THE EFFECT OF TEMPERATURE GRADIENT ON SOLIDIFICATION IN ALUMINUM-COPPER ALLOYS

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THE EFFECT OF TEMPERATURE GRADIENT ON SOLIDIFICATION IN ALUMINUM-COPPER ALLOYS

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ABSTRACT

A brief review of the methods available for the study of the solidification of metals is presented and discussed, along with a review of the most recent published literature on the solidification process.

The thermal analysis technique was used to study the effect of temperature gradient on the solidification of aluminum-copper alloys cast in green sand molds. Aluminum-copper alloys containing from 1 to 4% copper were melted in a high-frequency induction furnace and cast into horizontal bars, one inch in diameter and twelve inches long. Continuous cooling curves were recorded in the castings with a high-speed recorder.

Studies of the macrostructure of the bars were correlated with the solidification index and pouring temperature. The X-ray analysis technique was used to study the extent of macro-segregation in a number of selected test bars.

It was shown that a large solidification index favors the formation of an equi-axed structure and a small solidification index favors the formation of the columnar structure. X-ray diffraction analysis did not reveal any gross macro-segregation in any of the cast bars under the conditions used in this experiment. The existence of non-equilibrium eutectic was detected by thermal measurement in all castings containing more than 1.53% copper in this investigation.

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INTRODUCTION

The practical importance of the phenomena of solidification must have been recognized for a very long time. The difference between ice and water, for example, has had a profound influence on the history of mankind and the evolution of society. The possibility of melting a metal and allowing it to freeze in a mold to a desired shape has been an essential ingredient in our mastery of the art of shaping metals for thousands of years.

The importance of melting and freezing as applied to metals and alloys has been so great, in fact, that empirical solutions have been found for the multitude of practical problems that have arisen. This approach has been so successful that relatively little attention has been directed to arriving at an understanding of the fundamentals of the process. In 1924 the British Non-Ferrous Metals Research Association began a long-term study of the solidification of castings.

The basic problem, to which this thesis is devoted, is this: A mass of metal of known chemical composition, is melted, heated to a given temperature, and allowed to solidify in a green sand mold. What effect will the resulting temperature gradient have on the distribution of the chemical elements and the shape of the grains formed in the casting?

HISTORY

The effect of the structure assumed by most alloy castings at the time of solidification persists throughout it's life. The microstructure may be altered by heat-treatment, if the alloy is of a suitable constitution to respond to such treatment, but the macrostructure of a casting is rarely affected by heat-treatment.(1) This feature plays an important part in the behavior of the cast article in service.

Solidification is a process of nucleation and growth. The rate of solidification of a cast article is the resultant of the rate of nucleation and the rate of growth. The rate of growth at high temperature is very high and the rate of nucleation is low; at low temperature the reverse is true. Therefore, at a high temperature few nuclei have a chance to form before the rapid rate growth has completed the freezing process. Thus the final structure is coarse-grained. At low temperatures, many nuclei form before the freezing process is completed and the resulting structure is fine-grained.(2,3,4) If the rate of cooling is high, as in a metal mold, freezing will occur at a low temperature, and a fine-grained structure is formed. If the rate of cooling is low, as in a sand mold, freezing occurs at a high temperature and a coarse-grain structure is formed.

Considerable progress has been made in recent years toward an understanding of the solidification of metals. Chalmers, Winegard and their co-workers(5,6) have done considerable research regarding supercooling, dendritic freezing and the solid-liquid interface in alloy systems. R.W. Ruddle and his co-workers in England have conducted experiments relating to the solidification of castings.

In 1950 R.W.Ruddle(7) made a survey of the literature relating to the solidification of castings and to methods of controlling solidification. Ruddle's review is divided into two sections. The first covers the general work which has been done towards the application of scientific principles to the production of castings and ingots. The second part is concerned with a more fundamental study of the solidification rates of castings and the methods available for the investigation of solidification rates.

The fundamental principles of solidification of metals in molds can be investigated in four ways: 1. by mathematical analysis; 2. by electrical analogue; 3. by "pour-out" methods; 4. through temperature measurements taken in the solidifying casting and in the mold.

The mathematical approach to the problem becomes exceedingly difficult and often insoluble if all the factors affecting the solidification phenomena are considered. Even if simplifying assumptions are made, the equations are only solvable with great difficulty. In addition, the mathematical method requires much data concerning thermal properties at high temperature and especially in the liquid state. The data are very meager and much of the information which is available is of doubtful reliability at the present time.

The electrical-analogue method is the newest method of solving heat-flow problems. This method is not as restricted in its application as the mathematical method. However, it also requires knowledge of much unknown data. The main difficulty with both methods is that they are unable to provide information concerning the behavior of an alloy between the liquidus and the solidus temperature. This information is essential for a complete understanding of the factors involved in the solidification of metals. This is especially true of non-ferrous alloys, where the freezing ranges are large and the pouring temperatures are low.

A good deal of practical work on the solidification of steel and cast iron has been carried out in recent years using the "pour-out" technique. This method is of limited value because it enables one quantity, the rate of skin formation, to be measured. Its application to non-ferrous alloys having long freezing ranges would yield little information, since the formation of a solid skin takes place at some unknown point between the liquidus and the solidus. The results of such investigations throw no light on the beginning or end of solidification. Bochvar and Kuzina (8) have shown experimentally that the solid skin left in the mold will contain considerable liquid in aluminum-copper alloys. A further objection to this method, is that in many alloys it may not work at all. Hunsicker (9) examined a number of aluminum alloys, but was unable to obtain satisfactory solid shells. The "pour-out" method is a crude method of investigation and it may yield misleading results.

The measurement of temperature in the metal and in the mold is a much more versatile method and offers a number of advantages over the methods described above. This method requires a minimum of high-temperature data, and enables the progress of both the beginning and the end of solidification to be followed. It also shows the behavior in the zone where solidification is taking place. Temperature at various points in the casting and the mold can be measured at the same time, thus, permitting the calculation of the temperature gradient existing in both the casting and the mold. The temperature measurement method is the best technique for the investigation of solidification in non-ferrous alloys. This method had not been used extensively prior to 1950. Some results have been published by Briggs and Gezelius,(10) Baker,(11) Chvorinov,(12) and others.

In 1950 Ruddle(13) made a preliminary study of the solidification of super-pure aluminum and aluminum alloys containing 4, 8 and 30% copper using the temperature measurement technique. He reported that super-purity aluminum solidified by skin formation and 4% copper alloy solidified in a "pasty" manner. He was unable to determine the method of solidification of the 30% copper alloy. Ruddle calculated the solidification times for aluminum alloys using Chvorinov's formula and found that they compared favorably with the experimental data. Chvorinov's formula is expressed as:

$$T = (V/SA)^2/M^2$$

T = freezing time, hours; V = volume; SA = surface area; and M = constant.

A correlation of tensile properties of aluminum alloy plate castings with temperature gradients during solidification was also published by Ruddle in 1950.(3) He reported that plates having the steepest temperature gradient had considerably superior tensile properties. This was the case obtained in his ½ inch plate. He also concluded that plates thicker than ½ inch could not be soundly cast when rapidly poured, regardless of the size of the feeder employed. Ruddle did not discuss the affect that might be due to variation of grain size.

Cibula and Ruddle (4) made a study of the effect of grain size on the tensile properties of cast aluminum alloys. The grain size was varied in a 4½% aluminum-copper alloy by varying the pouring temperature of the casting. The tensile properties of this alloy were found to increase markely with decrease in grain-size.

Kondic and Shutt(14) investigated the macrostructure of super-pure and commercially pure aluminum using the temperature measurement method. They found that with super-pure aluminum, the number of grains in the cast structure was independent of the degree of superheating. With commercially pure aluminum, a greater number of crystals of different shapes in the same casting were obtained over a narrow range of superheating temperature. They also showed that on superheating the commercially pure aluminum to 950° C, and holding the melted metal at a temperature close to the liquidus temperature, caused a fine-grain structure to appear in the casting. They concluded that an increased rate of cooling refines the columnar structure of pure metals and modifies the equi-axed structure of impure metal, first, into a partly columnar and partly equi-axed structure, and secondly, at still higher rates of cooling, into a wholly columnar structure. Measurements of undercooling showed that any grain refinement of a pure metal with increased rates of cooling is accompanied by an increased degree of undercooling. The formation of equi-axed structure was found to be primarily due to the present of alloying elements.

Bishop, Brandt, and Pellini(15) investigated the solidification of steel ingots using thermal analysis. They were able to determine that solidification in a steel ingot proceeds in a wave-like fashion at rates which were determined by the carbon level, superheat, and mold thickness. They showed that increasing superheat produces a general coarsening of the macrostructure. They concluded that the classic relationship, thickness = a constant times the square root of the time, applies only to the first stage of solidification.

Winegard and Chalmers(16) discussed the mechanism of super-cooling and dendritic freezing in alloy systems in a publication in 1953. They were able to show that supercooling may result from the enrichment in the solute of the liquid immediately ahead of the advancing solid-liquid interface. They proposed that dendrites in ingot structure are produced as a result of constitutional supercooling and that dendritic equi-axed zone in the center of ingots is a result of nucleation in a large constitutionally supercooled region.

Morris, Tiller, Rutter, and Winegard(6) investigated the conditions for dendritic growth in alloys of lead containing from 0.25% to 5% tin, using the thermal analysis technique. It was shown that dendrite formation is favored by a rapid rate of solidification and a low temperature gradient. The results indicated that the factor controlling the beginning of dendritic growth is the ratio of the rate of solidification to the temperature gradient.

When an alloy solidifies differences in chemical composition may occur on either a small or large scale. If within the individual crystals or grains, it is called micro-segregation. Segregation may be observed on quite a large scale within the mass of solid metal, the composition on the outside, for instance, being quite different from the center of the mass. In this case, the difference in composition is referred to as macro-segregation.

Segregation can occur only in cast alloys that solidify over a range of temperature, with a difference in the composition of the liquid and the solid within this range under non-equilibrium thermal conditions. Ideal conditions are difficult to produce in a laboratory and are never attained in a metallurgical casting operation. In practice, this means the central portion of the crystal contains a different proportion of the solute atoms than is present in the outer parts of the crystals. If diffusion had taken place- as it would under strictly equilibium conditions of cooling- this gradient would not exist. All castings exhibit one or more forms of micro-segregation.(4) Michael and Bever(17) have recently shown that the copper content varies within the individual dendrites formed in alloys of aluminum containing from 2% to 5% copper using the radiographic technique.

Macro-segregation may be so gross that it is readily visible to the naked eye. This form of segregation can be readily observed in large ingots. Very little information has been reported concerning this type of segregation in castings.

Notable among the mathematical studies of segregation, is the recent work of Pfann on zone-melting.(18) In a publication in 1954, Pfann(19) confirmed his mathematical analysis using radioactive antimony. He showed that there was a sharp decrease in concentration at each remelt boundary and an increase in concentration in the last region to freeze.

Killatly, Taylor, and Winegard(20) investigated segregation during casting of lead-antimony alloys, using radioactive antimony. They were able to show that gravity segregation is minimized by fast cooling rates.

Winegard(21) investigated segregation in bronze using radioactive technique and found that the outside of small castings were high in tin when made to solidify from outside inward.

PROCEDURE

The Aluminum-Copper Alloys used in this experiment were made from high-purity aluminum of 99.996 % purity, and electrolytic copper of 99.99% purity. The alloys were prepared from a 67:33 aluminum-copper hardener made from the above materials. Spectrographic analysis showed a very slight trace of manganese, a trace of silicon, a trace of iron, and more than a trace of magnesium. Spectrographic analysis on two of the cast bars showed that the amount of the above elements did not increase in the alloys under the casting conditions used in this experiment.

A 20 K.W. Ajax high-frequency induction furnace was used to melt all of the heats poured in this investigation. The alloys were melted in a 12 pound magnesia crucible and cast into horizontal bars, 1 inch in diameter and 12 inches long. Risers 1 inch in diameter were placed at each end of the bar. The castings were poured directly into one of these risers.

The green sand molds were made from Tennessee bank sand blended with 41% Ottawa silica sand. The curves shown in the appendix was constructed by measuring the physical properties of various percentages of Tennessee sand and silica sand. The 59:41 mixture was selected because it gave the maximum strength with relatively high permeability. The sieve analysis of the Tennessee sand and the blended sand is shown in Table 1. A moisture determination was made prior to the preparation of each mold and maintained between 5 and 6%

The thermocouples were placed with the hot-junctions in the center of the mold cavity at the parting line, as shown in figure 1. These thermocouples were constructed from 22 gage chromel-alumel wire and were calibrated with pure zinc, tin, high-purity aluminum, and electrolytic copper. The results are shown in Table 2. A test bar of high-purity aluminum cast in a green sand mold showed the temperature reading to be 5° F. high. All thermocouples were used without protection except heats T-125A, T-127B, and T-128B. Heats T-125A was coated with a wash of alundum and heats T-127B and T-128B had a thin silica tube covering all the couple, except about 1/16 of an inch at the hot junction. These heats showed that the couples gave readings with unprotected thermocou-

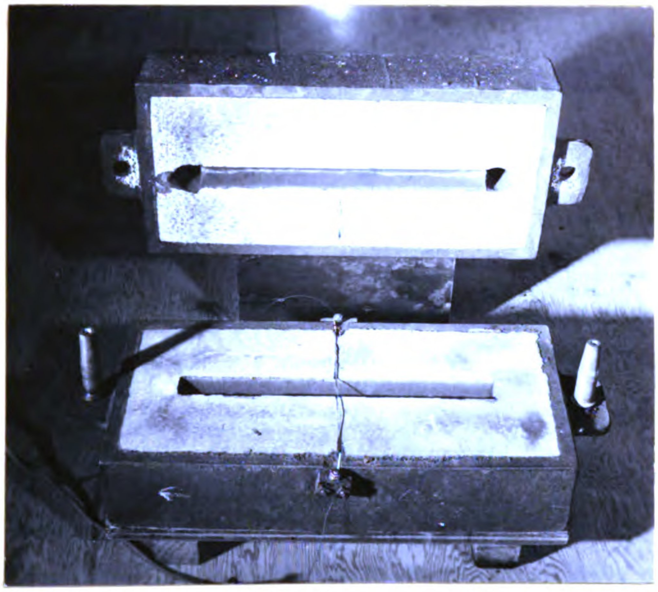

Figure 1. Mold and thermocouple

ples. The unprotected couples gave a more rapid reading and were used for this reason. A.B. Michael (21) has also shown this to be true in aluminum-copper alloys of the composition used in the experiment.

Continous cooling curves were recorded in the cast test bars with a Brown High Speed Electronik Recorder. The casting temperature was measured in the crucible just prior to pouring with a chromel-alumel thermocouple and a portable potentiometer.

Samples 1 inch long were taken from each bar, adjacent to the thermocouple and the beginning and end of freezing temperatures measured for comparison with the measurements taken in the casting. These measurements were made with the previous described recorder, and a 2 K.W. Lepel high-frequency furnace using glazed porcelain crucibles. These results are shown in Table 4.

Samples ½ inch long were taken from the casting adjacent to the thermocouple for macro-examination, and X ray diffraction analysis. Each sample was then marked on the top side so that its position in the mold could be identified. Turnings were taken from the face of the bar adjacent to this sample for chemical analysis.

The samples were ground on a belt sander and 1/0 paper, then polished with levigated alumina powder. A mixture of 10 ml. of HCl, 5 ml. of HF., and 95 ml. of distilled water was used to etch all samples for macro-examination, and Keller's etch was used for macro-examination. Photomacrographs were taken of selected samples and are shown in the discussion.

Fine drillings were taken with a 1/16 inch drill perpendicular to the face of selected specimens at the following positions: 1/16 inch from the mold-metal interface at the bottom, top, side, and at the center of the test specimens. A few samples were taken from the half-radius position between the top and center of the samples. The drillings were placed in a 5 mm. pyrex tube, evacuated and sealed. All X-ray samples were given a 2 hour solution treatment at 1000°F, and quenched in a beaker of water upon removing from the furnace. The drillings were removed from the pyrex tube, and dried in an erlenmeyer flask, using vacuum and heat, being careful not to heat the flask above hand-touching temperature.

X-Ray diffraction patterns were obtained of the filings using a Van Arkel Camera and unfiltered copper radiation. The position of the diffraction lines for the 422, 511-333 reflecting planes were measured with a Phillips Comparator for K_{α_1} and K_{α_2} radiation. The lattice constants were calculated for each plane and corrected by extrapolation. An example of the extrapolation curves is shown in the appendix. The copper content of the sample was determined from the curve shown in the appendix. This curve was constructed from lattice parameter measurements as described above for high-purity aluminum, test bar T-115 containing 0.90% copper, test bar T-1212 containing 1.53% copper, test bar T-135 containing 2.50% copper, test bar T-45 containing 3.01% copper; and a high-purity aluminum copper alloy containing 95.09% aluminum and 4.89% copper supplied by the Aluminum Company of America.

Chemical analysis was performed using the following electrolytic method. A 2 to 5 gram sample was dissolved in a mixture of 200 C.C. of distilled water, 10 C.C. of HCl, 20 C.C. of HNO_3. Approximately 2 C.C. of H_2SO_4 per gram of sample was added, and the solution evaporated to fumes of SO_3. The residue was then dissolved in distilled water with 3% HNO_3 and 3% H_2SO_4, and electrolyzed. The method was checked with an aluminum-copper alloy supplied by the U.S. Bureau of Standards and found to be within 2% error.

DISCUSSION

High-purity aluminum and electrolytic copper was used in this experiment to minimize the affect of residual elements. Kondic and Shutt(14) have demonstrated that minor impurities may completely outweight the thermal factors in controlling nucleation during solidification. The possibility of producing fine-grained aluminum alloy castings, by additions of small quantities of certain elements to the melt has long been known. The results of the spectrographic analysis show that there was no pick-up of undesirable elements under the casting conditions used in this investigation.

The test bars used in this work were designed so that a zone in the center of the casting would represent a "semi-infinite" casting. In the "semi-infinite" zone, all of the heat is lost in the direction of the side surfaces. Pellini(22) has shown this to be the case in similar bars cast in steel. All thermal measurements, macro-specimens, X-ray samples, and chemical analyses were taken from this zone.

Table V gives the compositions of the cast bars and the times of solidification. The cooling curves are shown in the appendix. A close observation of the cooling curves reveal that the recorded liquidus and solidus temperatures are inconsistent and in some cases higher than the solidification temperature of pure aluminum. Prior calibration of the thermocouple wire and recorder, indicated that the maximum temperature deviation should not be more than 5° F. The recorder was a continuous balancing instrument and was balanced manually prior to each operation.

The interpretation of the data was based on the solidification index to eliminate the above mentioned variation in temperature measurements in all the alloys, except the 1% copper alloys. The solidification index is defined as the difference between the observed liquidus and solidus temperatures, divided by the total time of solidification. This index has the dimensions of a cooling rate, but also reflects any isothermal part of the solidification process. Many of the other variables in the casting process will exert an influence on the solidification index. An increase in pouring temperature will cause a decrease in the solidification index due to an increase in the solidification time. Any changes in the mold material that affect its thermal properties will be reflected in the solidification index. An increase in the thermal conductivity of the sand will cause an increase in the solidification index. The structure of test bar T-137 is an example of the influence of some unknown variable on the solidification index. This bar contains equi-axed and columnar grains, whereas bar T-133 poured from 1300° F. contains all columnar grains. If the structures are interpreted on the basis of solidification index instead of pouring temperature, the duplexed structure would be predicted for this bar.

Cooling curves were determined from a remelted sample of each bar to see if the temperature measurements would be more consistent under different conditions. Samples of high-purity aluminum were run at various intervals, so that corrections could be made to the recorded values. The corrected values and the measurements recorded in the mold are shown in Table IV. Cooling curve determinations for aluminum indicated that the characteristics of the thermocouple did not change in any way that could explain the above conditions. The inconsistent temperature measurements appeared to be due to instrumental difficulties, but could not be verified.

The horizontal portion of the cooling curve at the liquidus, was observed in the alloys cast under the conditions used in this experiment. Michael and Bever(17) also observed this horizontal in their investigation of aluminum-copper alloy. They suggested the observation might be due to a transient balance at the thermocouple bead between the evolution of the heat of solidification and heat losses to the surroundings. Ruddle(13) investigated the solidification of aluminum alloys containing 4% copper and concluded that 50% of the metal solidifies in the first 10°C. of the freezing range in a 5 inch cylinder.

The cooling curves for all alloys containing more than 1.53% copper, have an arrest at approximately 1010°F, which is the temperature of the eutectic reaction. The eutectic halt increased with copper content. The photomicrograph in Figure 2 shows eutectic in the grain boundries of the 2.53% copper alloy. Michael and Bever,(17) reported observing the eutectic halt in 2% copper alloys under similar cooling rates. Mondolfo(23) reports that the maximum amount of copper that can be held in solution in sand cast aluminum-copper alloys is 2.5% at the eutectic temperature. These data suggest that even less copper might be held in solution in casting.

Figure 2 Test Bar 137 2.52% copper 500X

The presence of the eutectic due to non-equilbrium conditions during subsequence heat treatment, may cause partial melting in the boundries of an alloy, which according to the phase diagram, should be a solid solution having a higher solidus temperature. In the case of the homogenization for age-hardening, the time required for solution treatment would be much longer and at a lower temperature.

The presence of the eutectic in the grain boundries, might possibly have some subtle affects on the physical properties, and the feeding of casting during solidification. A non-equilibrium diagram is constructed from these data and shown in the appendix.

The influence exerted by copper on the nucleation rate can be observed from the photomacrograph in Figure 3. The 1% and 2% copper bars show a trace of columnar structure and the 3% and 4% copper bars are all equi-axed when cast from 1250°F. It is evident that a smaller solidification index is required to produce a columnar structure with increasing copper content. Table V shows the relation between copper content, the solidification index, temperature, and the macrostructure.

The effect that cooling rate exerts on the structure of a casting can also be seen from the photomacrograph as shown in Figure 3. Test bars that contain equi-axed and columnar grains always have the equi-axed structure in the cope side of the casting. This part of the mold has absorbed heat from the first metal entering the mold and has a lower cooling rate. This lower cooling rate in the top of the mold, accounts for the observed duplex structure in these bars.

Table V summarizes the solidification index measurements. The results indicate that a large solidification index favors an equi-axed structure and a small solidification index favors the columnar structure. There appears to be a transition solidification index, which must be exceeded to produce the equi-axed structure. This relation is shown in the curve in the appendix. This is in agreement with the conclusions of Kondic and Shutt,(14) that an increased rate of cooling modifies the equi-axed structure of impure metals into a partly columnar and partly equi-axed structure, and at still higher rates of cooling into a wholly columnar structure.

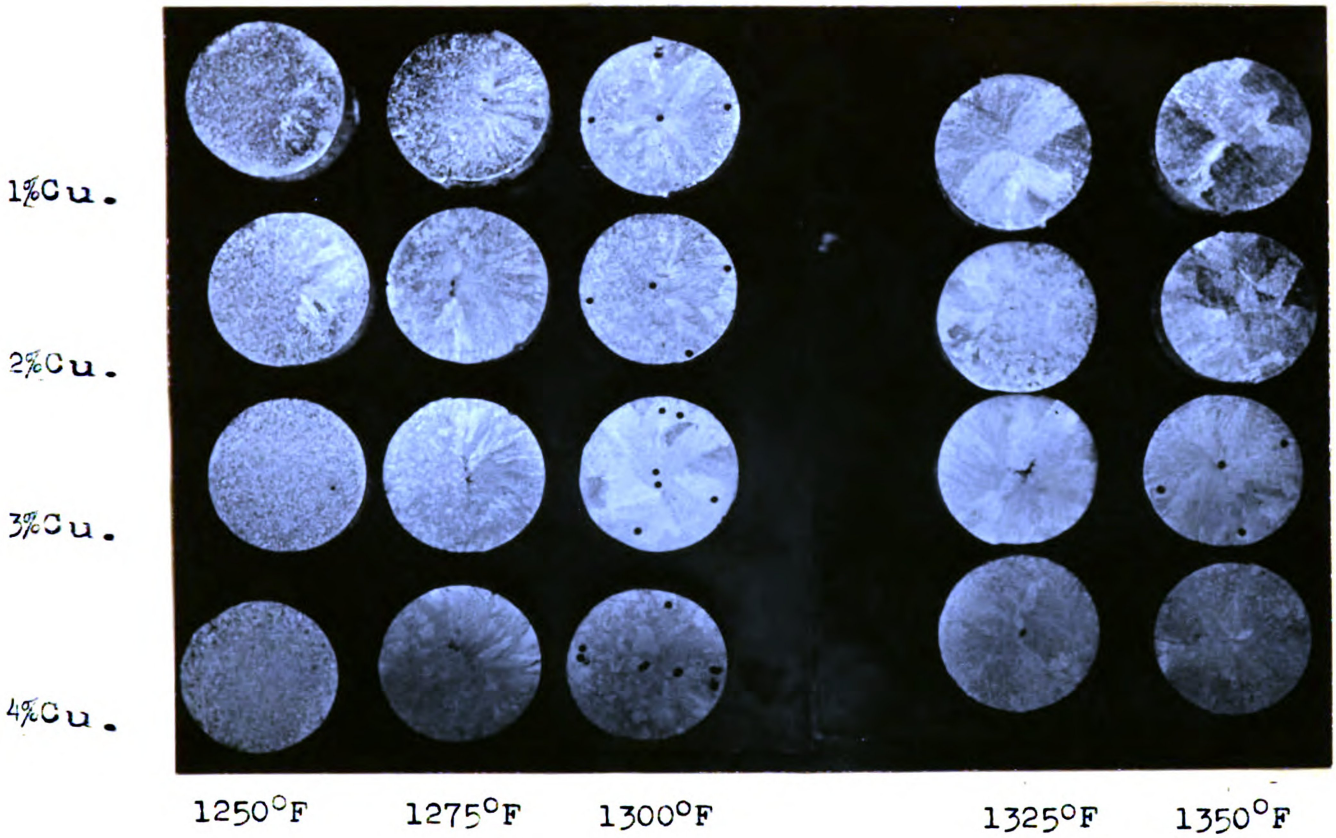

Figure 3. 3/4 actual size, cope on the left side.

The determination of the compositions of samples by lattice constants is a precise method. The method offers an additional advantage in that it requires a very small sample, on the order of a few milligrams. The method of elimination of systematic errors by extrapolation is simple and effective in back-reflecting cameras, such as used in this investigation. The values of θ obtained in this experiment, were between 60 and 90 degrees. This is the range where extrapolations are best. The results of lattice measurements on high-purity aluminum compared favorably with the values presented by Barrett.(24)

Table VI summarizes the results of the X-ray diffraction analysis taken for studies of macro-segregation. Examination of the data shows evidences of segregation, but does not reveal any particular pattern in relation to alloy content, pouring temperature, position, or the structure. The maximum variation was 0.40% copper in the 1 and 2% copper alloys cast from 1300°F. and 1350°F. respectively. Test bar T-140 poured from 1540°F. and having a columnar structure showed 0.31% maximum variation, whereas test bar T-143 cast from 1300°F had 0.25% maximum variation.

The photomicrograph shown in Figure 2, reveals that large amounts of segregation did take place on a micro-scale not susceptible to X-ray analysis. The dark area adjacent to the grain boundries and the existence of the eutectic in the boundries, are evidence that the liquid near the advancing interface is enriched in solute, in this case copper. The last metal to solidify lies in a region between the solidifying dendrites and has the composition of the aluminum-copper eutectic.

The existence of the eutectic in all regions of the cast bar, explains the small amount of macro-segregation detected by X-ray analysis. The drillings taken for X-ray analysis contain both high and low concentrations of copper and the lattice determination is the average of both the high and low concentration. The X-ray samples were homogenized at 1000°F for 2 hours to eliminate segregation within the individual sample.

Calculations of the solidification constant* used in Chvorinov's(12) method of calculating freezing times of castings were made for the two percent copper alloys poured from various temperatures. The relation between the solidification constant and the pouring temperature is shown in the appendix. Spot checks of selected bars of higher copper content indicate that these constants can be used to calculate the freezing times for all the castings poured in this experiment. The maximum difference between the calculated times and the observed times was on the order of 6%. Pellini(25) reported that the freezing time of steel castings can be calculated with a high degree of precision using Chvorinov's formula. Pellini's maximum deviation was 15% at high pouring temperatures. The results of this experiment suggest that Chvorinov's formula can be used to calculate the freezing times of aluminum-copper alloys.

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* See Appendix

CONCLUSIONS

The X-Ray diffraction studies reveal evidence that macro-segregation does take place in sand cast aluminum-copper alloys. The evidence indicates that the segregation does not follow any particular pattern in relation to the alloy content, pouring temperature, or structure.

Examination of some of the alloys reveals that segregation did take place on a micro-scale. Micro-examination also revealed the presence of the aluminum-copper eutectic in the grain boundries of the samples examined.

The thermal arrest associated with the aluminum-copper eutectic was also observed in all alloys having a copper content greater than 1.53%. The existence of the non-equilibrium eutectic might possibly alter industrial heat-treating practices of sand cast aluminum-copper alloys.

It was concluded that a large solidification index favors an equi-axed structure, and a smaller solidification index favors a columnar structure. The observations suggest that a transition cooling rate exists for the formation of the equi-axed and columnar structures. It also varies with copper content.

Macro-examination of the aluminum-copper alloys investigated in this experiment, showed that an increase in copper content increased the nucleation rate in these alloys.

Calculations of Chvorinov's solidification constants were made for the two percent alloys from various pouring temperatures. The solidification constant decreases with increasing pouring temperature.

RECOMMENDATIONS FOR FUTURE STUDIES

The crystal structure is important with respect to the physical properties of metals, but present knowledge of this subject is in a rudimentary state. The nucleation of solidification in alloys has received only scant attention and requires further experimental and theoritical treatment. Studies should be made on the doctorate level concerning the nucleation rates, and the rate of growth in alloys by a thermodynamical treatment or some other scientific method.

The existence of the non-equilibrium eutectic in the sand cast aluminum-copper alloys could possibly exert some profound effects on the heat-treatment of these alloys. It is recommended that future research to be conducted to determine what effect it might have on the temperature, and time required to solution treat these alloys for age-hardening and the effect it might possibly exert on their physical properties.

Additional experiments are also required before any definite conclusions can be made as to the existence of a transition solidification index for the formation of the equi-axed and columnar structure.

The calculation of the freezing time could be very valuable to industrial operations. This type of information could be used to determine shake-out cycles for sand castings, permanent molds, and die-casting. This information might be useful in the new continuous casting process. For these reasons, additional research would be desirable, concerning the variation of the solidification constant with various cooling rates.

APPENDIX

DATA

Table 1. Sand Analysis.

Sieve No.	Tennessee Sand Grams	%	Blended with 41% Ottawa Sand Grams	%
6	0.000	0.00	0.000	0.00
12	0.37	0.74		
20	0.16	0.32		
30	0.08	0.16	0.02	0.05
40	0.08	0.16	0.03	0.08
50	0.07	0.14	0.85	0.23
70	0.19	0.38	21.29	57.40
100	1.99	3.98	1.93	5.57
140	16.47	32.94	3.12	8.42
200	11.07	22.14	8.40	22.62
270	3.91	7.82	1.46	3.94
Pan	2.77	5.54	0.81	0.22

Table 2. Calibration of Thermocouple Wire and Recorder.

Material	Recorded Freezing Temp. Deg. F.	True Freezing' Temp. Deg. F.	Difference Deg. F.
Zinc	787.0	787.3	-0.3
Tin	450	449.4	0.6
High-purity	1220	1220.4	-0.4
Aluminum	1225*	1220.4	5.0
Copper	1977	1981.4	-4.6

' A.S. M. Handbock.
* Green Sand Mold.

Table 3. Variation in the Freezing Temperature of High-Purity Aluminum with the Operating Time of the Recorder.

Hours of Operation	Freezing Temperature Degrees F.
0.00	1220
0.50	1228
1.00	1233
1.00	1233*

* New Sample of High-Purity Aluminum.

Table 4. Determination of Liquidus and Solidus temperatures in green sand molds and remelted samples from the same casting.

Sample No.	Casting Temperature		Remelt Temperature	
	Liquidus Deg.F.	Solidus Deg.F.	Liquidus Deg.F.	Solidus Deg.F.
T-115	1230		1219	
T-114	1218		1216	
T-113	1228		1215	
T-112	1237		1213	
T-110	1222		1215	
T-111	1222		1216	
T-1212	1213	1010	1215	1015
T-1210	1221	1018	1218	1010
T-1211	1221	1018	1215	1012
T-129	1219	1018	1215	1012
T-125	1218	1018	1211	1010
T-124	1220	1018	1217	1015
T-123	1217	1020	1215	1015
T-121	1222	1020	1209	1010
T-128	1217	1012	1212	1013
T-120	1222	1028	1208	1008
T-122	1219	1021	1207	1007
T-127	1212	1015	1210	1015
T-136	1205	1015	1209	1014
T-137	1208	1009	1208	1010
T-135	1219	1028	1202	1010
T-134	1219	1033	1200	1010
T-133	1223	1031	1200	1013
T-132	1215	1028	1200	1010
T-147	1205	1020	1199	1010
T-145	1220	1028	1207	1010
T-144	1206	1022	1195	1010
T-143	1209	1022	1198	1012
T-142	1213	1033	1197	1012
T-141	1218	1032	1191	1009
T-140	1213	1033	1199	1008

Table 5. Summary of Data.

Sample No.	Chemical Analysis %	Moisture of Mold %	Pour. Temp. Degrees F.	Solid. Index Deg/Sec.	Structure
T-115	0.90	5.7	1325		Columnar
T-114	0.94	5.8	1275		Duplex
T-113	1.08	5.5	1400		Columnar
T-112	1.09	5.8	1300		Duplex
T-110	1.12	5.3	1250		Duplex
T-111	1.13	5.8	1500		Columnar
T-1212	1.53	5.3	1325	1.16	Columnar
T-1210	1.63	5.6	1275	1.19	Duplex
T-1211	1.68	5.3	1300	1.13	Columnar
T-129	1.76	5.6	1300	1.18	Columnar
T-125	1.78	5.9	1450	0.96	Columnar
T-124	1.99	5.9	1600	0.82	Columnar
T-123	2.00	5.4	1400	0.89	Columnar
T-121	2.00	5.6	1300	1.08	Duplex
T-128	2.00	5.8	1650	0.76	Columnar
T-120	2.01	5.2	1250	1.13	Duplex
T-122	2.03	5.6	1350	1.00	Columnar
T-127	2.14	5.9	1400	1.00	Columnar
T-136	2.50	5.7	1275	1.26	Duplex
T-137	2.52	5.7	1325	1.09	Duplex
T-145	3.01	5.4	1275	1.06	Duplex
T-135	3.09	6.0	1400	0.93	Columnar
T-147	3.18	5.8	1325	1.04	Columnar
T-134	3.27	5.8	1350	0.90	Columnar
T-133	3.32	5.8	1250	1.14	Equi-axed
T-132	3.35	5.7	1300	0.98	Columnar
T-140	3.81	6.0	1540	0.70	Columnar
T-143	3.93	5.5	1300	0.98	Duplex
T-144	3.97	5.3	1450	0.83	Columnar
T-142	3.98	6.0	1360	0.84	Columnar
T-141	4.26	6.0	1250	0.98	Equi-axed

Table 6. X-Ray Analysis.

Sample No.	Chemical Analysis %Cu.	Copper Content by X-Ray Analysis Top %Cu.	Bottom %Cu.	Center %Cu.	Side %Cu.	½ Position %Cu.
T-112	1.09	1.20	1.05	1.27	1.45	
T-121	2.00	1.94	1.94	1.89	1.98	
T-122	2.03	2.08	2.25	1.85	1.98	
T-129	1.76	1.75	1.70	1.72	1.80	
T-132	3.35	3.55	3.40	3.22	3.45	
T-140	3.81	3.94	3.88	3.85	3.94	3.63
T-143	3.93	3.95	4.00	4.10	4.05	3.85

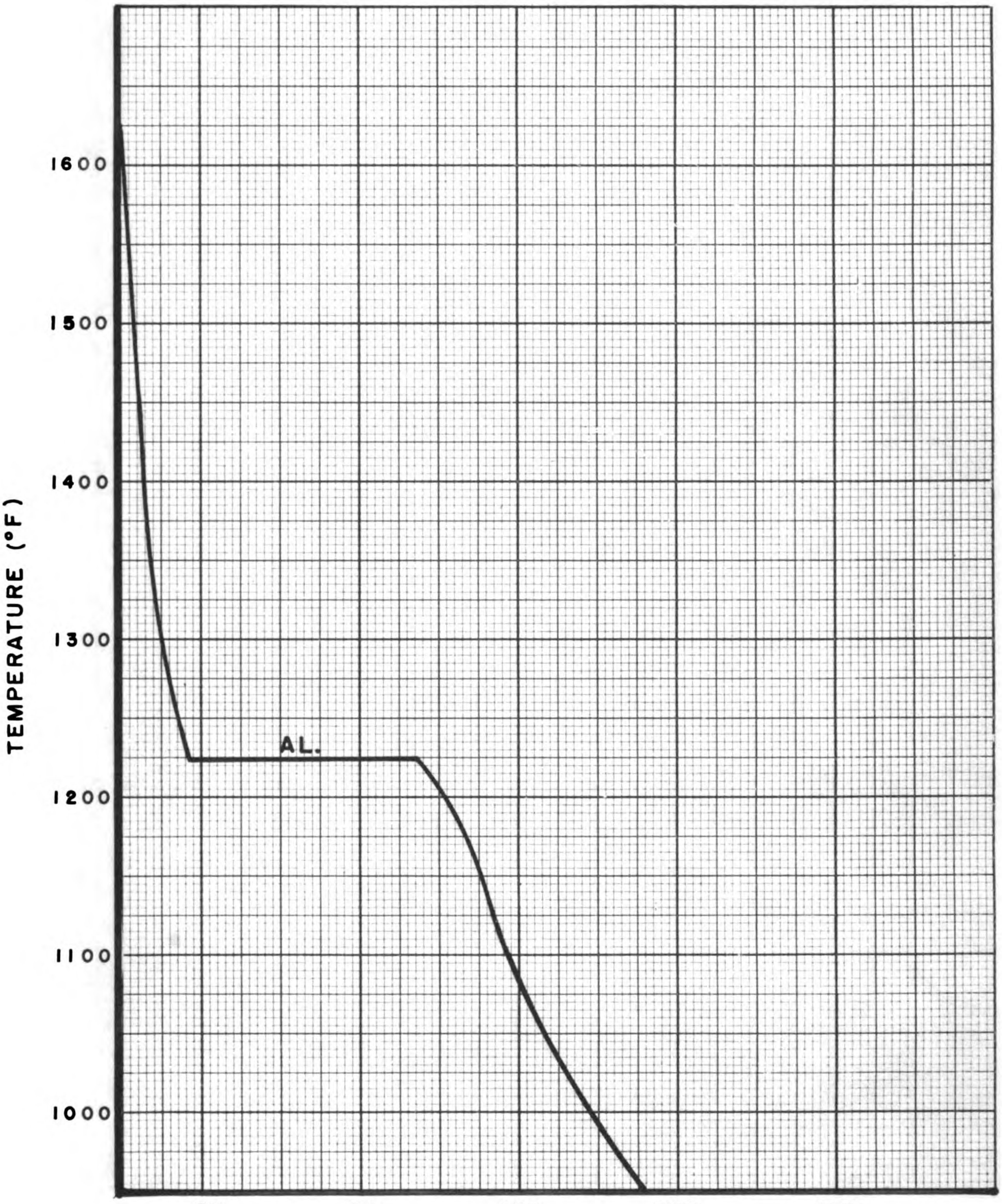
Table 7. Lattice Constants

Sample No.	Chemical Analysis	Lattice Constant Kx Units
High-Purity Aluminum	0.000% Cu.	4.0422
T-115	0.87% Cu.	4.0407
T-1212	1.53 %Cu.	4.0392
T-136	2.50 %Cu.	4.0370
T-145	3.01 %Cu.	4.0361
**	4.89 %Cu.	4.0318

**High-purity Aluminum Alloy supplied by the research Laboratory of the Aluminum Company of America.

COOLING CURVES

TIME - TEMPERATURE



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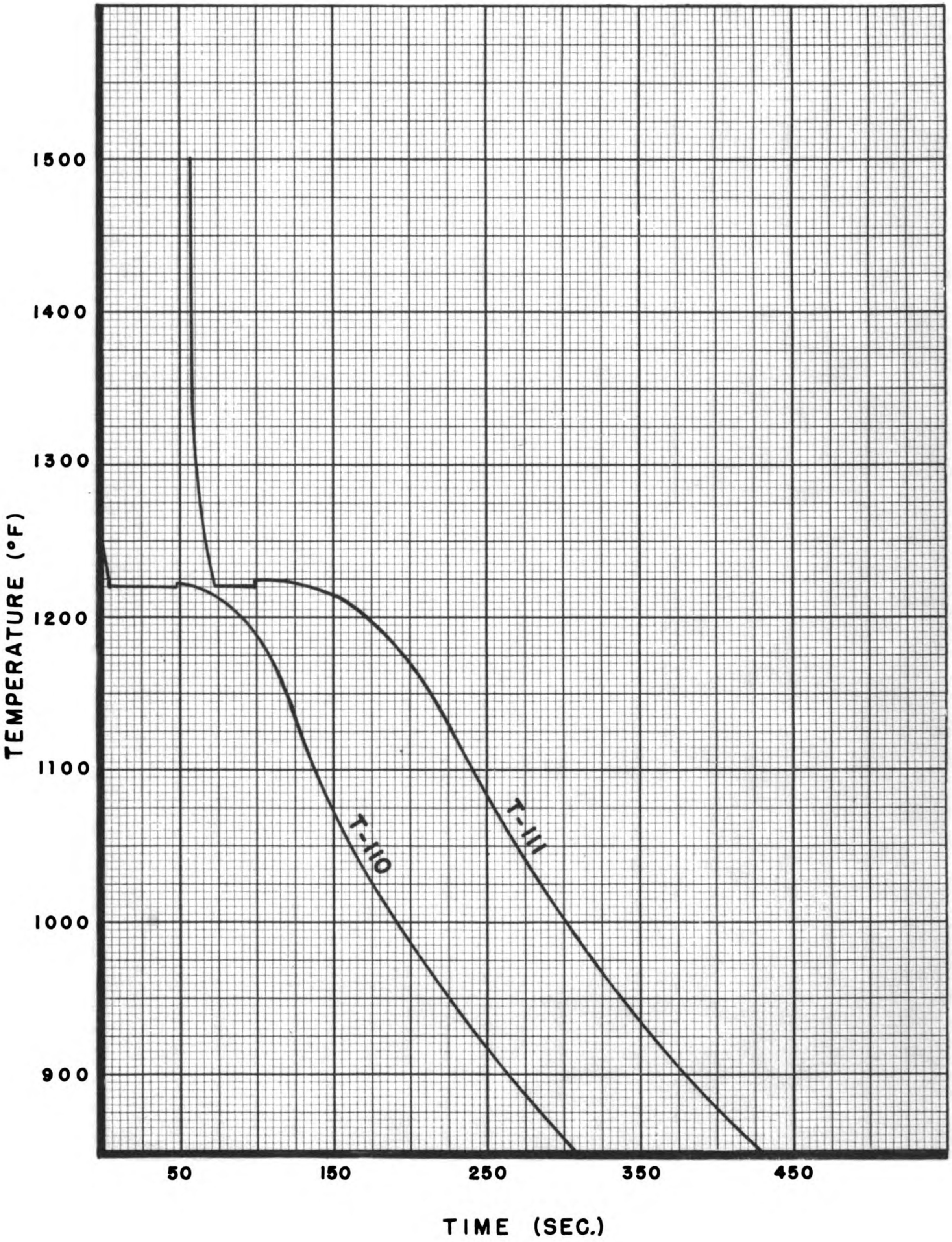
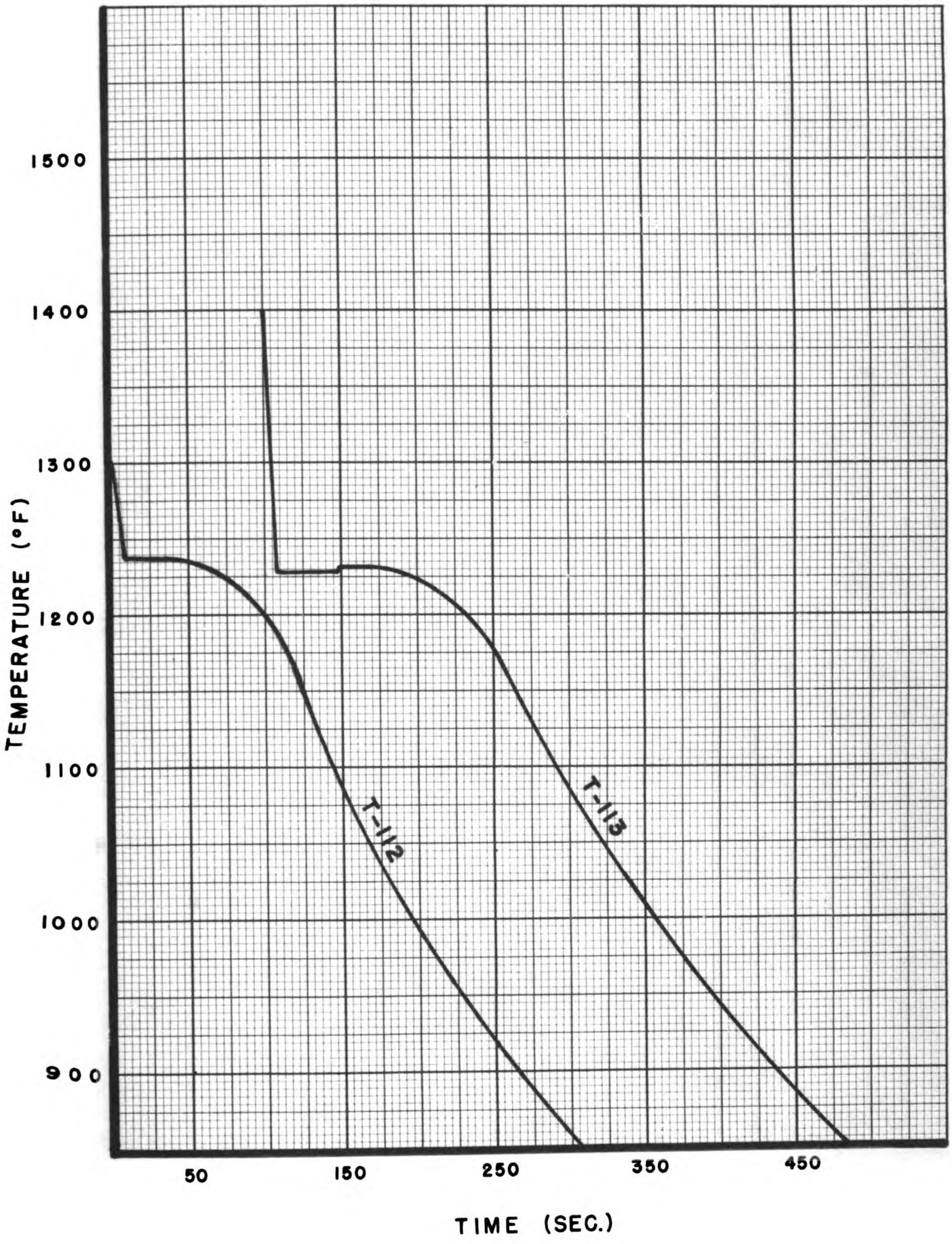
TIME - TEMPERATURE



COOLING CURVES
TIME - TEMPERATURE



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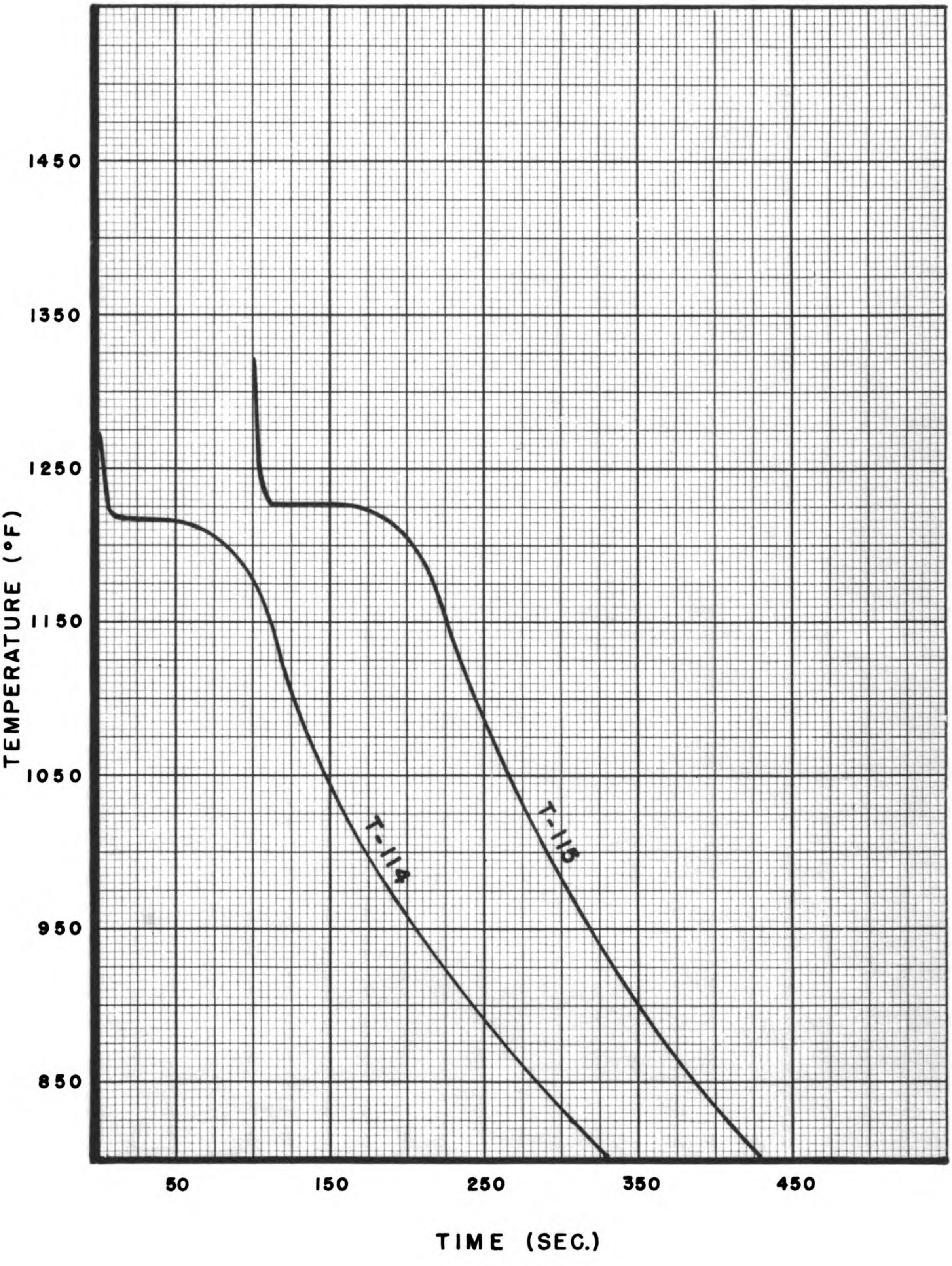
TIME - TEMPERATURE



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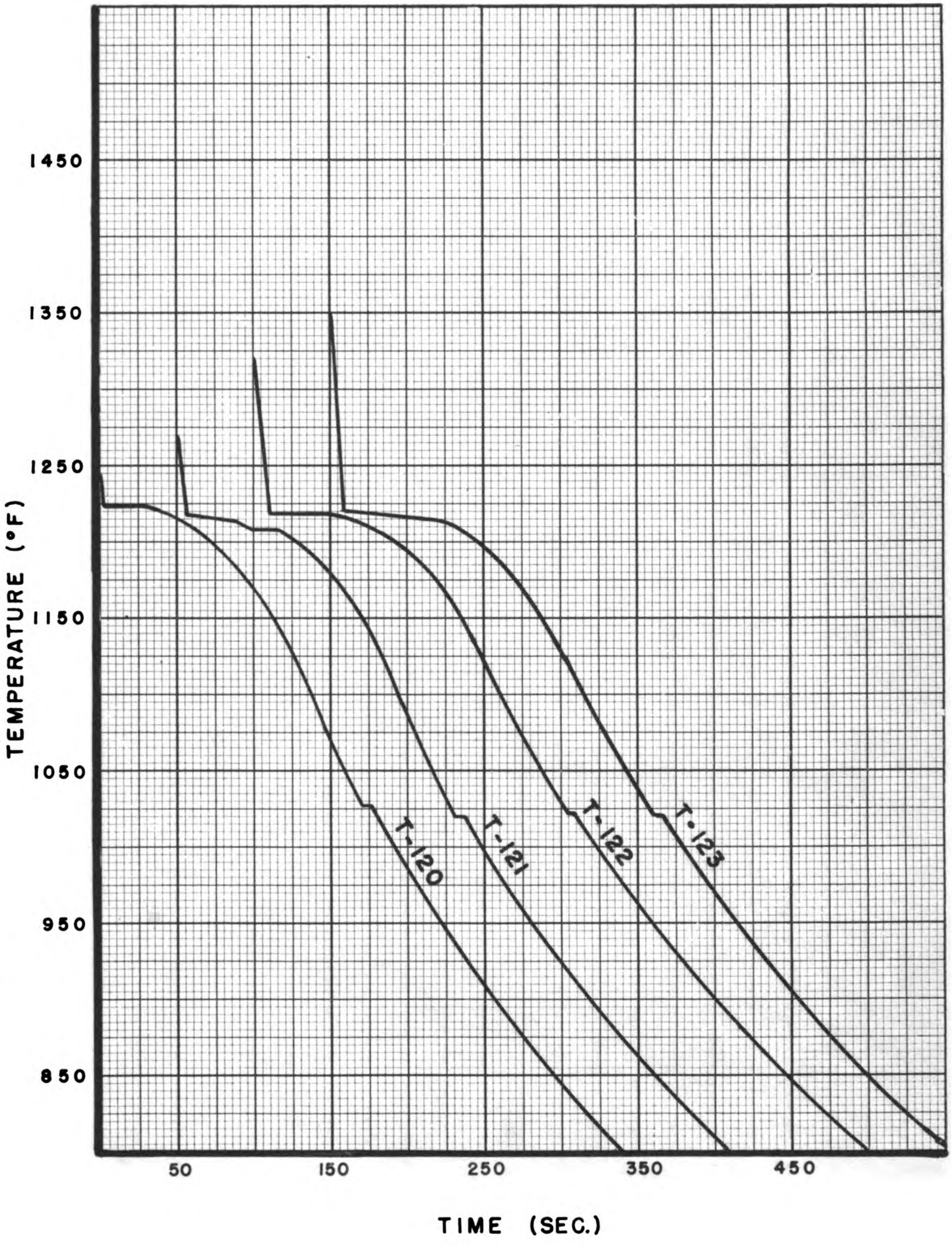
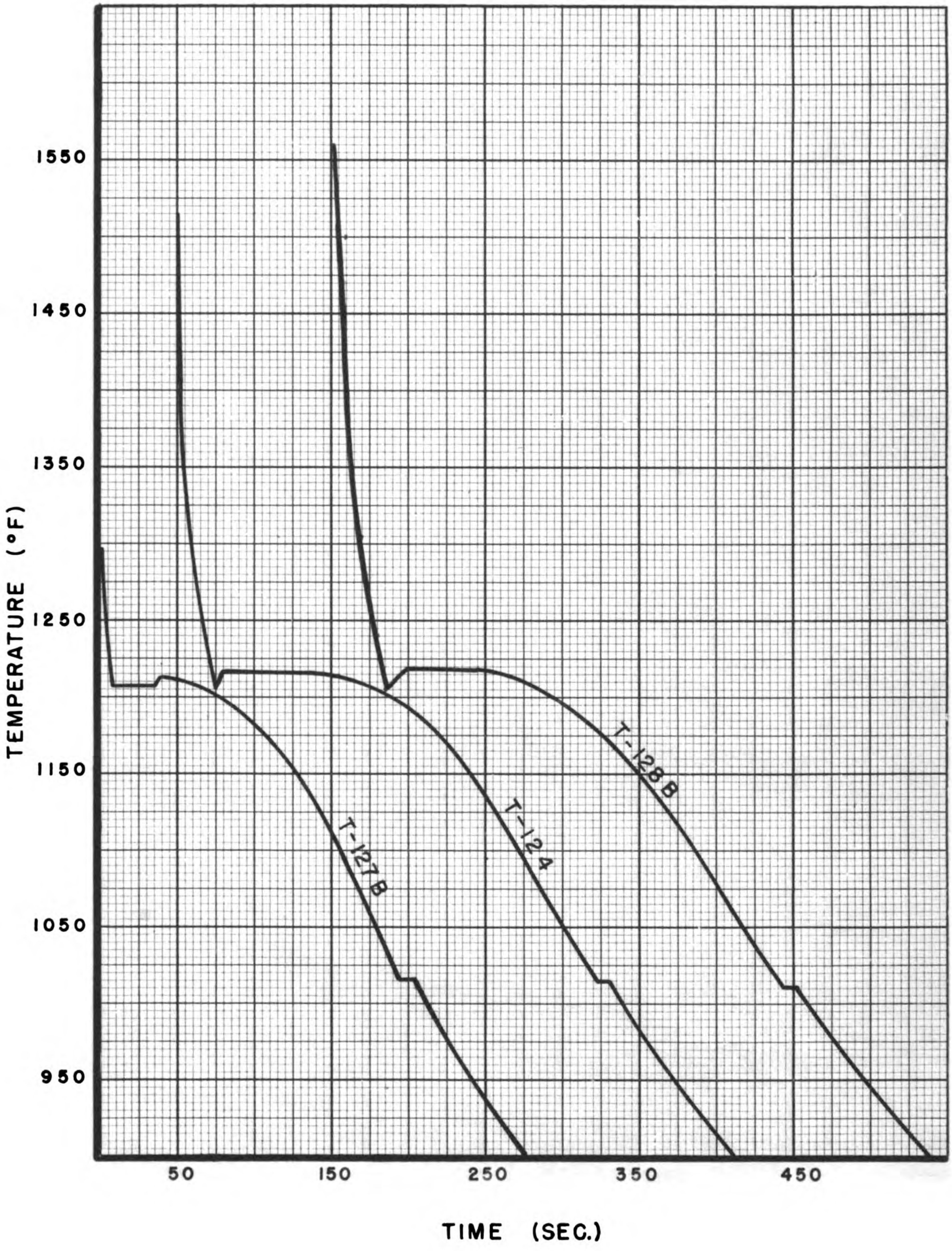
TIME - TEMPERATURE



COOLING CURVES

TIME - TEMPERATURE



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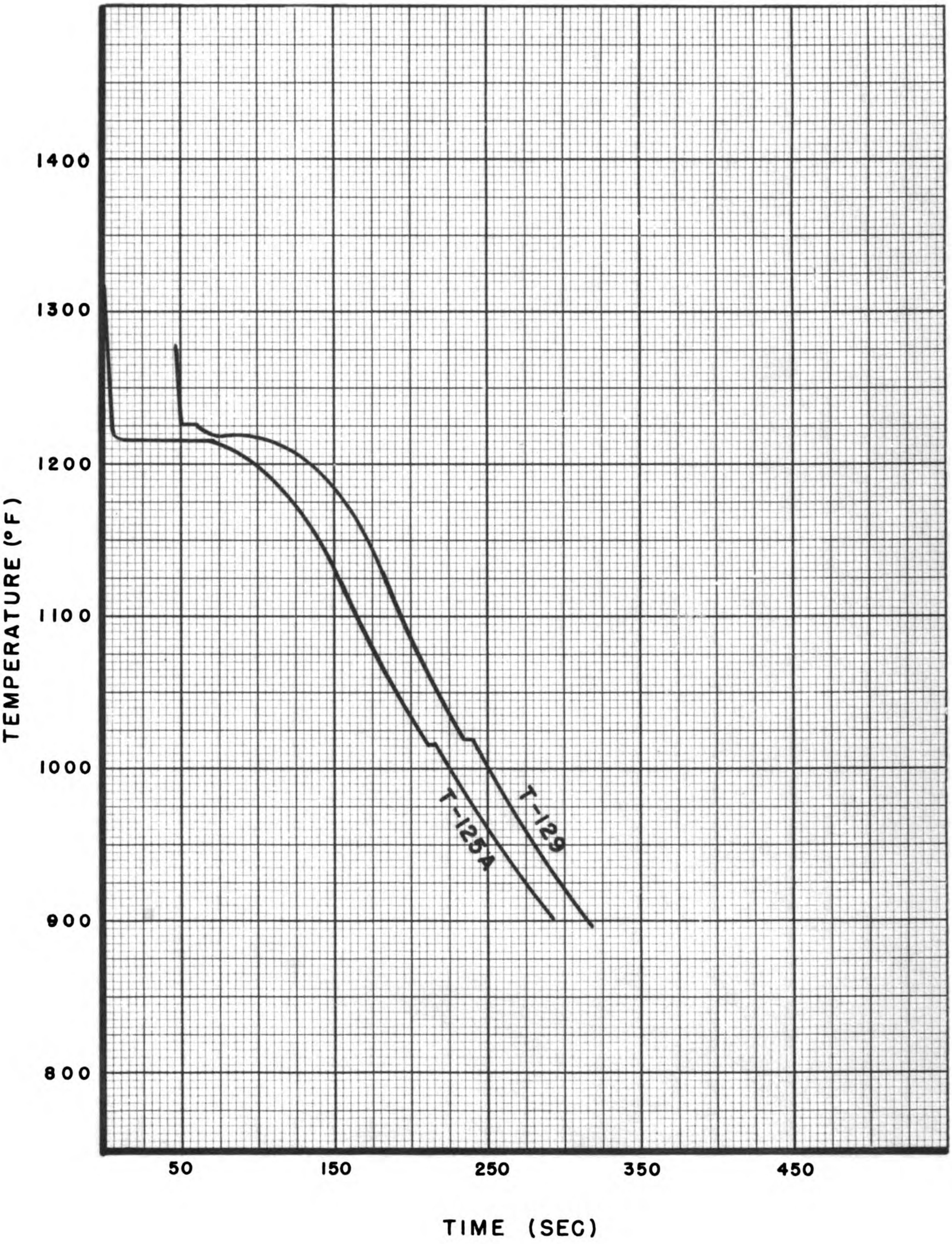
TIME - TEMPERATURE



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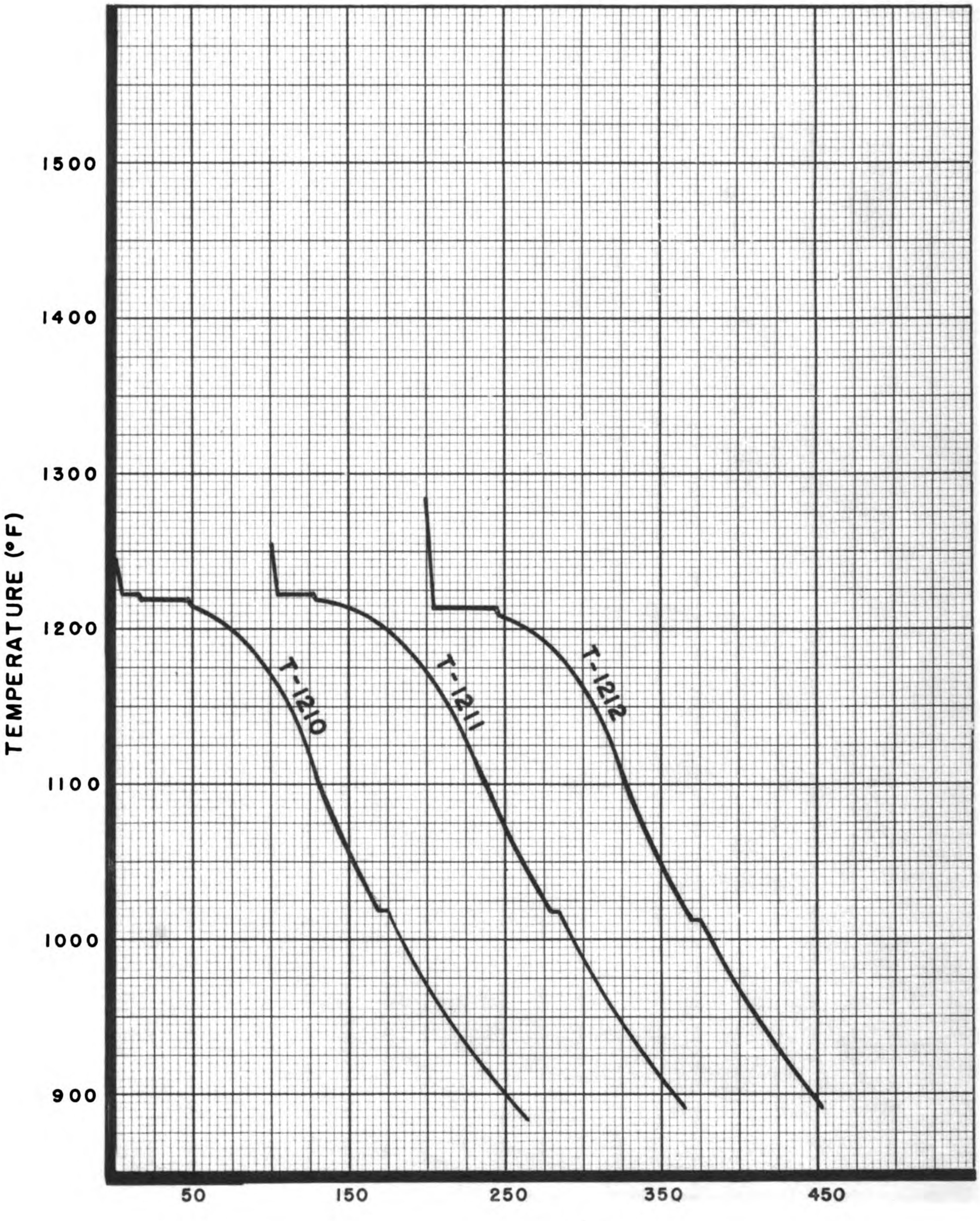
TIME - TEMPERATURE



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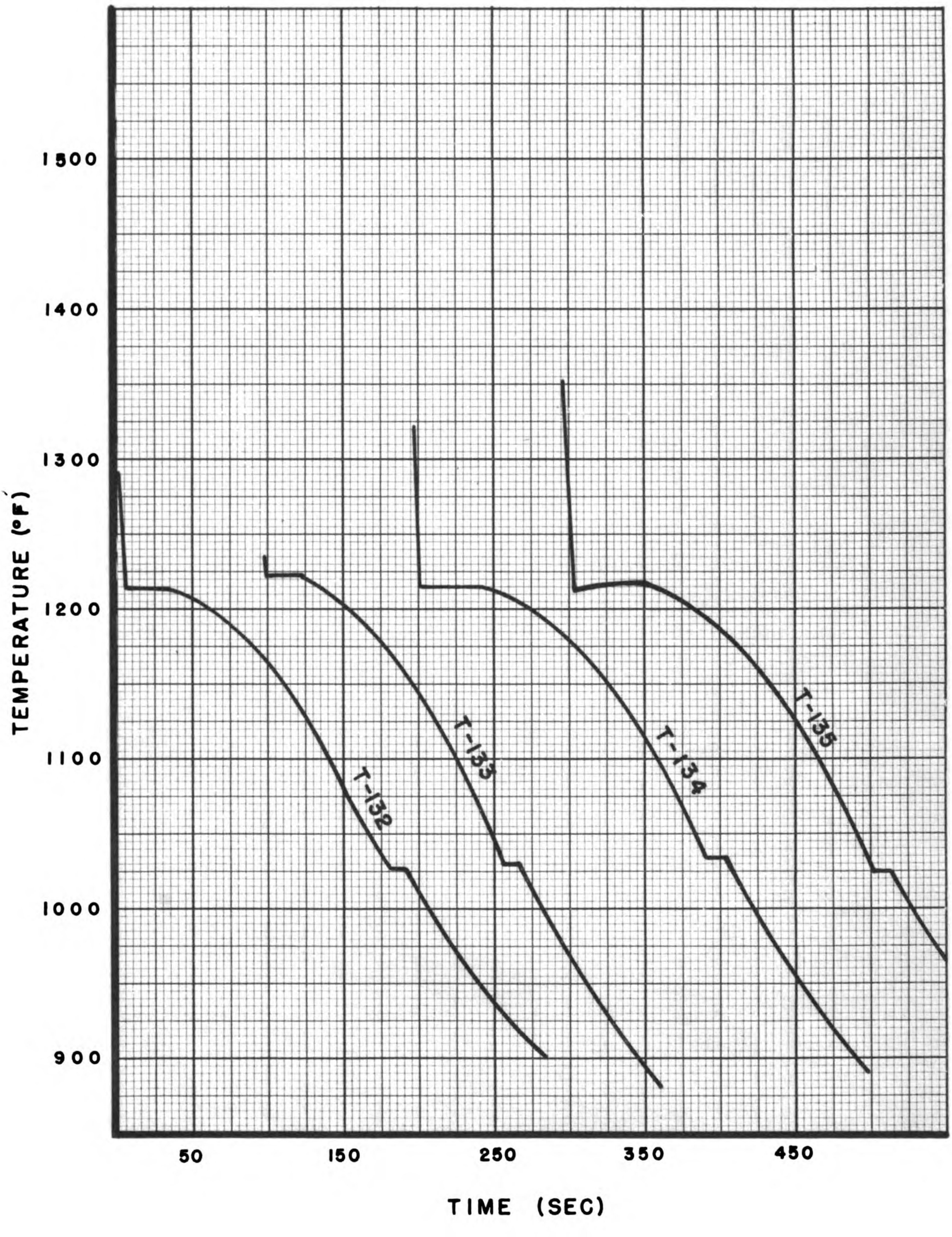

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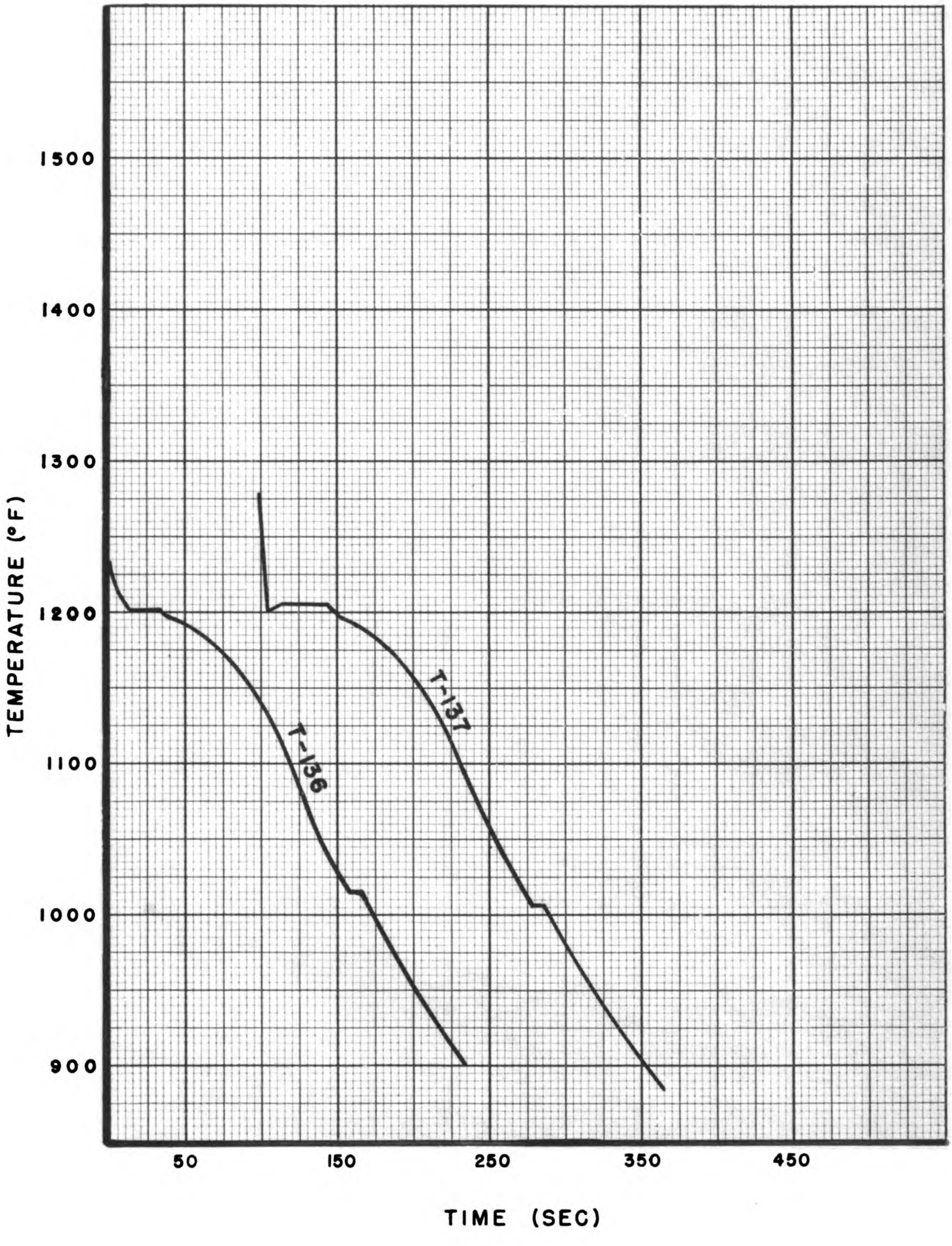
TIME - TEMPERATURE



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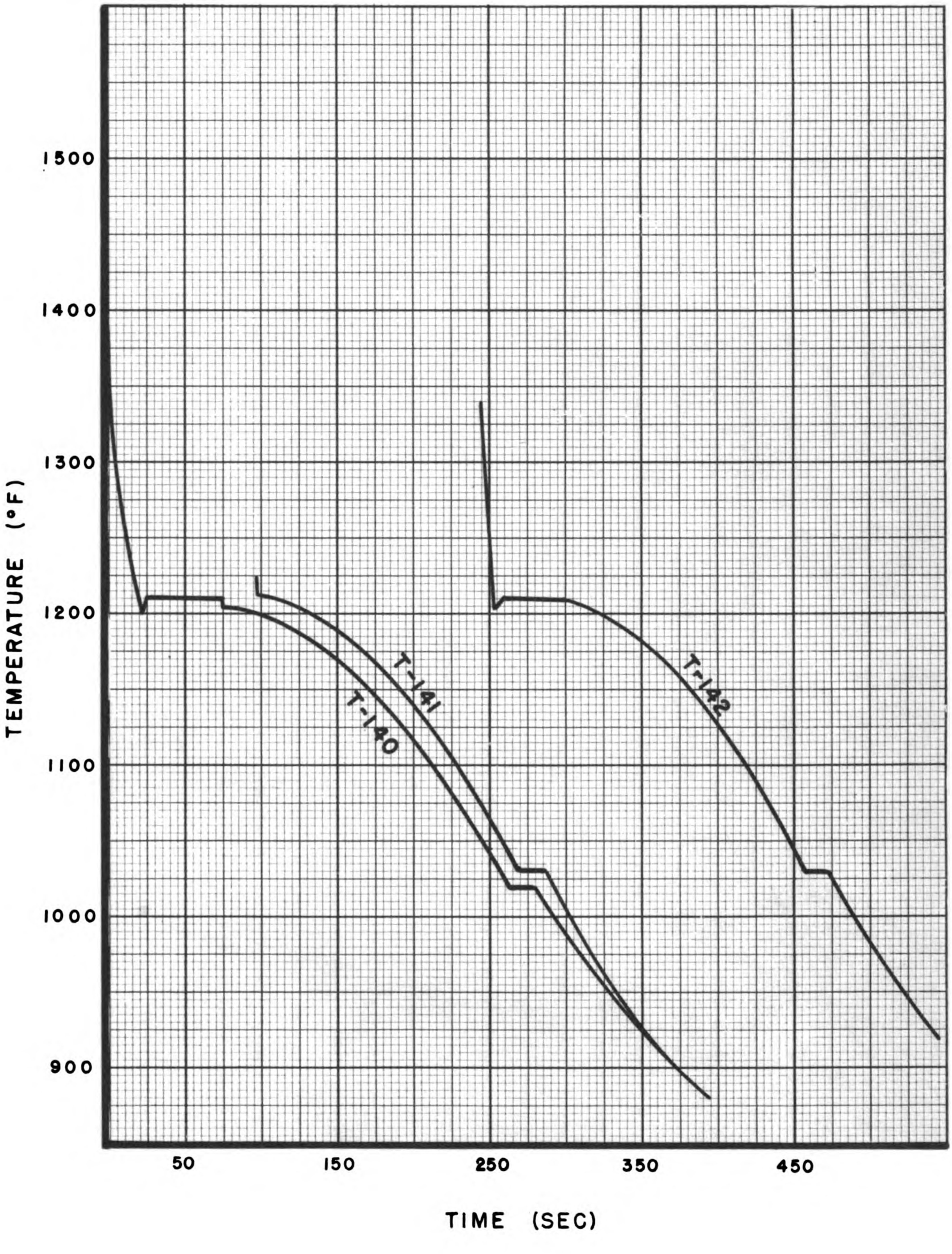
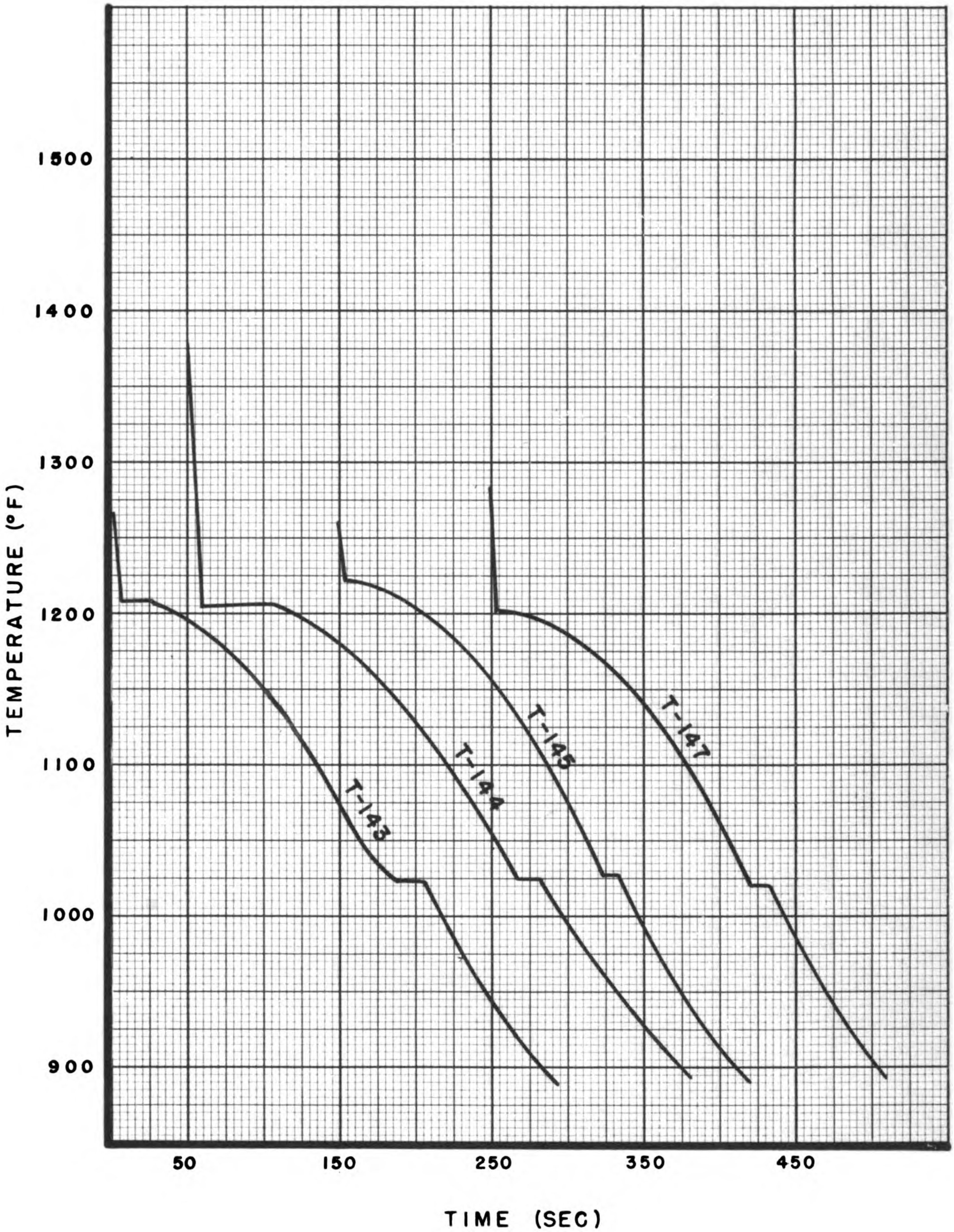
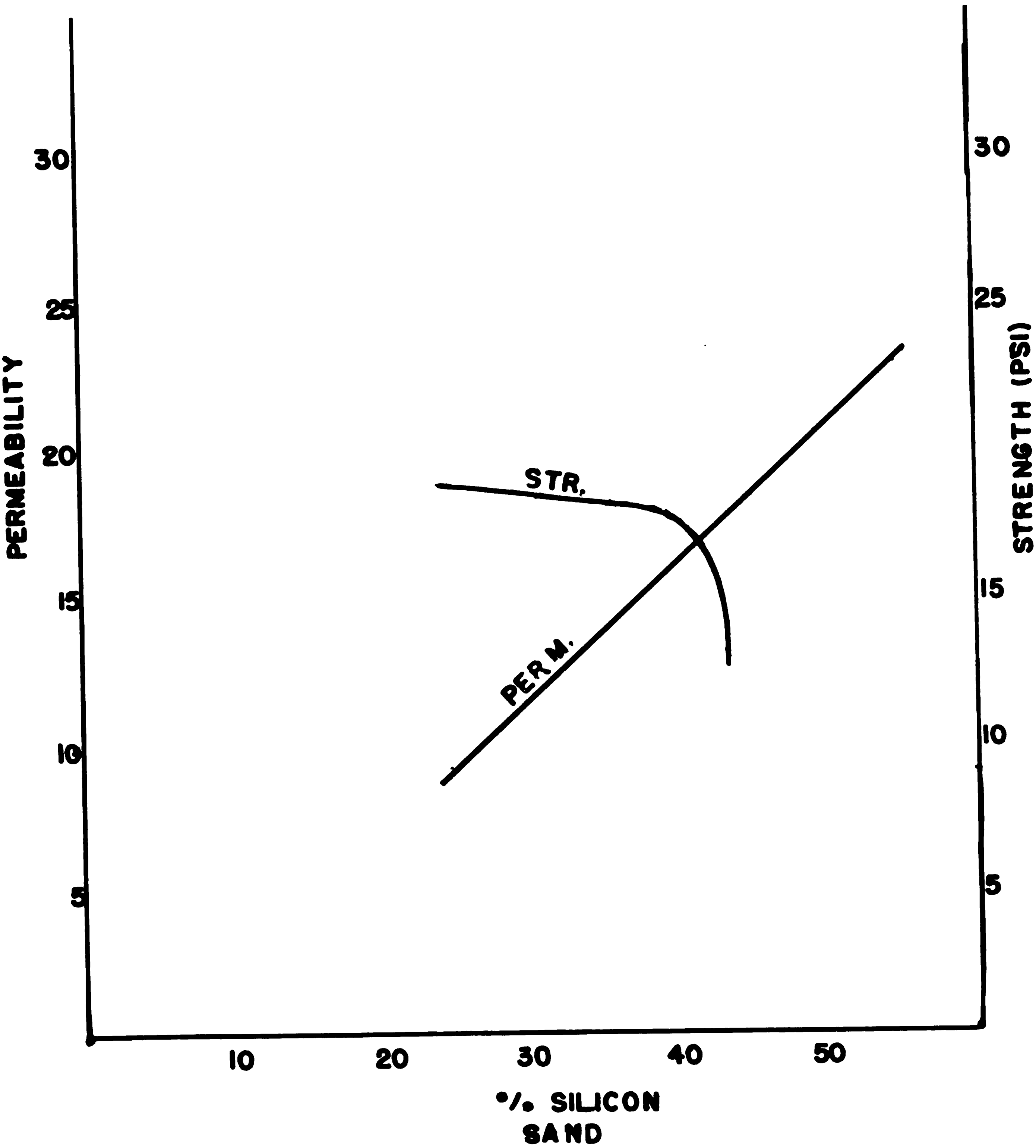


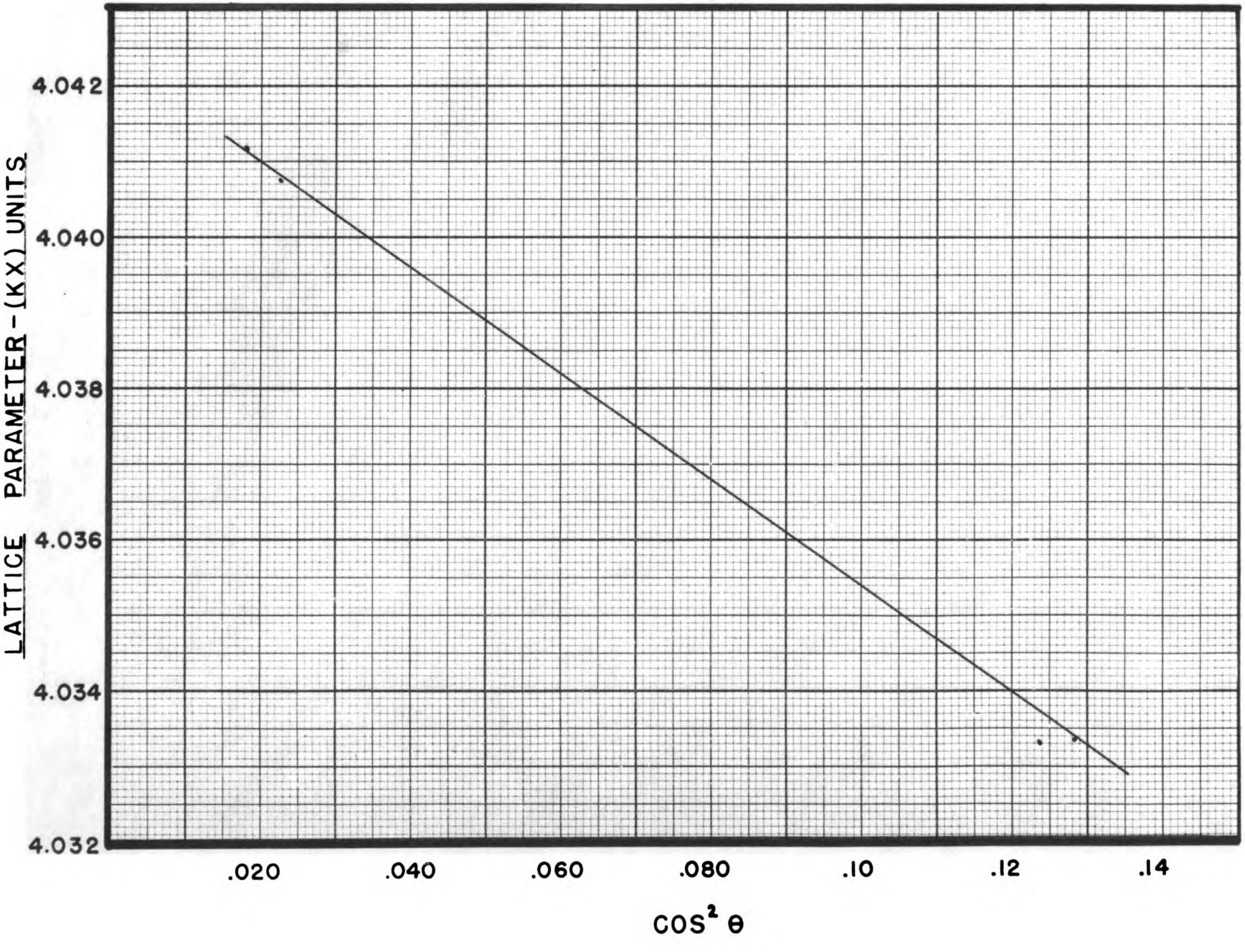
COOLING CURVES
TIME - TEMPERATURE



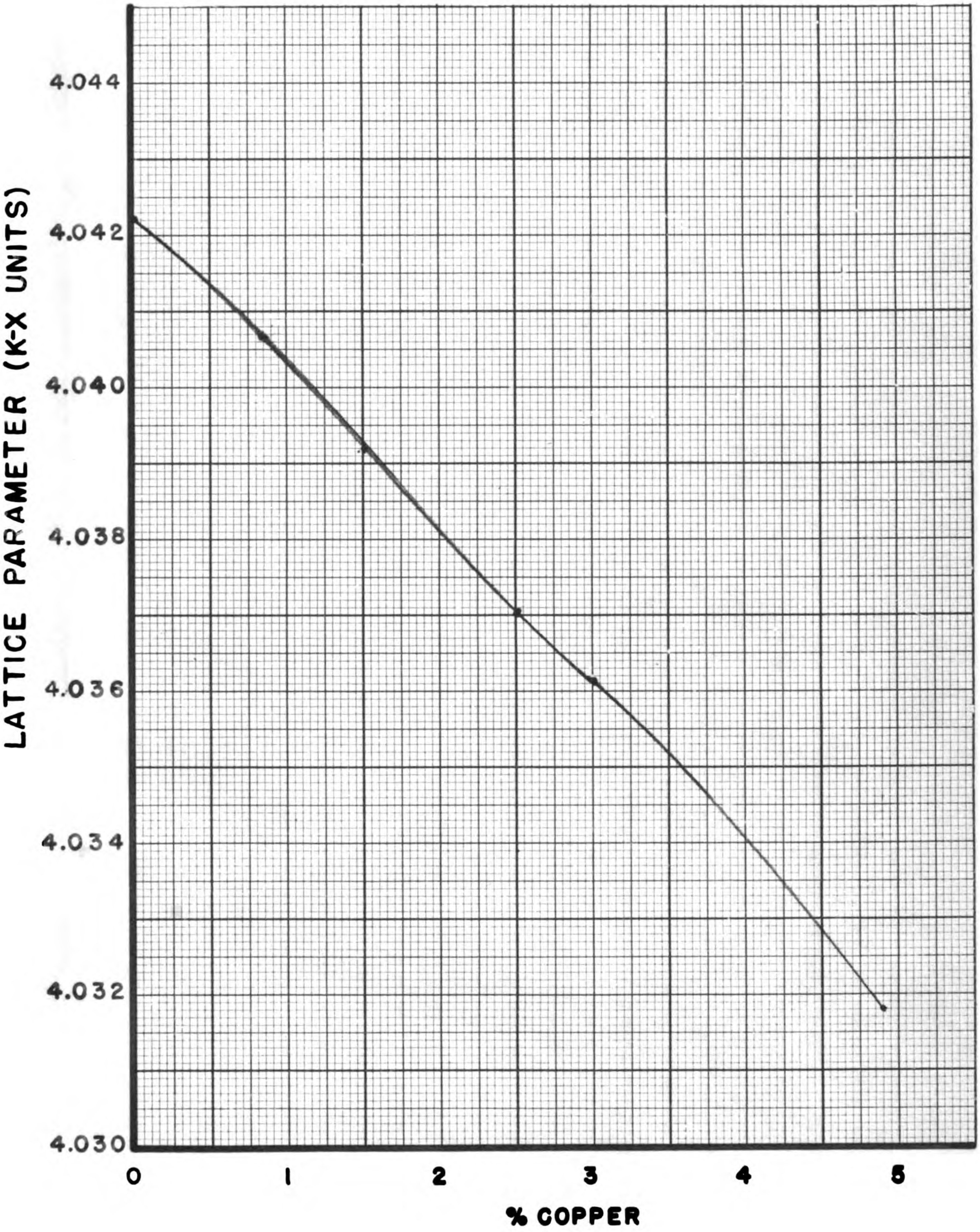
VARIATION OF STRENGTH & PERMEABILITY WITH ADDITION OF SILICON SAND



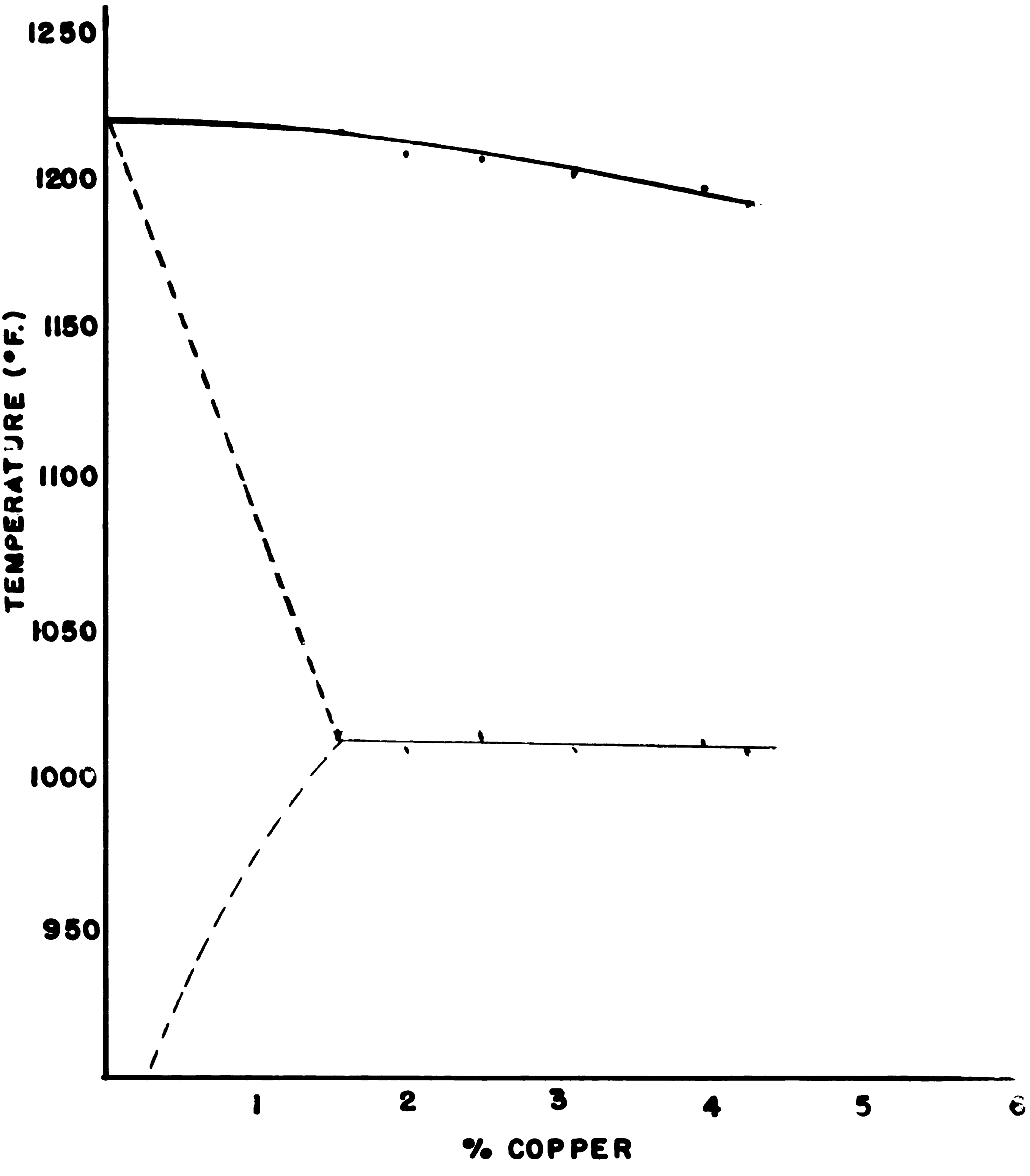
EXTRAPOLATION OF LATTICE PARAMETER
FOR HIGH PURITY ALUMINUM



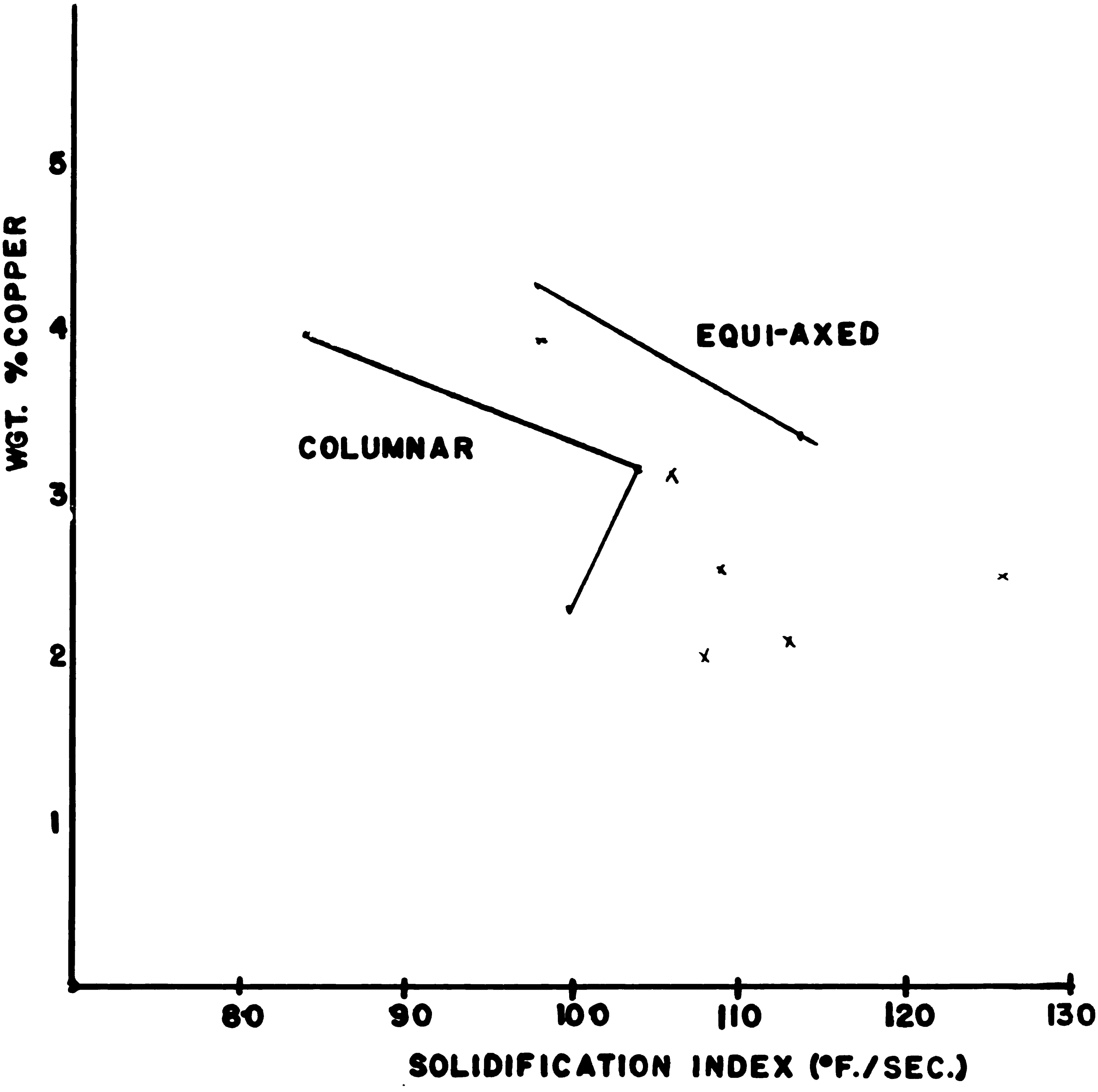
LATTICE PARAMETER
VS
COPPER CONTENT



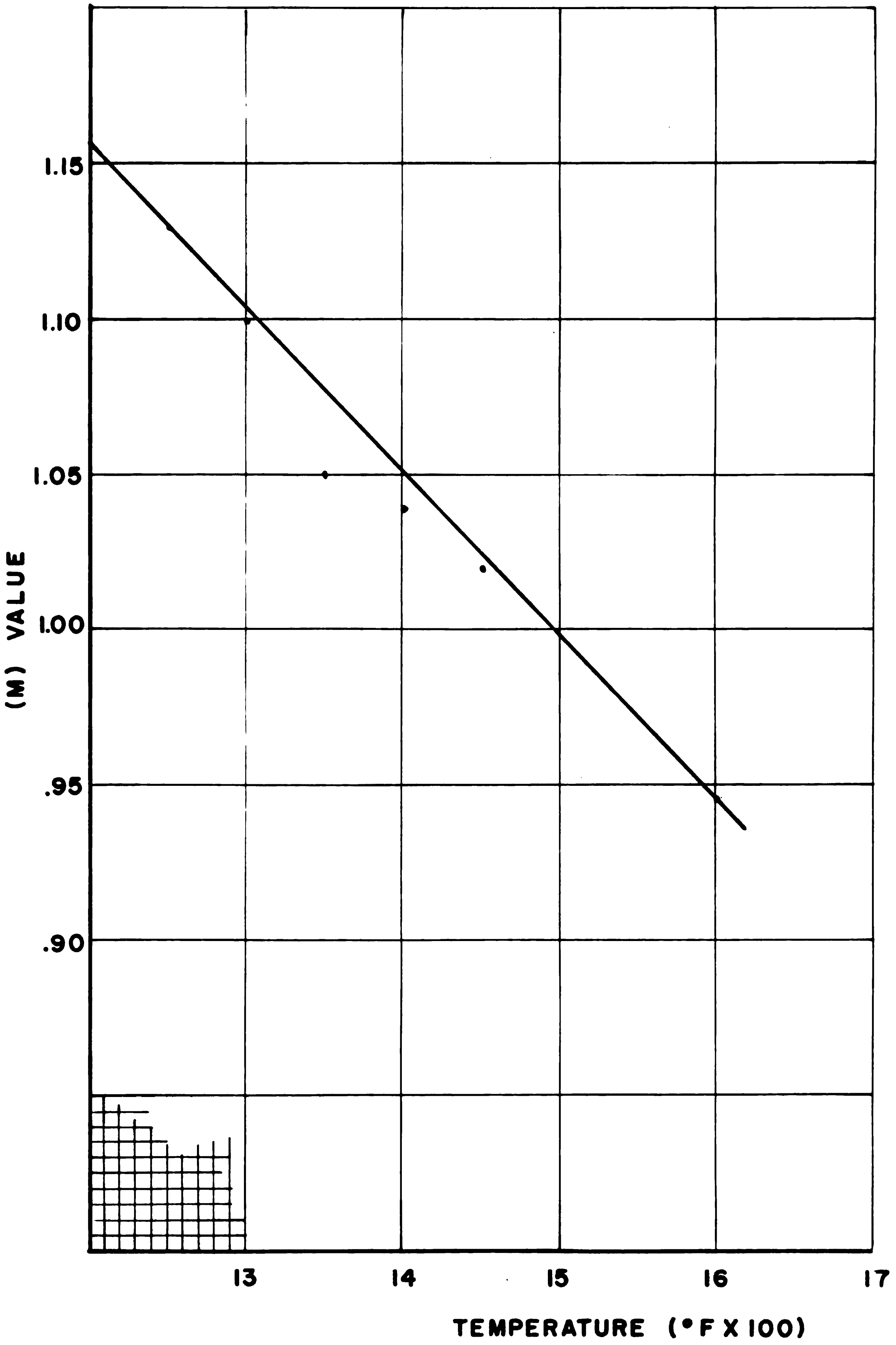
Non-Equilibrium Phase Diagram



RELATION OF COMPOSITION, STRUCTURE AND SOLIDIFICATION INDEX



SOLIDIFICATION CONSTANT(M) VS POURING TEMPERATURE



SAMPLE CALCULATIONS

$$\text{Solidification Index} = \frac{(\text{Liquidus Temp.} - \text{Solidus Temp.})^{\circ}\text{F.}}{\text{Solidification Time (Sec.)}}$$

Sample Calculation for T-140:

$$\text{Solid. Index} = \frac{(1213-1033)^{\circ}\text{F.}}{258.1\ \text{Sec.}} = 0.70\ ^{\circ}\text{F/Sec.}$$

Calculation of Lattice Constants:

$2\phi =$ Distance between like lines.

$\theta = \pi - \phi/2$

Example:

$2\Phi = \text{LINE } 8 - \text{LINE } 1 = 360.35 - 277.50 = 82.85^{\circ}$

$\theta = 180 - 41.425/2 = 69.285^{\circ}$

Lattice Parameter (a):

$$\text{SIN}^2\theta = \frac{\lambda^2}{4a^2}(h^2 + k^2 + l^2)$$

$$\text{SIN}\,\theta = \frac{\lambda}{2a}\sqrt{h^2 + k^2 + l^2}$$

$$a = \frac{\lambda}{2\,\text{SIN}\,\theta}\sqrt{h^2 + k^2 + l^2}$$

Example: (K_{α_1} radiation, 422 plane)

$a = 1.53795/2 \times 0.93538\sqrt{4^2 + 2^2 + 2^2} = 4.02600$ KX UNITS.

Calculation of Chvorinov's Constant (M):

$T \quad (V/SA)^2/M^2$

$M \quad \sqrt{(V/SA)^2/T}$

T Freezing time in Hours.
V Volume
SA Surface Area
M Constant

Example of a long cylinder:

$$T = \left(\frac{D^2L/4}{DL}\right)^2 / M^2 = (D/4)^2 / M^2$$

Example : (T-121)

$$M = \sqrt{(1/4)/185/360} = 1.102$$

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