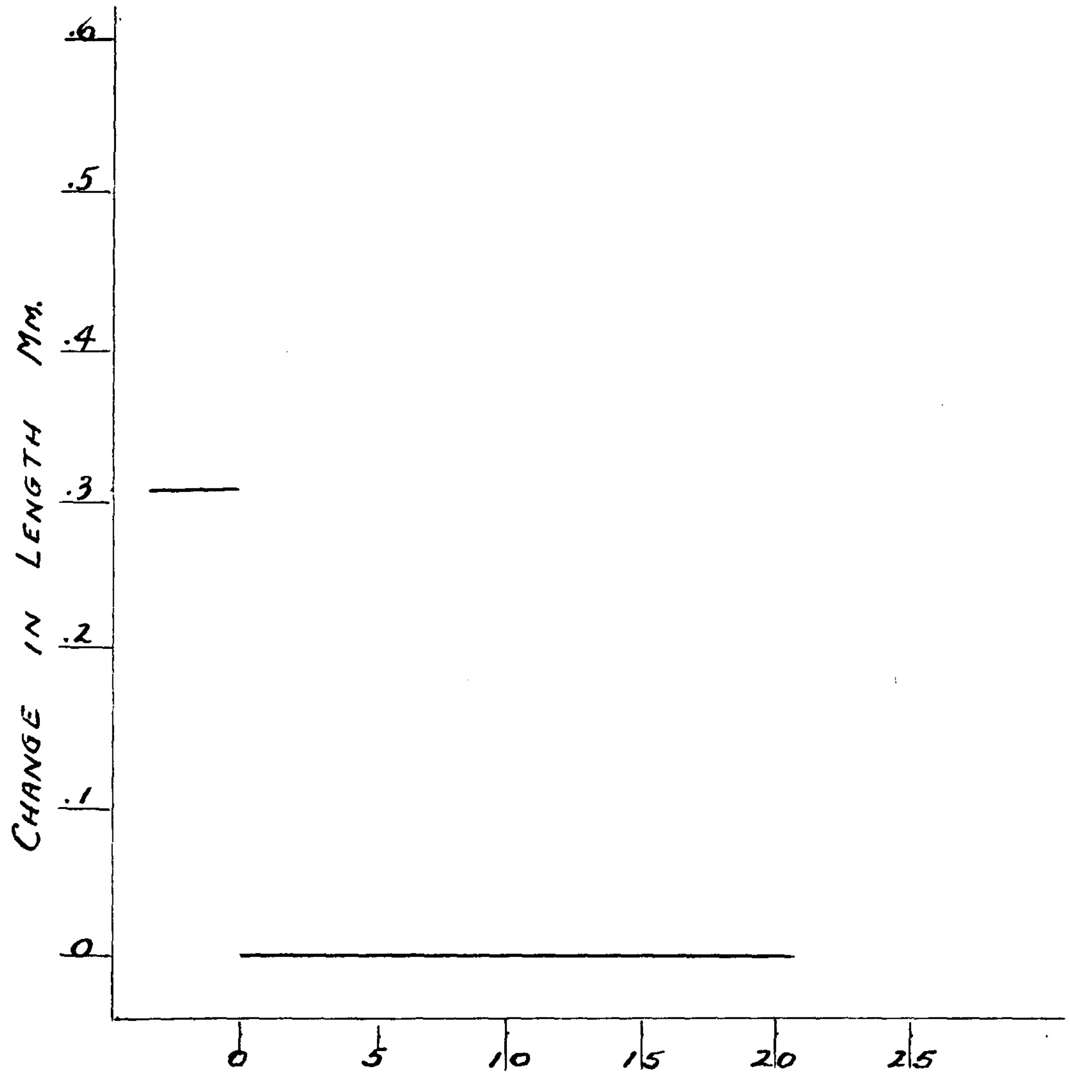


Figure 31

Dilatometer tracing of a pure aluminum specimen quenched from 300° C. into water at 50° C.

specimen than would be possible otherwise without the necessity of photographing the progress of the reaction with a motion picture camera.

The last point to be mentioned is the fact that the quartz tubes that hold the dilatometer specimens are very easily broken. Such breakage can become a major cost in the investigation since each of the tubes currently cost $30.

SUGGESTIONS FOR FUTURE INVESTIGATIONS

The author believes that certain factors not included in the scope of this investigation raise interesting questions for future experimenters to answer. For instance, the effect of the γ phase's grain size upon the kinetics of the eutectoid reaction in the zinc-aluminum system has never been investigated. The author feels that, since the transformation products are nucleated at random centers within the γ phase grains as well as along the grain boundaries, the kinetics of the eutectoid reaction would not be greatly affected by variations in the high-temperature phase's grain size.

Another study might be conducted on zinc-aluminum alloys containing larger amounts of copper than those employed in this investigation. Magnesium, which slowed down the eutectoid reaction when alloyed in relatively small amounts with the basic zinc-aluminum alloy, would provide a good subject for a similar investigation.

Studies, such as these, would lead to a better understanding of the eutectoid reaction and might reveal methods of controlling the reaction speed and/or products.

VITA

The author was born October 17, 1941, in Troy, New York. He received a B.S. Degree in Metallurgical Engineering in 1964 from the University of Missouri School of Mines and Metallurgy, presently known as the University of Missouri at Rolla.