

A STUDY OF THE CAUSES OF VARIABLE LIQUATION TEMPERATURE
IN COLUMBIUM STABILIZED AUSTENITIC STEEL

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A STUDY OF THE CAUSES OF VARIABLE LIQUATION TEMPERATURE IN COLUMBIUM STABILIZED AUSTENITIC STEEL

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This investigation was conducted to determine the causes of liquation at variable temperatures well below the bulk melting temperature of 18 Cr-8 Ni + Cb austenitic steel (AISI Type 347). Liquation temperatures as low as 2360°F and in excess of 2475°F were observed.

The liquation temperature was determined by metallographic examination of small specimens which had been heated rapidly to temperatures in the range from 2350°F to 2500°F, held for one minute and water quenched. Liquation first manifested itself in the form of a film in the grain boundaries or when larger amounts of melting occurred as a eutectic structure in the grain boundaries.

The variable liquation temperature of wholly austenitic Type 347 steel was due to variations in the amounts of columbium and carbon plus nitrogen which participated in complex eutectic melting reactions. Carbon in excess of columbium on an atomic basis for heats with low nitrogen contents had high liquation temperatures which increased slowly with increasing ratio of carbon to columbium. The products of solidification were austenite and CbC. Slightly reducing the carbon to columbium atom ratio below one resulted in a rapid drop in liquation temperature to about 2400°F where it leveled off for further reductions in the ratio of carbon to columbium. When the liquation temperature leveled off at the low level, the products of solidification were austenite, CbC, and Fe₂Cb. The data indicated a change from one complex eutectic reaction to another complex eutectic reaction as the atom ratio of carbon to columbium was reduced. Increasing amounts of both carbon and columbium slightly altered the ratio at which the observed effects occurred.

Limited studies of the influence of nitrogen indicated that nitrogen was approximately 60 percent more effective than carbon in raising liquation temperature and raised the liquation temperature to values in excess of those which could be reached from carbon alone. Nitrogen probably substituted for a portion of the carbon in the CbC phase and increased the amount of columbium necessary before melting occurred.

Variations in the amounts of chromium and nickel, which introduced ferrite into the microstructure, removed the sensitivity of liquation temperature to the amounts of columbium and carbon. Partition of columbium to ferrite, due to its much higher solubility for

that element, removed the columbium from the austenite where liquation occurs.

Liquation temperature would be expected to be sensitive to segregation in those heats with carbon, columbium, and nitrogen contents within the composition range where liquation temperature is sensitive to the amounts of those elements. In such material, melting, solidification, and hot working conditions should influence the degree of segregation and therefore influence liquation temperature.

The explanation of the causes for variable liquation temperature serves as a basis for understanding hot ductility and is applicable to welding problems in Type 347 steel. The probability of the same type of phenomena in other austenitic steels and the factors controlling it can be estimated from the principles developed.

PREFACE

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INTRODUCTION

The temperature of formation of a liquid phase in 18 Cr-8 Ni + Cb austenitic steel (AISI Type 347) was known to vary among different lots of the alloy ^{1*}. The liquid phase formed at temperatures as low as 2360°F in some heats while in others temperatures in excess of 2475°F were required. This thesis is based on an investigation to determine the causes of variable temperature of formation of the liquid phase (liquation temperature) in this steel under conditions of rapid heating.

Erratic difficulties have been encountered as a result of the welding of heavy sections of this steel due to cracking of the base metal in the heat-affected zone. Although it has not been a problem in light sections, heat-affected zone cracking has occurred with sufficient regularity in heavy sections to be a source of serious concern to users of the steel. The formation of a liquid phase during the thermal cycle associated with the welding operation has been one of the most widely accepted causes of such cracking.

In general the literature has shown the erratic nature of cracking to be due to variations between heats and possibly to variations within a heat of the steel with nominal composition within the usual specification range. If the base metal cracking was due to liquation, the variable nature of the liquation reaction could at least be partly responsible for diverse service experience. The commonly accepted method of evaluating the susceptibility of a material to cracking has been a hot ductility test². In this test, a material is subjected to a rapid heating and cooling cycle which approximates the thermal cycle experienced by material in the heat-affected zone of a weld. The tensile ductility of the material at various points in the thermal cycle has been correlated to the cracking susceptibility of the material³. Low ductility of

*The superscripts refer to literature listed under REFERENCES.

an alloy on cooling from a high terminal temperature was related to high cracking susceptibility. When high ductility was obtained in the same test, it was associated with low susceptibility to cracking.

Microstructural studies of a number of hot-ductility specimens which exhibited a range of ductilities had shown that specimens which had poor ductility always contained evidence of the formation of a liquid phase during the thermal cycle. For a given thermal cycle, some materials would exhibit evidence of liquation in their microstructure while others would not. The variations in behavior of alloys in the hot ductility test can be explained on the basis of variable liquation temperatures among the alloys. The determination of the factors controlling the liquation temperature of Type 347 steel under conditions of rapid heating was the objective of this investigation.

REVIEW OF THE LITERATURE

In order to obtain information from the literature on the subject of liquation in Type 347 stainless steel, it was necessary to review data published on the subject of cracking as a result of welding. In almost all cases, it was necessary to review these papers with the knowledge that variable liquation temperatures do exist in the alloy because most of the literature does not recognize their existence.

The problem of variable susceptibility to cracking of the base metal in the weld heat-affected zone has been the subject of literature surveys within the past four years by Linnert⁴, Fiorentino and Associates⁵, and recently by Borland and Younger⁶. These surveys have emphasized the large number of contradictory results which have been published concerning the problem. The main points shown by these surveys, however, are:

- 1) Some investigators believe cracking occurs during the welding operation.
- 2) Other investigators believe it occurs during subsequent heat treatment or service as a result of embrittlement caused by the welding operation.
- 3) All agree that it has only been a serious problem in heavy sections, particularly in main steam piping of electric power generation facilities.

Cracking During Welding

Over the years, grain boundary liquation has been cited numerous times^{7, 8, 9, 10, 11, 12, 13, 14, 15, 16} as the cause of cracking in the base metal heat-affected zone. These papers have cited evidence of melting at the grain boundaries in which cracks propagated. During welding, the temperature of the base metal at the weld interface must approach the temperature of the molten weld metal. Since the evidence of grain boundary liquation extended into the base metal, liquation

occurred at a temperature below that which existed at the weld interface, well below the bulk melting point of the base metal. The presence of a liquid phase in the grain boundaries allowed cracks to initiate and propagate under the action of the stresses developed in the base metal on cooling.

While these papers show that cracking may be associated with liquation, they do not recognize that variable liquation temperatures exist in the steel.

Cracking Subsequent to Welding

Those investigators^{17, 18, 19, 20, 21, 22} who found data indicating that cracking occurred during heat treatment or service subsequent to welding have generally considered liquation to have a minor influence on cracking. Their papers claim that the thermal and mechanical stresses existing in the heat-affected zone cause a strain induced precipitation of CbC. This precipitation occurs only in the portion of the base metal which has had a high temperature solution treatment such as produced by the welding operation. This precipitation of fine CbC particles raises the creep resistance of the grains to a very high level. Stresses imposed on this portion of the base metal during heat treatment or service caused deformation to be forced to the grain boundaries. Under these conditions, total deformation is slight before cracking is initiated. Such material would be very susceptible to premature failure due to stress concentrations. This approach to cracking in Type 347 steel offers little information relating to variable liquation temperature.

Other investigators^{23, 24, 25, 26, 27, 28, 29, 30, 31} have studied the influence of heat treatment on the carbide phases present in this steel. They have related the type, size, and distribution of the carbide phases to subsequent mechanical properties. Here again, these investigations provided little background regarding variable liquation temperature.

Effect of Chemical Composition

A number of investigations have been carried out on the influence of chemical composition on cracking susceptibility. Most of these investigations have been directly concerned with cracking in the weld deposited metal. In general, they have not been related to liquation. In most cases, they have been related to cracking susceptibility as measured in various ways.

Hoerl and Moore^{3 2} have made a statistical analysis of the effects of various elements on the cracking susceptibility of fully austenitic weld deposited metals. Their results showed that C, Mn, Cr, Nb, and N decreased cracking susceptibility, while Si, S, P, and Ni increased it. Goldschmidt^{3 3}, Rollason and Bystram^{1 5}, and Bishop and Bailey^{3 4} have concurred with Hoerl and Moore^{3 2} in that silicon increased susceptibility to cracking. Goldschmidt^{3 3} thought that this was due to the formation of an iron-columbium silicide, $Fe_4 Nb_5 Si_3$. Rollason and Bystram^{1 5} also agreed that sulfur increased the susceptibility of the material to hot cracking.

The analysis of Hoerl and Moore^{3 2} which showed that carbon decreased cracking susceptibility was in agreement with the finding of Rollason and Bystram^{1 5}, while Nippes et al^{3 5} and Medovar^{1 4} took the opposite point of view. Hull^{3 6, 3 7} studied the effects of various elements on the hot cracking tendency of austenitic Cr-Ni steels using the cast-pin tear test. He showed that N, Mn, Mo, W, and Cr decreased the susceptibility to hot cracking, while Co, V, Al, Ni, Ta, Si, Nb, Ti, C, Hf, Zr, and B caused increasing amounts of cracking. Perkins and Binder^{4 5} have concurred with Hull^{3 7} in his finding that nitrogen decreased cracking susceptibility.

In no case was it clear to what degree the cracking was due to liquation and to variable liquation temperatures. In all the tests, it could have been a major factor although other factors such as the ductility of the bulk material could have been more important. Hull's

experiments could have very easily measured liquation effects in alloys containing B, Cb, Hf, and Zr since there was some evidence that cracking occurred while a liquid phase was present. In most cases, however, the results tended to show that the amount of ferrite developed on solidification of the weld metal was the important factor in determination of the cracking susceptibility of an alloy. The presence of 7 to 10 percent ferrite yielded material with maximum cracking resistance.

Hot-Ductility Testing

The hot-ductility test² has been widely used to evaluate the weldability of Type 347 steel. This test reproduces the thermal cycle experienced by the base metal in the heat-affected zone during the welding operation. Curves of ductility are established as a function of temperature up to the temperature at which the steel has nil ductility. Specimens are then heated to the nil ductility temperature, cooled and broken to establish a curve for the ductility of the steel on cooling. Those materials which recovered ductility rapidly on cooling from the nil ductility temperature have been associated with low cracking susceptibility. Materials which were slow to recover ductility have been associated with high cracking susceptibility during welding and subsequent to welding³.

Kreischer³⁸ has stated that the stress required to fracture the specimens may have been as important as their ductilities. He cited several cases where anomalies existed between the results of hot-ductility tests and actual welding behavior. Re-evaluation of these results, with consideration given to the tensile strength, provided correlations with actual welding behavior.

It should be noted that due to the large number of tests required to completely establish ductility curves, the practice has been developed where specimens are heated to a specific terminal temperature,

cooled to some temperature and broken. High ductility has been taken as evidence of resistance to cracking while low ductility has been associated with susceptibility to cracking.

Liquation and Hot Ductility

A research investigation of the causes of base metal cracking in Type 347 steel at the University of Michigan has been sponsored by the Steam Power Panel of the ASTM-ASME Joint Committee on Effect of Temperature on the Properties of Metals at the request of and with the financial assistance of The Prime Movers Committee of The Edison Electric Institute. As part of the investigation, the microstructure of Type 347 stainless steel was shown to be related to the behavior of the steel in the hot-ductility test. Low ductility in this test was always associated with evidence of formation of a liquid phase during the thermal cycle. The liquid phase manifested itself in the room temperature microstructure in the form of a eutectic structure. The relationship existing between the hot ductility of Type 347 steel and the amount of the eutectic structure is shown in figure 1. Further studies showed that the temperature of formation of the liquid phase varied among the materials used in the investigation¹.

EXPERIMENTAL PROCEDURES

The general procedure involved melting and fabrication of small heats of Type 347 steel using variations in composition and hot working schedule from heat to heat. The liquation temperatures of the heats were then studied as a function of the compositional and processing variables. The detailed experimental procedures are described in the following sections.

Experimental Materials

The experimental materials made during this investigation were induction melted in the University of Michigan vacuum-induction furnace. The heats were made in alumina or magnesia crucibles using virgin melting stock. The melting stock was comprised of electrolytic iron, electrolytic nickel, aluminum reduced chromium, electrolytic manganese, 99.9 silicon powder, spectroscopically pure carbon, and 99.6 percent columbium roundels. The heats normally totaled 4000 grams, except in the cases where split heats were made. The split heats totaled 5000 grams of charged material. In split heats two or more ingots were poured in order to study the influence of variations of one element in material with a constant base composition.

The materials were normally processed by holding at 2100°F for two hours followed by rolling at 2100°F to ½ inch square bar stock in 20 passes with 5 reheats. The total amount of reduction of the ingots was about 95 percent when this procedure was followed. The smaller ingots from the split heats were reduced to ½ inch bar stock in 10 passes with 2 reheats, giving a total reduction of about 90 percent. The hot working temperature and total amount of reduction were varied only to study the effects of variable hot working practice.

Heating Structure Test

The heating structure test consisted of exposing samples of a material to a series of temperatures for a given time and subsequent observation of the microstructure of the samples to determine the temperature at which liquation occurred in the material.

The samples used in the heating structure test measured approximately $\frac{1}{4}$ " x $\frac{1}{4}$ " x $\frac{3}{8}$ ". After these samples were cut from the material to be studied, a hole $\frac{1}{16}$ " in diameter was drilled about $\frac{2}{3}$ of the way through each sample along the length of the sample. Using a percussion welding technique with 28 gage wire a chromel wire was welded to one side of the drilled hole and an alumel wire welded to the other side. With this arrangement, the sample acted as the bead of the thermocouple. The wires were then passed through a two-hole ceramic insulator approximately 12" long. This insulator was then butted up against the sample so that no section of the thermocouple was exposed to direct radiation.

The thermocouple was attached to a high speed, variable range, variable span recorder. The recorder was adjusted to give full scale deflection of 10 millivolts from a zero point of 45 millivolts (2005°F) to provide sensitivity in measuring peak temperatures. In order to attain this sensitivity, it was necessary to sacrifice heating rate data in the range from room temperature to 2000°F.

The specimen was inserted into the hot zone of a "glo-bar" furnace and in 45-50 seconds reached the exposure temperature. The exposure temperature was adjusted by changing the position of the specimen in the hot-zone of the furnace. The specimen was held at temperature for one minute, removed and water-quenched. During the time the specimen was at the exposure temperature, the temperature was kept within a range of 5°F. The peak temperature which the sample attained during the one minute exposure was recorded as the exposure temperature. For example, if the sample varied in temperature between 2440°F and 2445°F, then 2445°F was listed as the exposure temperature.

Light Microscopy

Metallographic samples were mechanically polished on wet silicon carbide papers through 600 grit and on cloths impregnated with 6 and 1 micron diamond paste. The final polish was obtained on a Syntron ultrasonic polishing unit using a solution of Linde B powder and water.

The etchant used on the samples was composed of 6 parts phosphoric acid (85 percent) and 1 part distilled water. The specimens were etched electrolytically at 6 volts and at a current density of approximately 1.5 amperes per square inch. The time required to obtain a satisfactory etch was approximately 10 seconds. This time had to be increased to 20 seconds when ferrite was present in the microstructure.

An immersion etch in concentrated hydrofluoric acid (55 percent) for two minutes was sometimes employed in the evaluation of the microstructures. This etch made it possible to distinguish between coarse Fe_2Cb particles and CbC particles as is shown in figure 2. The hydrofluoric acid rapidly attacked the Fe_2Cb while leaving the CbC untouched. The distinction was not possible when the phosphoric acid-distilled water etch was used.

Determination of Ferrite Content

The amounts of ferrite present in the materials were determined by the use of a Magne-Gage. This instrument essentially consisted of a magnet mounted on a spring. It measured the force required to pull the magnet from the surface of a material. The amount of magnetic phase present, in this case ferrite, determined the attractive force between the material and the magnet.

The calibration of the Magne-Gage was established by making use of the method of lineal analysis to measure the volume percent ferrite in the microstructure of samples containing various amounts of ferrite. The plot of volume percent ferrite versus Magne-Gage reading yielded a linear relationship as shown in figure 3.

The ferrite determinations were made by taking four Magne-Gage readings on each sample. These readings were averaged and the average value converted into percent ferrite by use of the calibration curve. It should be noted that care was taken to avoid readings near the surface of the material since a magnetic oxide layer was present on these surfaces.

X-Ray Diffraction

A slight modification of the extraction technique reported by Binder ²⁶ was used in the isolation of the excess phases present in the alloys. The specimen surfaces were ground on wet silicon carbide paper to remove any surface oxide layers. The sample was then digested in a solution composed of 75 grams CuCl_2 , 50 milliliters of concentrated hydrochloric acid, and 225 milliliters of distilled water for approximately 24 hours. The solution was filtered to separate the residue which was washed with distilled water and dried. The extract was placed in a 0.5 mm glass capillary tube which in turn was placed in a 114.6 mm diameter Debye-Scherrer camera and subjected to nickel-filtered copper radiation for 6 hours. The X-ray films were measured using a comparator to the nearest 0.005 cm. The values obtained were compared with standard patterns to identify the phases present in the residue.

Lattice parameter measurements of the CbC phase were made by calculating "a" values by use of the Bragg equation. The Nelson-Riley method of extrapolation ³⁹ was used to determine the lattice parameter of the extracted phase. The lattice parameter dropped with increasing amount of nitrogen present in the phase and it was used as a qualitative measure of the nitrogen content of the phase.

Electron Diffraction

In certain cases, the amount of Fe_2Cb in the extracted residue was too small to permit positive identification by X-ray diffraction. In

the cases where it was thought that this phase should be present and where its presence was not indicated in the X-ray films, an electron diffraction technique was employed.

This technique consisted of making a dilute water solution of the extracted residue. A drop of this solution was placed on a collodion covered nickel grid. The water was then allowed to evaporate. The grid was placed in a 50 kv electron microscope and scanned with the electron beam. The individual particles on the grid emitted an electron diffraction pattern. The diffraction patterns were indexed to determine the identity of the particles from which they were obtained. In most cases, only two phases were present in the residue, CbC and Fe_2Cb , and these phases had different crystal structures. Because the diffraction patterns were widely different it was not considered necessary to place an internal standard on the grid.

MICROSTRUCTURE OF TYPE 347 STEEL

The evaluation of the results of this study required a clear understanding of the microstructure of Type 347 steel. The results are primarily expressed in terms of microstructures which vary with the composition and condition of the steel prior to and as a result of exposure to high temperatures.

As-Cast Condition

During solidification, austenite was the first phase to solidify followed by a eutectic. This eutectic was composed of a mixture of austenite and CbC and was located at the grain boundaries (figure 4). Some additional CbC was usually present within the austenite grains. The size of the CbC particles in the eutectic structure increased as the cooling rate decreased. The eutectic structure of small ingots (200 grams) was rather fine (figure 4), while larger 4000 gram ingots had a much coarser eutectic structure (figure 2).

With compositions in which the columbium content was unusually high, such as the 1.39 percent columbium of heat 1241, Fe_2Cb also formed within the eutectic structure (figure 2). For compositions within the specification range for Type 347 steel, Fe_2Cb was not found in the microstructure except in isolated patches near the ingot surface (figure 5). This phase apparently formed at this position due to carbon depletion.

Ferrite formed in some heats and appeared in the as-cast microstructure as separate grains (figure 2b).

As-Rolled Condition

In the rolled condition, the microstructure of this alloy consisted of CbC particles in an austenitic matrix. Usually, the particles were

located in stringers. These stringers became more pronounced as the amount of hot reduction increased. The stringers resulted from the break-up of the eutectic patches of CbC and austenite which existed in the as-cast state. Figure 6 shows an example of the microstructure of the steel as a function of the amount of hot reduction.

A precipitation of secondary particles of CbC sometimes occurred on cooling of the rolled bar stock from the hot working temperature. The amount of this precipitation increased as the cooling rate was decreased. The hot working operation caused any ferrite present in cast state to become elongated in the direction of rolling.

After High Temperature Exposure

Exposure Below the Liquation Temperature

High temperature exposure of Type 347 alloys at temperatures just below the liquation temperature resulted in the solution of many CbC particles which were present in the as-cast or as-rolled condition. The amount of the CbC taken into solution increased with exposure temperature. This is in agreement with the data of Irvine, Murray, and Pickering¹⁹ (figure 7) which show that the solubility of columbium in austenite increases with increasing temperature. Other investigators^{40, 41} are in agreement with the data presented in figure 7. If the carbon and columbium levels of the material are low enough, then after high temperature exposure below the liquation temperature the microstructure would be completely austenitic. In most alloys, however, all CbC particles within the matrix are not dissolved at the liquation temperature for the short exposure times and rapid heating rates used in this study.

Exposure Above the Liquation Temperature

When samples of Type 347 steel were held at temperatures above the temperature at which liquation occurred, pronounced changes took

place in the microstructure. The amount of liquid formed in the alloy varied directly with the exposure temperature (figure 8). Depending upon the exposure temperature, the liquid phase was manifested in the room temperature microstructure either as a grain boundary film or as a eutectic structure located in the grain boundaries. The grain boundary film was present after exposure to temperatures just above the liquation temperature (figure 8b), while the eutectic structure became evident in the microstructure after exposure to temperatures about 20°F above the liquation temperature and increased in amount with increasing temperature of exposure.

The number of CbC particles in the microstructure decreased with increasing exposure temperature and approached zero as the alloy shifted from the austenite plus CbC plus liquid region into the austenite plus liquid region. The CbC particles usually disappeared from the microstructure by dissolving in austenite although there was evidence that in some cases the CbC reacted with austenite to form a liquid. These areas were manifested in the room temperature microstructure in the form of eutectic "rosettes" located within austenite grains (figure 8d).

With increased temperature, the microstructures of the alloys used in this investigation changed from austenite and CbC to austenite, CbC, and liquid. On further heating, the CbC phase disappeared leaving only austenite and liquid stable at higher temperatures.

Effects of Variable Cooling Rate on the Microstructure

Rapid Cooling

When samples of this alloy were air cooled or water quenched from exposure temperatures above the liquation temperature of the material, the structure of the eutectic was quite fine. In many cases, it was not possible to resolve the different particles in the eutectic structure by optical methods. Depending upon the exposure tempera-

ture and alloy composition, undissolved CbC particles were or were not present within the matrix. In experimentally determining the phase relations, the presence or absence of these particles was used to establish whether the alloy was located in the austenite plus liquid region or the austenite plus CbC plus liquid region at the exposure temperature.

In high columbium-low carbon alloys, X-ray analysis of extracted residues showed that an Fe_2Cb phase was present as part of the eutectic structure after the samples were air cooled or water quenched from above the liquation temperature. No positive method of identifying this phase in the optical microstructure has been developed for the cases where the particle size of this phase was small. The comparison of a great many samples of the alloy which experienced rapid cooling from above the liquation temperature did reveal, however, subtle differences in the eutectic structure between materials which contained the Fe_2Cb phase and those which did not.

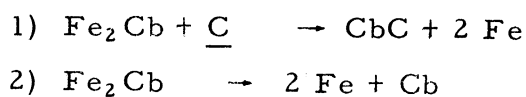
In those materials which contained the Fe_2Cb phase, the eutectic was dark grey or greyish-brown in color after etching with the phosphoric acid and water solution (figures 9a and 9b). The eutectic structure in those materials which did not contain the Fe_2Cb phase was light grey in nature. This distinction was not always readily obvious to the casual observer.

Rapid cooling of specimens from exposure temperatures below the temperature of formation of a liquid phase resulted in a microstructure composed of austenite and CbC. The amount of CbC decreased with increased exposure temperature due to solution of CbC.

Slow Cooling

The comparison of samples water quenched or air cooled from a temperature above the liquation temperature with samples furnace cooled from the same temperature showed marked differences in the microstructure (figure 9). Only two phases, CbC and austenite, were

found in the microstructure of furnace cooled specimens. There was no evidence of the presence of the Fe_2Cb phase in these specimens. The CbC particles, for the most part, were located in the grain boundaries in a coarse eutectic arrangement (figures 9c and 9d). This contrasted sharply to the very fine eutectic structure evident in the rapidly cooled specimens (figures 9a and 9b). During slow cooling, the CbC particles agglomerated and increased in size. The Fe_2Cb phase which formed on solidification of the liquid in high columbium-low carbon materials transformed into austenite and dissolved columbium or reacted with carbon in solution to form austenite and CbC . The reaction was one of the following:



The applicable reaction occurred just below the liquation temperature. The instability of the Fe_2Cb phase at these temperatures indicated that the liquid phase was enriched in columbium and the resulting Fe_2Cb was not in equilibrium with the matrix.

Identification of Fe_2Cb

The presence of Fe_2Cb in Type 347 alloys was first noted in an alloy containing 1.39 percent Cb and 0.04 percent C . Since that discovery, the phase has been found in alloys containing as little as 0.73 percent Cb . Prior to this time, this phase had not been reported in austenitic alloys containing less than 1.8 percent Cb .²⁶

A number of investigators^{22, 23, 24, 25, 29, 31} have made X-ray analyses of the excess phases present in Type 347 alloys. Several individuals^{15, 24, 42, 43} have attempted to analyse materials containing the eutectic structure. None of the investigators have reported the presence of the Fe_2Cb phase. The reason for their failure to detect this phase probably was either the result of an improper method of extraction or a slow cooling rate from the liquation temperature

which caused the Fe_2Cb to dissolve. Most commonly used extraction solutions dissolve the Fe_2Cb phase. Bromine in methyl alcohol is a common example of a solution which will dissolve this phase.

Figure 10 shows the electron diffraction patterns obtained from Fe_2Cb and CbC particles which were extracted from a sample rapidly cooled after exposure for one minute at a temperature in excess of its liquation temperature. The particles from which the patterns were obtained are also shown. This figure shows the Fe_2Cb phase to be present as a thin film which was almost transparent. The diffraction pattern obtained from the particle was typical of the type obtained from thin films.

The CbC and Fe_2Cb electron diffraction patterns were indexed as shown in figure 11. The lattice parameter values reported by Wallbaum⁴⁴ were used to index the pattern obtained from the Fe_2Cb phase.

RESULTS AND DISCUSSION

The composition and prior history of this steel were varied to determine the causes of the variable liquation temperature. It was found that the liquation temperature was controlled by the columbium, carbon, and nitrogen contents of the alloy. The only exceptions were compositions which allowed ferrite to be stable in the microstructure.

Effects of Carbon and Columbium on Liquation Temperature

During the course of the investigation, several factors pointed to carbon and columbium contents as being the principal factors which controlled the temperature of formation of the liquid phase in Type 347 alloy. The liquid phase often formed 150°F or more below the bulk melting temperature of the alloy. It had been noted many times that a high columbium level in conjunction with a low carbon level always resulted in a low liquation temperature in fully austenitic materials. In an effort to pinpoint the effects of varying contents of carbon and columbium on liquation temperature, a series of heats (Table I) were made in which the levels of these elements were intentionally varied.

Influence of Carbon Content

For a given columbium content, the liquation temperature first rose sharply with increasing carbon content (figure 12) and then tended to level off. A change from strong to weak dependence of liquation temperature on carbon content occurred at an approximate columbium to carbon ratio of 7.7. This value corresponded to the ratio of the molecular weights of columbium to carbon. At this ratio, sufficient carbon was available to satisfy the stoichiometry of CbC. Increased carbon content above that required to give equal atomic percentages of columbium and carbon did not raise the liquation temperature an appreciable amount.

An essentially constant liquation temperature (2400°F) existed for those compositions containing less carbon than indicated at the

intersection of the curves of constant columbium content with the 2400°F isotherm (figure 12).

Influence of Columbium Content

The liquation temperature dropped rapidly with increasing columbium content for all carbon levels (figure 13) from 0.05 percent to 0.10 percent. The slope of the curve increased as the carbon content was reduced. This indicated a stronger dependence of liquation temperature on columbium content at lower carbon levels. Again, an essentially constant liquation temperature of 2400°F is indicated by the horizontal portion of each of the curves. The 2400°F isotherm intersects the curves of constant carbon content at increasing columbium to carbon ratios with increased carbon content. These ratios range from 8.7 for the 0.05 percent carbon curve to 13.0 for the 0.10 percent carbon curve.

Figures 12 and 13 which show the dependence of carbon and columbium on liquation temperature were derived from a set of isothermal sections of the austenite corner of the austenite-columbium-carbon system. These diagrams will be presented in the following section.

Isothermal Sections

In order to clarify the phase relationships which exist in Type 347 alloys, a series of isothermal sections of the austenite corner of the austenite-columbium-carbon system have been prepared. The carbon and columbium contents as well as the liquation temperatures of the alloys used in the construction of the isothermal sections are listed in Table I. The isothermal sections were constructed at five different temperatures which covered the range from 2350°F to 2450°F. These diagrams are shown in figures 14a through 14e. They apply to the phase relationships existing in the alloys which were

heated rapidly to a high temperature and held for one minute. These sections should not be taken as indicating the equilibrium state.

The isothermal diagrams were constructed from the determination of the phases present in the specimens of a material after exposure to temperatures in the range from 2350°F to 2500°F. From these determinations, the temperature of formation of the liquid phase could be estimated. Check redeterminations of liquation temperatures of several alloys have shown the reproducibility of liquation temperature to be within 10°F. Metallographic examination of the specimens also revealed the approximate temperature at which the CbC phase disappeared from the structure. This permitted location of the boundary between the austenite plus CbC plus liquid region and the austenite plus liquid region.

Vacuum melted materials were used in the construction of the isothermal sections of figure 14. The nitrogen content of these materials with two exceptions was approximately 0.003 percent. This level of nitrogen was considerably below the nitrogen level of commercial materials. It will be shown in the following section that the nitrogen content of Type 347 steel played an important role in determining liquation temperature.

Figure 14a shows the isothermal section of the austenite corner of the austenite-columbium-carbon system at 2350°F. All of the materials with just three exceptions were situated in the austenite plus CbC region. Two of the alloys were completely austenitic at this temperature, while one alloy was located in the austenite plus CbC plus Fe₂Cb region. At 2380°F (figure 14b), a liquid plus austenite plus CbC region has formed in the low carbon area of the diagram. With increasing temperature, this region moved to higher carbon contents as shown in figures 14c through 14e.

An austenite plus liquid region was detected in one heat at 2420°F. The region would have been present at lower temperatures in material

with very low carbon content. The heats used in this study, however, had carbon contents which were too high to be situated in the austenite plus liquid region at temperatures below 2420°F. At 2450°F, this region moved to higher carbon and lower columbium contents. A number of the alloys used in this study were situated in this region at 2450°F as shown in figure 14e.

The liquid phase formed in a number of the alloys at about 2400°F (figure 14c). X-ray diffraction patterns obtained from residues extracted after exposure to temperatures above 2400°F to increase the amount of liquid showed the presence of Fe₂Cb. Fe₂Cb was not detected in alloys which required a higher temperature than 2400°F for liquation. This indicated that, in the alloys which liquate at 2400°F, a metastable equilibrium was approached at the temperature of formation of the liquid phase. This metastable equilibrium existed between austenite, CbC, liquid, and Fe₂Cb.

The phase relationships of figure 14 indicate that wholly austenitic Type 347 steel, the composition of which is in accordance with ASTM Specification A376-55T, would exhibit a liquid phase during exposure at 2420°F. The specified carbon content is 0.08 percent maximum and the specified columbium range is 10 times the carbon minimum and one percent maximum. Such alloys would exhibit varying amounts of liquation at 2420°F if no other factor was involved. As will be shown in the next section, commercial materials usually have higher liquation temperatures due to the presence of nitrogen.

Effect of Nitrogen

Commercially made Type 347 steel usually exhibits a liquation temperature which is between 30°F and 60°F higher than experimental vacuum melted materials of the same base composition (Table II). In order to investigate the possibility that differences in nitrogen content were responsible for the observed difference in liquation temperature,

a split laboratory heat was made to which CrN was added. This heat had an aim base composition of 12.5 percent Ni, 18.0 percent Cr, 1.5 percent Mn, 0.5 percent Si, and balance Fe. The carbon, nitrogen, and columbium compositions of the materials were as follows:

<u>Ingot</u>	<u>C (percent)</u>	<u>N (percent)</u>	<u>Cb (percent)</u>
1308-1	0.055	0.003	0.75
1308-2	0.054	0.049	0.77
1308-3	0.056	0.115	0.75

The first ingot (1308-1) was poured without any nitride addition. This ingot was used to determine the liquation temperature of the alloy with the indicated base carbon and columbium levels. This ingot also served to establish the normal nitrogen level of vacuum melted laboratory material. An addition of chromium nitride was made to the melt and the second ingot (1308-2) was poured. This material contained 0.049 percent nitrogen. This nitrogen content was approximately the same as the level in commercial air melted heats. A second nitride addition was made and the third ingot was poured. This ingot contained 0.115 percent nitrogen. This level was considerably above that of commercial materials and selected to show what effects high nitrogen content would have on the steel.

Influence of Liquation Temperature

The liquation temperatures of the nitrogen containing materials were as follows:

<u>Ingot</u>	<u>N (percent)</u>	<u>Liquation Temperature</u>
1308-1	0.003	2405°F
1308-2	0.049	2455°F
1308-3	0.115	2470°F

These data show that liquation temperature was strongly dependent on nitrogen content, particularly at levels below 0.05 percent. Since commercial air-melted materials usually have much higher nitrogen

contents than vacuum melted materials, it is reasonable that the observed differences in liquation temperature between laboratory vacuum heats and commercial heats having the same carbon and columbium levels are due to differences in nitrogen content. Support is given to this conclusion by Perkins and Binder⁴⁵ who showed that the solidus temperature of Type 347 weld metals increased with increasing nitrogen content.

The degree of the influence of nitrogen on liquation temperature can best be indicated by a diagram of liquation temperature versus carbon or nitrogen added to materials with similar carbon and columbium levels. Heats 1306 and 1308 had the same base composition and similar levels of carbon and columbium. These levels were:

<u>Heat</u>	<u>C (percent)</u>	<u>Cb (percent)</u>
1306	0.056	0.79
1308	0.055	0.76

Both of these materials had liquation temperatures of 2405°F. The addition of carbon or nitrogen to heats of this composition raised their liquation temperatures (figure 15). The data presented in figure 15 suggest that nitrogen was approximately 60 percent more effective than carbon in raising the liquation temperature.

Lattice Parameter Determinations

Part of the nitrogen in the alloy replaced carbon in the CbC phase to form a Cb(C, N) phase. This is demonstrated by figure 16 which shows that the lattice parameter of the extracted carbide phase from ingots 1308-1, 1308-2, and 1308-3 decreased as a function of the nitrogen content of the alloy. Duwez and Odell⁴⁶ have shown that the lattice parameter of the face centered cubic Cb(C, N) dropped from 4.47 Å for CbC to 4.38 Å for CbN. The data of figure 16 are in agreement with this change in the composition of the carbide phase in the experimental alloys.

The analysis can be carried one step further, allowing some comments concerning the role of nitrogen in Type 347 alloys. In figure 17, the lattice parameter of the extracted $\text{Cb}(\text{C}, \text{N})$ phase has been plotted as a function of liquation temperature for materials which had a columbium to carbon ratio greater than 7.7. These materials had insufficient carbon present to tie up all the columbium as CbC . This figure shows that as the lattice parameter of the carbide phase decreased, the liquation temperature of the material increased. This decrease in lattice parameter was due to the replacement of carbon by nitrogen in the CbC phase. Any nitrogen present in the steel in addition to carbon ties up columbium as a compound. The presence of nitrogen, therefore, reduces the amount of uncombined columbium present in the steel. The substitution of nitrogen for carbon in the $\text{Cb}(\text{C}, \text{N})$ compound increases the stability of the compound and thereby makes its solution more difficult. Both the reduction of uncombined columbium and the greater difficulty of solution of $\text{Cb}(\text{C}, \text{N})$ would raise the liquation temperature of the steel.

Liquation Reaction

A consistent picture of the liquation reaction in Type 347 steel can be evolved from the data acquired during the investigation. The evidence of liquation during high temperature exposure was the presence of a eutectic structure which was primarily located at the grain boundaries. Dependent upon the composition of the alloy, the eutectic was composed either of austenite and CbC or austenite, CbC , and Fe_2Cb .

A number of alloys exhibited a liquation temperature of approximately 2400°F . These alloys contained a eutectic structure composed of austenite, CbC , and Fe_2Cb after rapid cooling from temperatures above 2400°F . The Fe_2Cb phase was not stable since it disappeared from the eutectic structure on re-exposure to temperatures just below 2400°F for rather short periods of time.

The existence of a liquation temperature which within experimental error was constant for these alloys indicated the existence of columbium segregation within the materials on rapid heating to temperatures just below 2400°F. The conditions of heating were such that insufficient time was allowed to level out the regions of concentrated amounts of excess columbium. The columbium content of these regions reached sufficiently high levels to allow the compositions of these regions to intersect a solidus surface at approximately 2400°F. This surface separated the austenite plus CbC plus Fe₂Cb phase field from the austenite plus CbC plus liquid field.

In those alloys which liquated above 2400°F, the temperature of formation of the liquid phase was controlled by the amount of columbium in excess of that combined with carbon and nitrogen and by the stability of the columbium compound present in those regions in which liquation was initiated. In these alloys, insufficient local levels of excess columbium did not allow the formation of the Fe₂Cb phase on heating. Figure 12 showed that the liquation temperature of Type 347 steel was raised by increased carbon content. Increasing carbon markedly increased liquation temperature approximately to the point where the carbon content on an atomic basis was equal to the columbium content. Increased carbon content beyond this point was not nearly as effective in raising the liquation temperature. Therefore, increasing carbon content raised the liquation temperature from 2400°F by reducing the amount of excess (uncombined) columbium.

The local level of excess columbium necessary to form the liquid decreased with increased exposure temperature. When this level approached zero, the rate of solution of the columbium compound [CbC or Cb(C, N)] was of prime importance in determination of liquation temperature. It has already been shown that in the absence of nitrogen increasing carbon content in excess of that required to give equal atomic percentages of columbium and carbon had little influence

on liquation temperature. Figure 15 showed that nitrogen was apparently about 60 percent more effective than carbon in raising the liquation temperature. This was due to the decreasing amounts of excess columbium and decreasing solubility of the Cb(C, N) phase with increasing nitrogen (figure 17).

The phases formed on solidification of the liquid were not the same in all cases. The products of solidification of the liquid were a function of the composition of the liquid. In those alloys which liquated at 2400°F, the amount of columbium in the liquid was more than required to form CbC and saturate the austenite so the Fe₂Cb phase precipitated from the liquid. In heats which exhibited liquation above 2400°F, no Fe₂Cb was found. In these alloys, the liquid composition was such that little columbium was present above that which would combine with carbon and nitrogen or which would dissolve in austenite on solidification.

Influence of Chromium and Nickel

In order to study the effects of different levels of chromium and nickel on the liquation temperature of Type 347 alloys, a series of heats was made in which the amounts of these elements present in the material were varied. The aim levels of these two elements were at each side of the composition range listed by ASTM Specification A376-55T which applies to Type 347 pipe for high temperature central station service. The respective levels were 9 percent and 13 percent nickel and 17 percent and 20 percent chromium. In addition, each of the four combinations were made at two columbium to carbon ratios, one low ($0.5/0.1 = 5$) and one high ($1.0/0.04 = 25$).

The aim compositions of these heats are shown in Table III. Long time experience in the vacuum induction melting of austenitic stainless steel has shown that the recovered amounts of chromium and nickel have been consistently within 0.8 percent of the aim analysis.

For this reason, it was not considered necessary to have actual chemical analyses made for these elements. In the absence of anomalous results, it was also not considered necessary to have analyses made for carbon and columbium. The aim carbon and columbium levels of a number of heats have been reported in Table IV along with their analysed contents. Comparison of the aim and recovered levels of these elements showed their recoveries were consistent when proper melting techniques had been used.

As expected because the extremes of the composition ranges for chromium and nickel were selected, ferrite formed in some of the heats. The ferrite contents of the as-rolled materials are reported in Table III in addition to the ferrite levels of the materials after a one minute exposure at 2450°F. This temperature was selected to serve as a basis for comparison of the ferrite contents after a high temperature exposure.

Influence on Liquation Temperature

As will be shown later, the presence of ferrite had a marked effect on liquation temperature. Due to the presence of ferrite in five of the eight heats with variable chromium and nickel, it was difficult to draw any independent conclusion regarding their effect on liquation temperature.

Comparing heats 1267 and 1271 of Table III, it can be seen that these heats differ only in nickel content. The aim columbium and carbon contents of both heats were 0.5 percent and 0.10 percent, respectively, and both contained 17 percent chromium. The heats showed no significant difference in liquation temperature although the nickel level of heat 1267 was 13 percent while in heat 1271 it was only 9 percent. Therefore, the variation in nickel content caused no apparent change in liquation temperature.

All of the heats which contained the higher level of chromium, 20 percent, also contained ferrite. For this reason, no independent

conclusions can be drawn regarding the influence of chromium level on liquation temperature. It would be rather surprising, however, if chromium had any influence on liquation temperature other than that caused indirectly through variations in amount of ferrite associated with differences in level of chromium.

Influence of Ferrite Content

Figure 18 shows the influence of chromium to nickel ratio on the ferrite content after high temperature exposure of the alloys listed in Table III. The ferrite content of the materials increased with increasing value of the chromium to nickel ratio, however, there were separate curves for the heats with low and high columbium to carbon ratios. This was not unexpected since the ferrite content of any alloy would be a function of the relative proportions of the ferrite forming elements and the austenite forming elements.

The ferrite contents of the alloys of Table III were correlated on one curve (figure 19) when the relative ferrite forming and ferrite suppressing characteristics of all the elements present in the alloys were combined as proposed by Schaeffler.⁵¹ Schaeffler developed the function to predict the relative amounts of austenite and ferrite in stainless steel weld deposits. This function was the ratio of chromium equivalent to nickel equivalent. These equivalents are calculated from the following formulas:

$$\text{Chromium equivalent} = \% \text{ Cr} + \frac{3}{2} (\% \text{ Si}) + \frac{1}{2} (\% \text{ Cb})$$

$$\text{Nickel equivalent} = \% \text{ Ni} + 30 (\% \text{ C}) + \frac{1}{2} (\% \text{ Mn})$$

Increasing value of the ratio of chromium equivalent to nickel equivalent was associated with increasing amounts of ferrite.

Influence of Ferrite Content on Liquation Temperature

A correlation existed between the amount of ferrite present in a material after exposure for one minute at 2450°F and the liquation tem-

perature of the material (figure 20). The liquation temperature initially dropped as the ferrite content increased from zero to low volume percents. Increased amounts of ferrite raised the liquation temperature to high values even for the materials with columbium to carbon ratios of 25 which had low liquation temperatures in the absence of ferrite.

The liquation temperatures of the heats with varying ferrite contents (Table III) when plotted as a function of the ratio of chromium to nickel (figure 21) behaved in the same manner as when plotted as a function of ferrite content (figure 20). This seems to support the earlier statement that chromium and nickel contents, per se, had little direct effect on liquation temperature. Their influence on the liquation temperature occurred through the amount of ferrite they caused to form in the alloy.

The influence of ferrite on liquation temperature can be explained by the affinity of ferrite for columbium. At a temperature of 2450°F, approximately 10 weight percent columbium was soluble in ferrite⁵⁰ (figure 22), while its solubility in austenite was only about 0.7 percent. During exposure of materials to elevated temperatures, the ferrite absorbed columbium because of its higher solubility for that element. The segregation of the columbium in the two heats with the largest amounts of ferrite was so extensive that no CbC particles were evident in their microstructures (figure 23).

In materials in which small amounts of ferrite existed, columbium tended to segregate to the ferrite during solidification and subsequent hot working. On cooling from the hot working temperature, the amount of ferrite present in the material decreased and rejection of columbium to the surrounding austenite occurred. These local levels of columbium reached sufficiently high values to cause liquation to occur in the material on heating in the heating structure test at a lower temperature than would be expected for a wholly austenitic alloy.

When the amount of ferrite in a material was high enough so that

the ferrite did not become saturated with columbium, there was no rejection of columbium to the austenite. Consequently, the lower liquation temperatures were not observed. The ferrite absorbed enough of the columbium present in the materials so that the liquation temperatures were actually raised to very high values.

The explanations proposed could also apply to the observed effect of ferrite in Type 347 austenitic steel weld metals. It had been noted that completely austenitic weld metals were very susceptible to cracking. Modification of the composition of the welding rods so that 4 to 10 volume percent ferrite was present in the weld metal at room temperature suppressed this cracking susceptibility completely. Curran and Rankin⁴⁷ have attributed the effectiveness of ferrite in preventing weld metal cracking to the gathering of harmful segregates around the ferrite particles instead of in the grain boundaries and thereby negating their ability to form cracks. Parks¹³ attributed the beneficial effect of ferrite to a redistribution of harmful segregating elements such as silicon and phosphorus through a process of selective adsorption and reprecipitation.

Empirical Relations

Numerous attempts have been made during this investigation to arrive at some compositional function which when plotted versus liquation temperature would yield a smooth curve. Most of the functions which were tried yielded unsatisfactory diagrams. An example of such a diagram is shown in figure 24 where the liquation temperature of wholly austenitic materials has been plotted versus the amount of excess columbium. The amount of excess columbium was calculated from the following formula:

$$\text{Excess columbium} = \text{columbium content} - 7.7 (\text{percent carbon}).$$

There was, in general, a drop in liquation temperature with increasing amounts of excess columbium. The band of the data, however, was

quite wide. This was probably due to the fact that the amount of excess columbium necessary to cause liquation at a given temperature varied with the carbon content of the material.

The first satisfactory compositional function for both wholly austenitic and for ferrite containing materials was the ratio of chromium equivalent to nickel equivalent. This function is plotted versus liquation temperature in figure 25. The nickel equivalent has been modified in this case to include a factor of plus 50 (% N). The data define a curve which decreases rapidly with increasing value of the ratio. A discontinuity in the curve appeared at the value of the ratio of chromium equivalent to nickel equivalent of 1.42. At greater values of the ratio, the liquation temperatures of the materials were quite high.

The logic of the dependence of liquation temperature on such a function is rather complex. The ratio of equivalents apparently takes into account the varying influence of the levels of carbon, columbium, and nitrogen on liquation temperature. In addition, however, the function includes the chromium and nickel contents of the alloys. We have already stated that chromium and nickel, per se, probably have little effect on liquation temperature and, therefore, it would not be expected that the inclusion of their levels should aid in the data correlation. Chromium and nickel levels do, however, play an important role in determining the ferrite content of the materials, which, as we have seen, does have a pronounced influence on liquation temperature. Therefore, the function plotted in figure 25 took into account all the known factors which influence liquation temperature.

The deletion of the chromium, nickel, manganese, and silicon contents from the function resulted in terms which took into account only the carbon, nitrogen, and columbium levels of the materials. When this function, $\frac{1}{2}(\% \text{Cb})/30(\% \text{C}) + 50(\% \text{N})$, was plotted versus the liquation temperature a better correlation was obtained (figure 26) than when the other four elements were included. This suggested that the

carbon, nitrogen, and columbium contents of a material were the principal elements which controlled liquation temperature of wholly austenitic alloys. The two data points which did not fall on the curve were from materials which contained considerable amounts of ferrite. These materials had abnormally high liquation temperatures as a result of the presence of the ferrite. The complete function including the Cr, Ni, Mn, and Si terms would predict the presence of sufficient ferrite to cause abnormally high liquation temperatures.

Influence of Variable Processing Conditions

The liquation temperature of Type 347 steel has been studied as a function of variable solidification and hot working conditions using the laboratory ingots. Variation of pouring temperature was used to determine whether the resulting variation in the amount of the eutectic structure in cast ingots was associated with differences in liquation temperature. The conditions under which the ingots were hot worked were varied to determine if liquation temperature could be changed.

Influence of Varying Pouring Temperature

During the investigation, it had been noted that an increase in the pouring temperature resulted in an increase in the amount of eutectic structure present in the as-cast material. In order to determine whether the amount of eutectic present in the as-cast condition had any relation to the liquation temperature of the alloy, a split heat was made in which the pouring temperature was varied. The composition of the heat selected was one which had a low liquation temperature. It was thought that suppression of the eutectic reaction in the cast ingot might result in an increase in the liquation temperature of the material.

This heat had an aim analysis of:

<u>Cr</u>	<u>Ni</u>	<u>Mn</u>	<u>Si</u>	<u>C</u>	<u>Cb</u>	<u>Fe</u>
18.0	12.5	1.5	0.5	0.04	1.0	Bal.

The first ingot was poured after superheating 25°F above the freezing point of the alloy. The second ingot was poured after superheating 175°F above the freezing point.

The two ingots contained different amounts of eutectic in the cast state but did not show any difference in liquation temperature. Both ingots exhibited evidence of melting in the grain boundaries of the material after exposure at 2400°F. It has been concluded that variations in pouring temperature caused no significant change in the liquation temperature of this heat.

In light of the better understanding of the effects of carbon and columbium on liquation temperature gained later in the investigation, the composition of this heat was not conducive to showing any effects variations in amount of eutectic might have on liquation temperature because the composition laid on the flat portion of the curves of figure 12. A better composition would have been one which laid on the steep portion of these curves. This figure indicates that for a given columbium to carbon ratio (7.7) the liquation temperature may decrease slightly with increasing amount of eutectic in the as-cast state. The amount of eutectic present in the cast condition will increase with increasing columbium and carbon.

Influence of Variable Hot Working Practice

In order to study the effects of variable hot working practice on the liquation temperature of Type 347 alloys, three split heats of the same aim composition were made. These heats were made in the University vacuum melting furnace and totaled 4000 grams each. The aim chemical composition of the material was as follows:

<u>Cr</u>	<u>Ni</u>	<u>Mn</u>	<u>Si</u>	<u>C</u>	<u>Cb</u>	<u>Fe</u>
18.0	12.5	1.5	0.5	0.08	0.80	Bal.

With the exception of nitrogen, this composition was typical of commercially produced alloys. The two ingots obtained from each of the three

heats were cut in half so as to obtain four small ingots from each heat. The small ingots were coded in such a manner as to describe from which heat they came, whether they were part of the first or second ingot poured during that heat, and whether they were the top or bottom half of that ingot.

The necessity for this came about because of the small capacity of the vacuum melting furnace. Since the capacity of the furnace was limited, it was necessary to randomize the small ingots in order to allow one to distinguish between any effects of variable hot working practice and any effects brought about by position of the ingot such as whether the first ingot poured behaved like the second or whether the top half of an ingot acted in the same way as the bottom half.

The ingots were reduced zero percent, 30 percent, 60 percent, and 90 percent at 1800°F, 2000°F, and 2200°F. The material was held for two hours at temperature prior to rolling. After the allotted reduction was completed, each ingot was allowed to air cool to room temperature.

The liquation temperature of the material was determined for material in each of the processing conditions. These temperatures (Table V) were above the 2420°F which was expected. This indicated that the actual composition was somewhat different than the aim composition.

A statistical analysis was made of the results reported in Table V to determine if there were significant differences in liquation temperature as a function of prior history. The "F" test^{48,49}, was used to analyse the results. This test measured the difference of two estimates of the same variance. This difference was measured in the form of a ratio which was compared to the ratio of the variances expected for a given confidence level. This test was used to test each of the variables used in the experiment: temperature of reduction, amount of reduction, position of ingot, and heat of material. The position of ingot variable

was broken down to distinguish between the two ingots poured from each heat and between the upper and lower halves of the ingot.

The details of the statistical analysis are given in the Appendix. The results of the analysis showed that prior history had no significant effect on liquation temperature in the materials studied. The analysis further showed that there were no significant differences in composition among the heats used in the study. Furthermore, the two ingots poured from each heat acted in a similar manner. The only factor which was shown to contribute to variability of liquation temperature was the difference between the upper and lower halves of the ingots. The statistical analysis showed that the difference in variance estimate between the halves of the ingots was greater than would be expected in nine cases out of ten if there was no real difference in liquation temperature between the halves of the ingots. While this difference was not statistically significant at the 95 percent confidence level, it did suggest that a difference in liquation temperature probably existed within the ingots.

The average liquation temperature for the lower halves of the ingots is higher than that of the upper halves of the ingots. This implies that segregation of columbium and/or carbon was taking place during solidification of the material. Such segregation would be expected to be magnified as the size of an ingot is increased. For larger ingots, segregation would probably result in decreasing liquation temperature from ingot surface to center as well as from bottom to top as shown in the small ingots used in this study.

Segregation

A distinct possibility exists that segregation is a cause of variable liquation temperature in Type 347 steel. Since columbium is a heavy element special care has to be taken during melting of the steel to obtain a uniform distribution of this element within the molten metal. The temperature range between the liquidus and solidus is quite wide and on solidification the steel exhibits a eutectic structure which is rich in columbium. This also could be a source of segregation. In addition to the segregation of columbium, carbon and nitrogen are known to vary sufficiently in their distribution within an ingot to considerably affect the liquation temperature of materials whose compositions lie in the region where liquation temperature is sensitive to the amounts of carbon and nitrogen present.

In several of the heats made early in this investigation gross segregation of columbium was encountered as a result of improper melting techniques. One such example (figure 27) of gross segregation was subjected to microprobe analysis. The columbium level of this area was determined to be in excess of 10 percent. On recognition of the existence of this segregation special precautions were introduced to insure a uniform distribution of columbium in the molten metal.

The high degree of reproducibility of liquation temperatures indicates that a rather uniform composition was obtained within the ingots. The data of the previous section, however, suggested the possibility of a difference in liquation temperature between the top and bottom halves of the ingots used in the study of variable hot working practice. The high degree of reproducibility of liquation temperature was probably due to the fact that the samples used to determine liquation temperature were taken from adjacent regions in the material. It should be noted, however, that the samples used for chemical

analysis were also taken from the same region so that the chemical compositions reported are for the same material as used for determining the liquation temperature.

In commercial practice there have been numerous cases which suggested variable weldability among pieces from the same heat and within a given piece. In general, however, hot ductility tests have not shown much difference within a given heat. For this reason it is suspected that welding and service conditions rather than segregation accounts for many of the cases of apparently erratic weldability.

Examination of figures 12 and 13 indicates that for chemical compositions which lie in the range where liquation temperature varies rapidly with changes in carbon or columbium, segregation would undoubtedly influence liquation temperature. The liquation temperatures of compositions which lie on the flat portions of the curves of figure 12 probably would not vary appreciably unless segregation was very pronounced.

Based on general experience, segregation should be recognized as a likely potential source of variable liquation temperature in commercial practice.

Relation of Results to Hot Ductility Results

In the hot ductility test specimens of a material are heated to a certain terminal temperature, cooled to a second temperature and broken in tension. The ductility of the specimens is a function of the terminal temperature used in the test. If the terminal temperature used is below the liquation temperature of the material high ductility will be obtained. The liquation temperature of Type 347 steel, however, varies with composition. Therefore if different heats are exposed to a given terminal temperature some heats will exhibit liquation while others will not.

If a series of hot ductility specimens are heated to a given terminal temperature above the liquation temperature of the particular material and broken at different temperatures on cooling from the terminal temperature the rate of ductility recovery can be measured. The rate of recovery of ductility will be a function of the amount and composition of the liquid formed. The amount of liquid formed will increase as the difference between the terminal temperature and the liquation temperature increases (figure 8). The composition of the liquid will be a function of the composition of the material and terminal temperature used in the test.

Under conditions of rapid cooling such as exist in the hot ductility test (approximately 200°F per second) the liquid phase probably will be supercooled. It is suggested that for a given terminal temperature alloys with low liquation temperatures will exhibit a greater amount of supercooling than alloys with high liquation temperatures due to the presence of a greater amount of liquid. This would manifest itself in the hot ductility test as a slower rate of ductility recovery on cooling from the terminal temperature. It is also probable that the amount of supercooling of the liquid phase is dependent on its composition.

CONCLUSIONS

The variable liquation temperature of wholly austenitic 18 Cr-8 Ni + Cb steel under conditions of rapid heating is due to variations in the amounts of columbium and carbon plus nitrogen within the normal range of composition of this steel. These participate in complex eutectic melting reactions which occur at temperatures well below the bulk melting temperature of the steel. Increased amounts of columbium cause a lowering of the liquation temperature at constant levels of carbon and nitrogen while increased amounts of carbon and nitrogen at constant columbium content cause an increase in liquation temperature.

In the virtual absence of nitrogen, increasing carbon in excess of columbium on an atomic basis raised the liquation temperature slightly and the products of solidification were austenite and CbC dispersed in a eutectic pattern. When the atom ratio of carbon to columbium was decreased below one, the liquation temperature dropped very rapidly. When this ratio reached a certain value, which varied somewhat with carbon and columbium content, the liquation temperature decreased only slightly with further increases in columbium and the products of solidification were austenite, CbC, and Fe_2Cb .

The phase relations were so complex that they were not fully established. The data obtained indicate that compositional changes in carbon and columbium caused a change from one eutectic reaction to a second more complex eutectic reaction, thus altering the liquation temperature. Detailed studies of the influence of nitrogen on the phase relations were not carried out. The probability, however, is that by substituting for a portion of the carbon in the CbC phase it increases the amount of columbium which can be tolerated before melting occurs and therefore increases the liquation temperature under conditions of rapid heating.

Limited data indicate that nitrogen is approximately 60 percent more effective than carbon in raising liquation temperature and raises the liquation temperature to values in excess of that which could be obtained from increased carbon alone. The liquation temperature of wholly austenitic alloys can be predicted from the following formula when the value of the function, $f = \frac{1}{2}(\% \text{Cb}) / 30(\% \text{C}) + 50(\% \text{N})$, is less than 0.20.

$$\text{Liquation Temperature } (^{\circ}\text{F}) = 2500 - 500 f$$

When the value of f surpasses 0.20, wholly austenitic materials exhibit a liquation temperature of approximately 2400°F .

Variations in the amounts of chromium and nickel to introduce ferrite into the microstructure removed the sensitivity of liquation temperature to the amounts of columbium, carbon, and nitrogen. This was due to the segregation of columbium to the ferrite as a result of its much higher solubility in ferrite than in austenite.

Variable liquation temperatures in Type 347 steel due to segregation would be expected in those heats with carbon, columbium, and nitrogen contents within the composition range where liquation temperature is sensitive to the amounts of these elements. In such material melting, solidification, and hot working conditions would be expected to influence the degree of segregation.

The variable hot ductility of Type 347 steel which caused the initiation of this investigation is due to the composition induced variations in liquation temperature.

APPENDIX

Design of the Experiment

The study of the influence of prior hot working history on liquation temperature required that any significant effects of other variables be identified. The evaluation of four different amounts of hot reduction at each of three temperatures required twelve ingots. The limited capacity of the vacuum induction furnace necessitated the melting of three different heats of material. Two ingots were obtained from each of the heats. These large ingots were cut in half so as to obtain four small ingots from each heat.

The strong influence of carbon and columbium contents on liquation temperature made it necessary to design the experiment in a manner so that any differences in the levels of these elements among the heats would be established. In short it was necessary to know that any variation in liquation temperature among the bars was due to differences in prior history and not to variations in composition. The experiment was designed so that any effects of hot working procedure on liquation temperature could be separated from effects resulting from differences in composition among the heats or among the ingots. Variations between the top and bottom halves of the large ingots could also be established. The design of the experiment is shown in Table IV.

Analysis of Variance

Estimates were made of the variance of liquation temperature as a function of:

- (1) temperature of reduction
- (2) amount of reduction
- (3) heat of material
- (4) order of pouring of the ingot
- (5) top or bottom half of the ingot.

The "F" test provided a method for determining whether the difference in the estimates of two variances was larger than might be expected by chance if they had been drawn from the same population.

The difference was measured in the form of a ratio in this test. The 95% confidence interval was arbitrarily selected as the interval outside of which the ratio of the variances had to lie to be considered significant.

The following table presents the data of Table V in the coded form. The liquation temperatures have been coded by subtracting 2400°F from each. The first number in the line directly below the coded temperature refers to the heat, the letter following this number refers to the first (A) or second (B) ingot poured from each heat, and the second letter refers to the upper (U) or lower (L) half of the ingot.

Coded Data

<u>Temperature of Reduction</u>	<u>Hot Reduction, Percent</u>				<u>Total</u>
	<u>0</u>	<u>30</u>	<u>60</u>	<u>90</u>	
1800°F	50° 5BL	50° 3AL	45° 4AU	40° 3BU	185
2000°F	35° 4BU	40° 5AU	45° 3BL	45° 4AL	165
2200°F	40° 3AU	50° 4BL	50° 5BU	45° 5AL	185
Total	125	140	140	130	535

Influence of Hot Working History

In order to determine if the temperature and/or amount of reduction had any influence on liquation temperature, the following analysis has been used.

Coded Data

Influence of Temperature and Amount of Reduction
on Liquation Temperature

Temperature of Reduction	Hot Reduction, Percent				Total
	0	30	60	90	
1800°F	50	50	45	40	185
2000°F	35	40	45	45	165
2200°F	40	50	50	45	185
Total	125	140	140	130	535

$$\Sigma x = 535$$

$$(\Sigma x)^2 = (535)^2 = 286,225$$

$$\Sigma x^2 = (50)^2 + (50)^2 + (45)^2 + \dots + (45)^2 = 24,125$$

$$\Sigma (\text{Temperature Totals})^2 = (185)^2 + (165)^2 + (185)^2 = 95,675$$

$$\Sigma (\text{Reduction Totals})^2 = (125)^2 + (140)^2 + (140)^2 + (130)^2 = 71,725$$

$$\text{Temperature Sum of Squares} = \frac{3(95,675) - 286,225}{12} = 66.67$$

$$\text{Reduction Sum of Squares} = \frac{4(71,725) - 286,225}{12} = 56.25$$

$$\text{Total Sum of Squares} = \frac{12(24,125) - 286,225}{12} = 272.92$$

The results may be summarized as follows:

<u>Source of Estimate of Variance</u>	<u>Sum of Squares</u>	<u>Degrees of Freedom</u>	<u>Mean Square</u>	<u>F</u>	<u>F(0.05)</u>
Temperature of Reduction	66.67	2	33.33	1.33	5.14
Amount of Reduction	56.25	3	18.75	0.75	4.76
<u>Error</u>	<u>150.00</u>	<u>6</u>	25.00		
Total	272.92	11			

Since the "F" values obtained were less than the values expected at the 95 percent confidence level, there was no significant effect of variations in temperature of reduction or amount of reduction on the liquation temperature of this material.

Influence of Position

Since neither temperature nor amount of reduction have any significant effect on liquation temperature, we may re-arrange the data of Table V to show any influence of position on liquation temperature.

Coded Data

Influence of Variations in the Order of the Ingot or Between Top and Bottom Halves of the Ingot on Liquation Temperature

<u>Ingot Half</u>	<u>Order of Ingot</u>		<u>Total</u>
	<u>A</u>	<u>B</u>	
Upper	40	40	250
	45	35	
	<u>40</u>	<u>50</u>	
	125	125	
Lower	50	45	285
	45	50	
	<u>45</u>	<u>50</u>	
	140	145	
Total	265	270	535

$$\Sigma x = 535$$

$$\Sigma x^2 = 24,125$$

$$(\Sigma x)^2 = 286,225$$

$$(\text{Ingot Half Totals})^2 = (250)^2 + (285)^2 = 143,725$$

$$(\text{Ingot Totals})^2 = (265)^2 + (270)^2 = 143,125$$

$$(\text{Position Totals})^2 = (125)^2 + (125)^2 + (140)^2 + (145)^2 = 71,875$$

$$\text{Ingot Half Sum of Squares} = \frac{2(143,725) - 286,225}{12} = 102,083$$

$$\text{Ingot Sum of Squares} = \frac{2(143,125) - 286,225}{12} = 2.083$$

$$\begin{aligned} \text{Interaction Sum of Squares} &= \frac{4(71,875) + 286,225 - 2(143,725) - 2(143,125)}{12} \\ &= 2.083 \end{aligned}$$

$$\text{Error Sum of Squares} = \frac{12(24,125) - 4(71,875)}{12} = 166.67$$

The results can be tabulated as follows:

<u>Source of Estimate of Variance</u>	<u>Sum of Squares</u>	<u>Degrees of Freedom</u>	<u>Mean Square</u>	<u>F</u>	<u>F (0.05)</u>
Ingot Halves	102.083	1	102.083	4.90	5.32
Ingots	2.083	1	2.083	0.10	5.32
Interaction	2.083	1	2.083	0.10	5.32
Error	166.667	8	20.833		
<u>Total</u>	<u>272.916</u>	<u>11</u>			

Again, the "F" values calculated were less than the values expected at the 95 percent confidence level. There does, however, appear to be an actual difference in liquation temperature between the top and bottom halves of the ingots although the ratio of the variance was within the 95 percent confidence interval.

Influence of Heat of Material

In order to show that there were no differences in liquation temperature among the different heats of steel used in the investigation of variable hot working history, the data of Table V have been regrouped

in the following form.

Coded Data

Influence of Differences Among Heats of Material and Between
Ingot Halves on Liquation Temperature

Ingot Half	<u>Heat of Material</u>			<u>Total</u>
	3	4	5	
Upper	40 <u>40</u> 80	45 <u>35</u> 80	40 <u>50</u> 90	250
Lower	50 <u>45</u> 95	45 <u>50</u> 95	50 45 95	285
Total	175	175	185	535

$$\Sigma x^2 = 24,125$$

$$(\Sigma x)^2 = 286,225$$

$$\Sigma (\text{Ingot Half Totals})^2 = 143,725$$

$$\Sigma (\text{Heat Totals})^2 = (175)^2 + (175)^2 + (185)^2 = 95,475$$

$$\Sigma (\text{Position Totals})^2 = 2(80)^2 + (90)^2 + 3(95)^2 = 47,975$$

$$\text{Ingot Half Sum of Squares} = 102.083$$

$$\text{Heat Sum of Squares} = \frac{3(95,475) - 286,225}{12} = 16.667$$

$$\begin{aligned} \text{Interaction Sum of Squares} &= \frac{6(47,975) + 286,225 - 2(143,725) - 3(95,475)}{12} \\ &= 16.667 \end{aligned}$$

$$\text{Error Sum of Squares} = \frac{12(24,125) - 6(47,975)}{12} = 137.500$$

Again, the results may be tabulated as follows:

<u>Source of Estimate of Variance</u>	<u>Sum of Squares</u>	<u>Degrees of Freedom</u>	<u>Mean Square</u>	<u>F</u>	<u>F (0.05)</u>
Ingot Halves	102.083	1	102.083	4.67	5.99
Heats	16.667	2	8.333	0.36	5.14
Interaction	16.667	2	8.333	0.36	5.14
Error	137.500	6	22.917		
<hr/>	<hr/>	<hr/>			
Total	292.917	11			

Since $0.36 < 5.14$ there was no significant difference in liquation temperature among the heats of steel. This analysis, as did the preceding analysis, shows that a probable difference in liquation temperature exists between the upper and lower halves of the ingots. An insufficient number of data have been taken to establish this as fact.

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TABLE I

LIQUATION TEMPERATURES OF MATERIALS USED IN CONSTRUCTION
OF ISOTHERMAL SECTIONS

<u>Heat</u>	<u>C (percent)</u>	<u>Cb (percent)</u>	<u>Liquation Temperature, ° F</u>
1223	0.05	0.99	2400
1226	0.13	0.69	2460
1234	0.11	0.62	>2440
1235	0.02	0.22	>2450
1237	0.14	0.85	>2450
1239	0.04	0.31	>2450
1240	0.04	0.73	2400
1241	0.04	1.46	2360
1258A	0.05	1.0	2400
1258B	0.05	1.0	2400
1265	0.05	1.0	2410
1267	0.10	0.5	2460
1271	0.10	0.5	>2460
1272	0.10	1.0	2420
1283	0.08	0.80	2440
1305-1	0.05	0.54	2400
1305-2	0.09	0.54	2440
1305-3	0.128	0.58	2445
1306-1	0.056	0.79	2405
1306-2	0.102	0.78	2435
1306-3	0.148	0.79	2440
1307-1	0.056	0.98	2400
1307-2	0.095	1.01	2425
1307-3	0.132	1.02	2440
1308-1	0.055	0.75	2400
1308-2	0.054	0.77	2455
1308-3	0.056	0.75	2470

Note: The data from Heats 1308-2 and 1308-3 were plotted at points determined by the percent carbon plus 1.6 times percent nitrogen. Heat 1308-2 contained 0.049 percent nitrogen and Heat 1308-3 contained 0.115 percent nitrogen.

TABLE II
 COMPARISON OF ACTUAL AND PREDICTED LIQUATION TEMPERATURES
 OF COMMERCIAL MATERIALS

<u>Material</u>	<u>C (percent)</u>	<u>Cb (percent)</u>	<u>Predicted Liquation Temperature, °F(1)</u>	<u>Actual Liquation Temperature, °F</u>
A	0.07	0.84	2400	>2450
B	0.07	0.86	2405	>2450
C	0.053	0.83	2400	2455
D	0.06	0.68	2405	2445
E	0.05	0.96	2400	>2450
F	0.057	0.81	2400	2435
G	0.067	0.74	2405	2450

(1) Predicted Liquation Temperature, °F = 2500-500 $\left[\frac{1}{2}(\%Cb)/30(\%C)+50(\%N) \right]$

TABLE III

INFLUENCE OF CHROMIUM AND NICKEL CONTENTS ON LIQUATION TEMPERATURE

Heat	Aim Chemical Composition (Weight Percent)						Liquation Temperature, °F	Ferrite (Volume Percent)	
	C	Cb	Cr	Ni	Mn	Si		As-Rolled	Overheated
1264	0.04	1.0	20.0	13.0	1.5	0.5	2400	2	2
1265	0.04	1.0	17.0	13.0	1.5	0.5	2410	0	0
1266	0.10	0.5	20.0	13.0	1.5	0.5	2440	<1	<1
1267	0.10	0.5	17.0	13.0	1.5	0.5	2460	0	0
1268	0.04	1.0	20.0	9.0	1.5	0.5	>2455	18	29
1269	0.04	1.0	17.0	9.0	1.5	0.5	>2455	1	6
1270	0.10	0.5	20.0	9.0	1.5	0.5	>2460	6	13
1271	0.10	0.5	17.0	9.0	1.5	0.5	>2460	0	0

TABLE IV

CHEMICAL COMPOSITION OF MATERIALS

Heat	Composition (Weight Percent)						Aim	Aim	N
	Cr	Ni	Mn	Si	C	C	Cb	Cb	
1223	18.3	13.0	1.47	0.40	0.05	0.065	0.99	0.85	
1226	18.4	13.0	1.50	0.68	0.11	0.11	0.69	0.85	
1234	18.6	12.9	1.09	0.69	0.09	0.09	0.63	0.85	
1235	18.7	13.0	1.33	0.72	0.02	0.0	0.22	0.85	
1237	18.4	13.3	1.32	0.70	0.12	0.10	0.85	0.85	
1239	18.7	13.3	1.30	0.48	0.04	0.05	0.31	0.30	
1240	18.1	12.7	1.22	0.62	0.04	0.05	0.73	0.70	
1241	17.9	12.8	1.31	0.70	0.04	0.05	1.39	1.40	
1258A	18.0 ^x	12.5 ^x	1.5 ^x	0.5 ^x		0.04		1.0	
1258B	18.0 ^x	12.5 ^x	1.5 ^x	0.5 ^x		0.04		1.0	
1264	20.0 ^x	13.0 ^x	1.5 ^x	0.5 ^x		0.04		1.0	
1265	17.0 ^x	13.0 ^x	1.5 ^x	0.5 ^x		0.04		1.0	
1266	20.0 ^x	13.0 ^x	1.5 ^x	0.5 ^x		0.10		0.5	
1267	17.0 ^x	13.0 ^x	1.5 ^x	0.5 ^x		0.10		0.5	
1268	20.0 ^x	9.0 ^x	1.5 ^x	0.5 ^x		0.04		1.0	
1269	17.0 ^x	9.0 ^x	1.5 ^x	0.5 ^x		0.04		1.0	
1270	20.0 ^x	9.0 ^x	1.5 ^x	0.5 ^x		0.10		0.5	
1271	17.0 ^x	9.0 ^x	1.5 ^x	0.5 ^x		0.10		0.5	
1272	18.0 ^x	12.5 ^x	1.5 ^x	0.5 ^x		0.10		1.0	
1283	18.0 ^x	12.5 ^x	1.5 ^x	0.5 ^x		0.08		0.8	
1284	18.0 ^x	12.5 ^x	1.5 ^x	0.5 ^x		0.08		0.8	
1285	18.0 ^x	12.5 ^x	1.5 ^x	0.5 ^x		0.08		0.8	
1305-1	18.0 ^x	12.5 ^x	1.5 ^x	0.5 ^x	0.05	0.04	0.54	0.6	
1305-2	18.0 ^x	12.5 ^x	1.5 ^x	0.5 ^x	0.09	0.07	0.54	0.6	
1305-3	18.0 ^x	12.5 ^x	1.5 ^x	0.5 ^x	0.128	0.10	0.58	0.6	
1306-1	18.0 ^x	12.5 ^x	1.5 ^x	0.5 ^x	0.056	0.04	0.79	0.8	
1306-2	18.0 ^x	12.5 ^x	1.5 ^x	0.5 ^x	0.102	0.07	0.78	0.8	
1306-3	18.0 ^x	12.5 ^x	1.5 ^x	0.5 ^x	0.148	0.10	0.79	0.8	
1307-1	18.0 ^x	12.5 ^x	1.5 ^x	0.5 ^x	0.056	0.04	0.98	1.0	
1307-2	18.0 ^x	12.5 ^x	1.5 ^x	0.5 ^x	0.095	0.07	1.01	1.0	
1307-3	18.0 ^x	12.5 ^x	1.5 ^x	0.5 ^x	0.132	0.10	1.02	1.0	
1308-1	18.0 ^x	12.5 ^x	1.5 ^x	0.5 ^x	0.055	0.04	0.75	0.8	0.003
1308-2	18.0 ^x	12.5 ^x	1.5 ^x	0.5 ^x	0.054	0.04	0.77	0.8	0.049
1308-3	18.0 ^x	12.5 ^x	1.5 ^x	0.5 ^x	0.056	0.04	0.75	0.8	0.115

Note: Superscript ^x indicates aim analysis

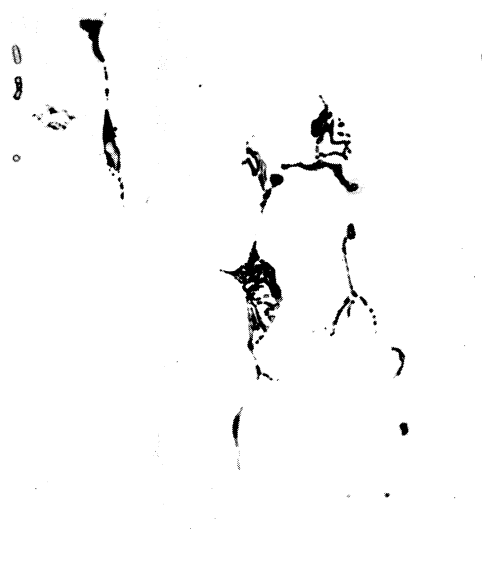
TABLE V
 INFLUENCE OF VARIABLE HOT WORKING PRACTICE ON LIQUATION TEMPERATURE

Temperature of Reduction	Hot Reduction, Percent		
	0	30	60
1800°F	2450°F	2450°F	2445°F
	1285 BL	1283 AL	1284 AU
2000°F	2435°F	2440°F	2445°F
	1284 BU	1285 AU	1283 BL
2200°F	2440°F	2450°F	2450°F
	1283 AU	1284 BL	1285 BU
			90
			2440°F
			1283 BU
			2445°F
			1284 AL
			2445°F
			1285 AL

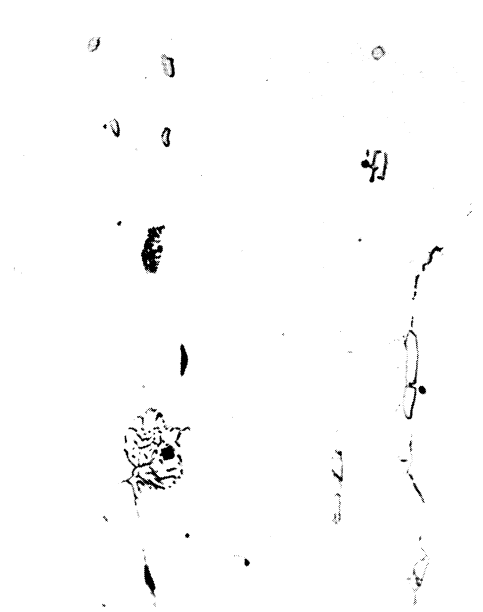
1283, 1284, 1285 are heat numbers
 A and B distinguish the first and second ingots poured from each heat
 U and L distinguish the upper and lower halves of the ingots



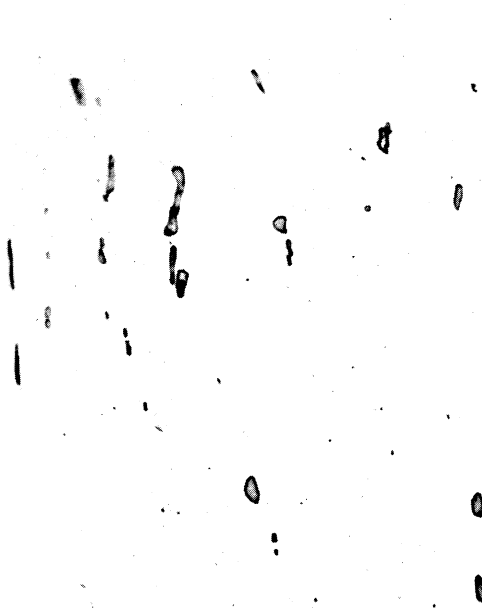
(a) 2% R. A.



(b) 24% R. A.



(c) 27% R. A.



(d) 86% R. A.

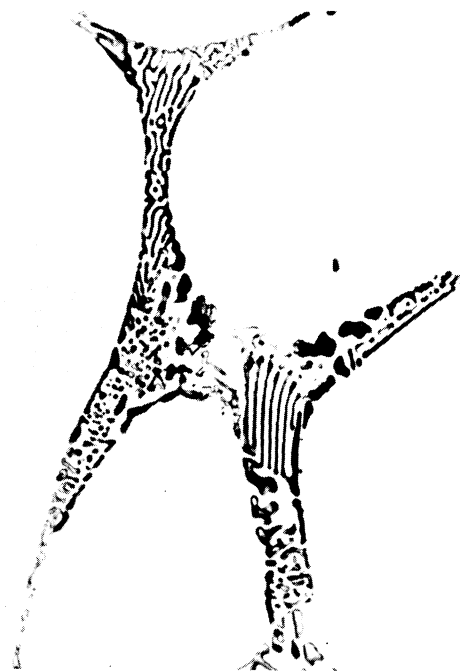
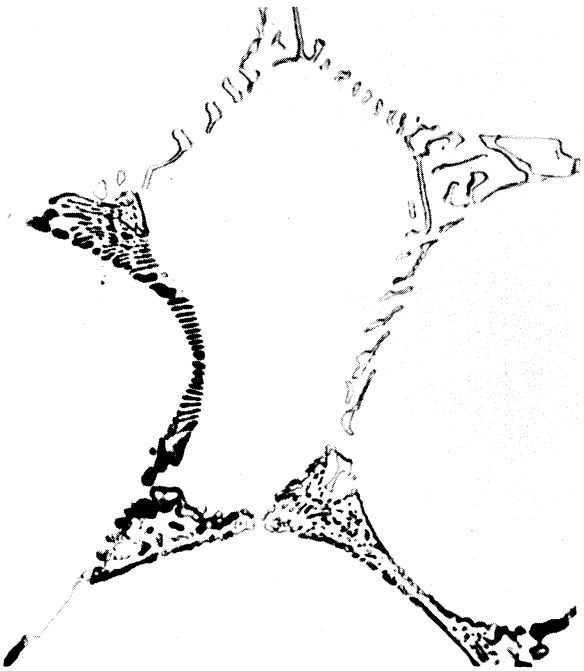
Figure 1. Relation of ductility in hot ductility test to presence of eutectic structure. X500



(a) Eutectic composed of CbC, Fe_2Cb , and austenite. H_3PO_4 electrolytic etch.



(b) Precipitation of Fe_2Cb at ferrite-austenite interface. H_3PO_4 electrolytic etch.



(c) and (d) Eutectic after having been exposed to an immersion etch in HF following an electrolytic etch in H_3PO_4 . Light constituent - CbC, dark constituent - Fe_2Cb , Matrix - austenite.

Figure 2. Micrographs of heat 1241 showing identification of various phases by selective etching. X500

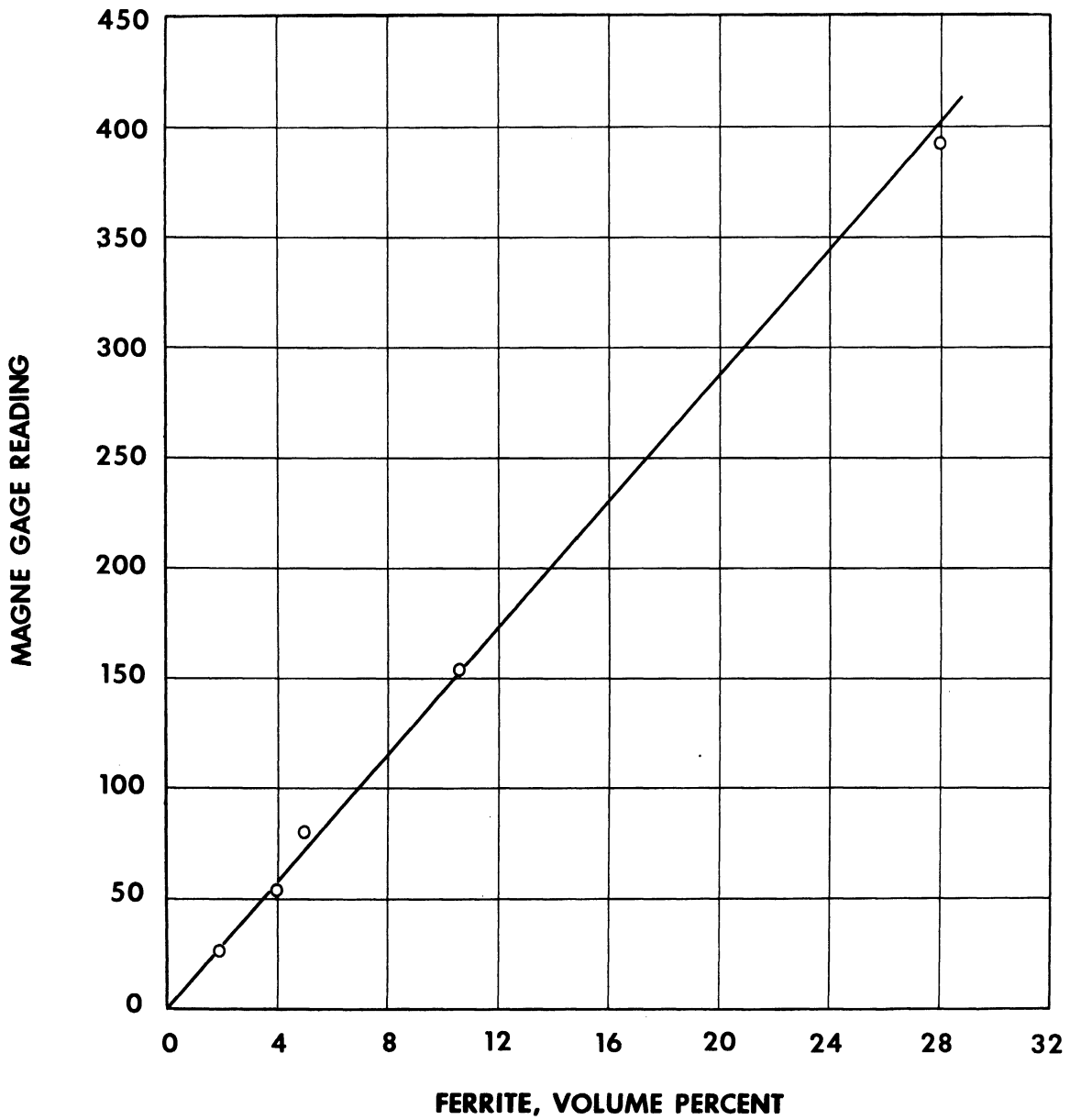
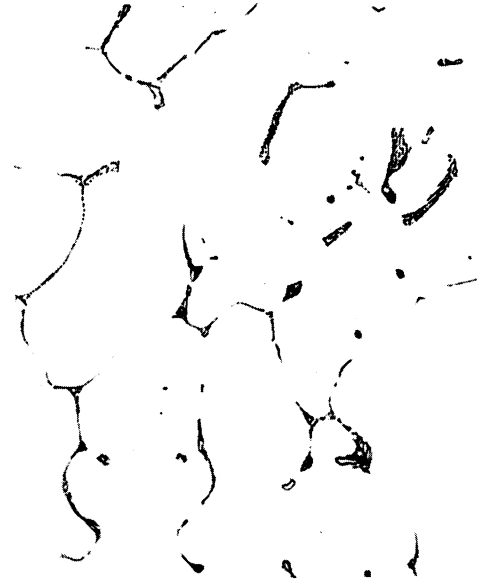


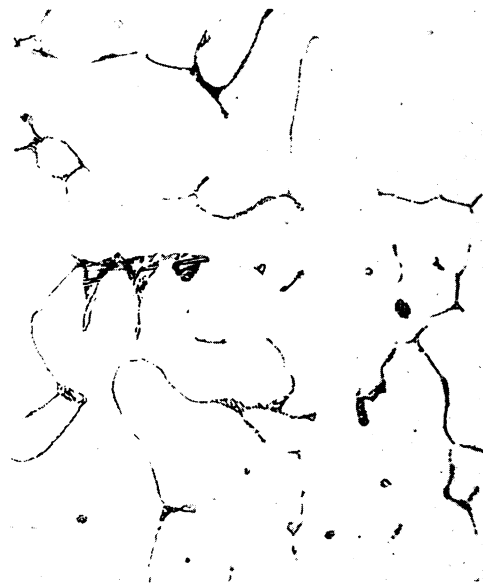
Figure 3. Relation between amount of ferrite and magne-gage reading.



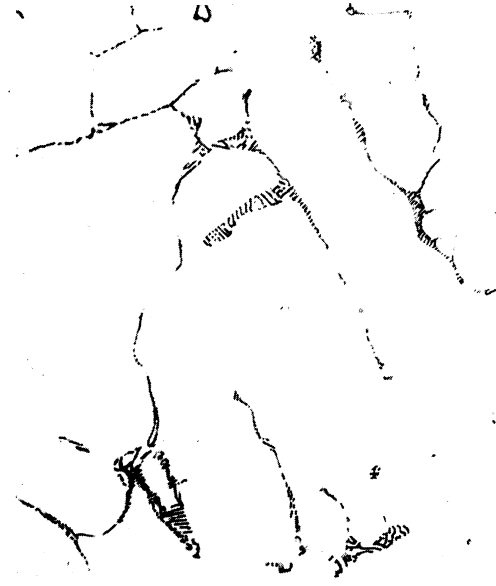
(a) 0.10 C, 0.60 Cb



(b) 0.10 C, 0.70 Cb



(c) 0.10 C, 0.80 Cb



(d) 0.10 C, 0.90 Cb

Figure 4. Typical examples of as-cast microstructure of Type 347 steel. X500

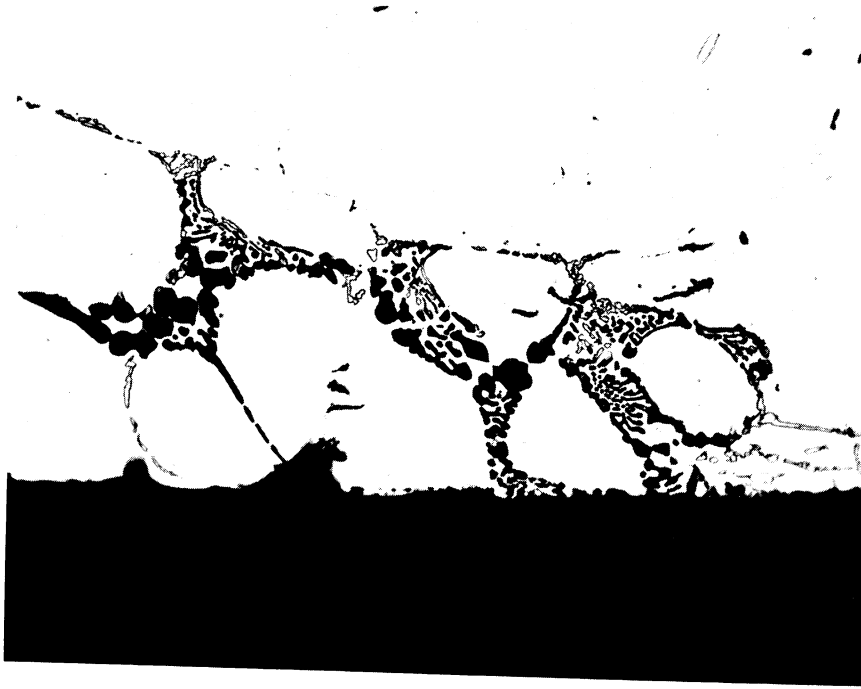
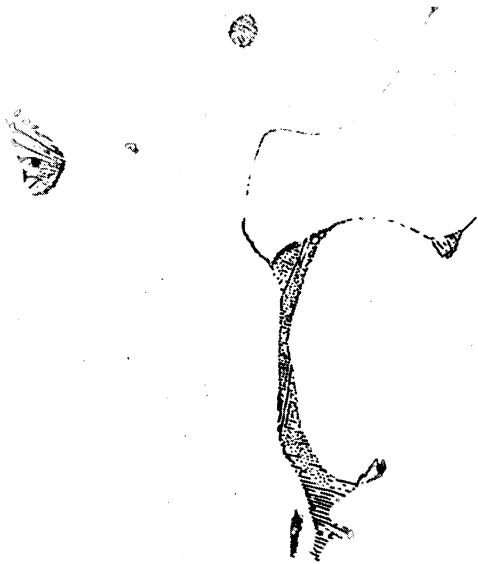


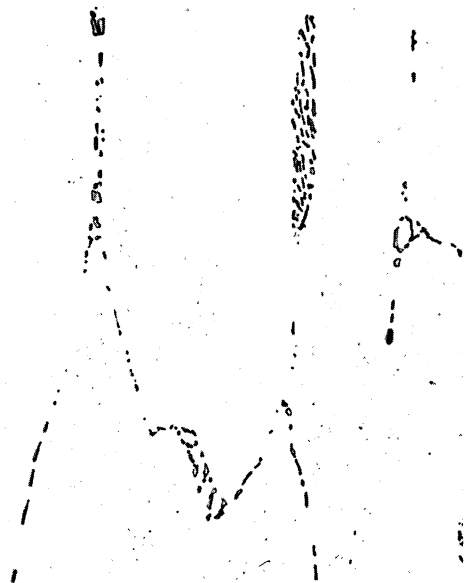
Figure 5. Example of the presence of Fe_2Cb phase near the ingot surface in a Type 347 steel. X500



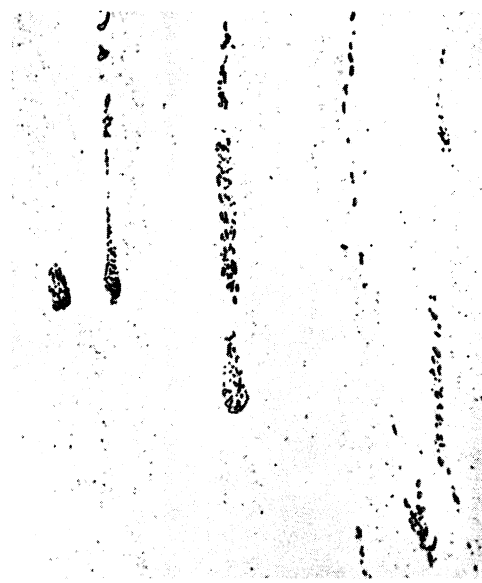
(a) As-Cast



(b) Reduced 30%



(c) Reduced 60%



(d) Reduced 90%

Figure 6. Effect of varying amounts of hot reduction at 2100°F on the carbide topology in Type 347 steel. X500

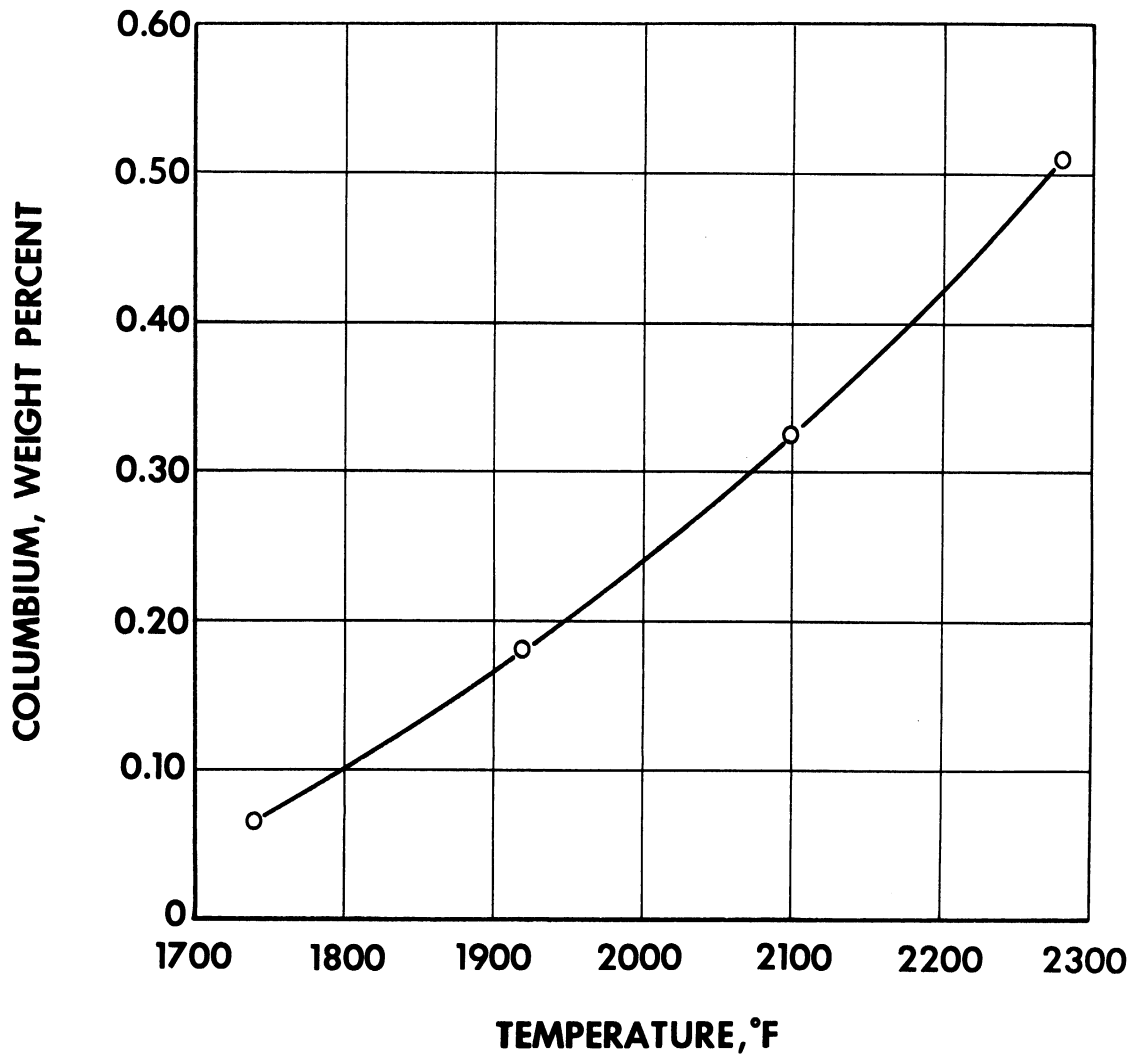
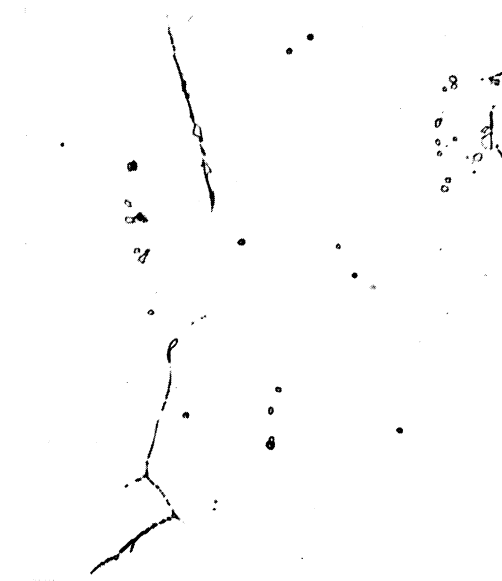


Figure 7. Solubility of columbium in austenite as a function of temperature.



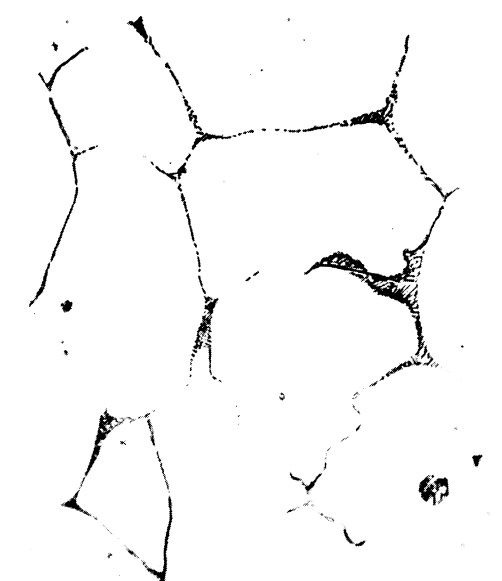
(a) One minute at 2398°F



(b) One minute at 2426°F

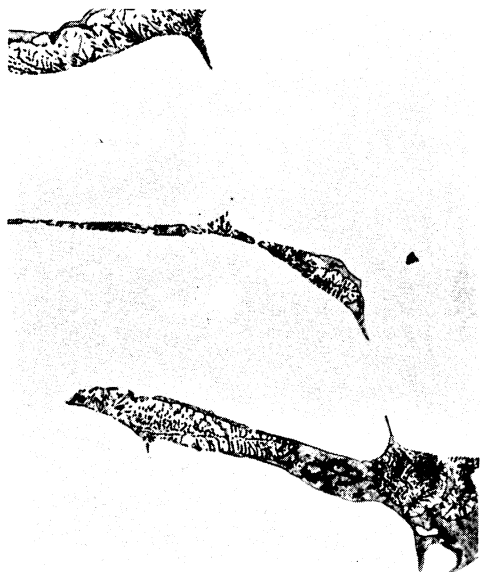


(c) One minute at 2452°F



(d) One minute at 2495°F

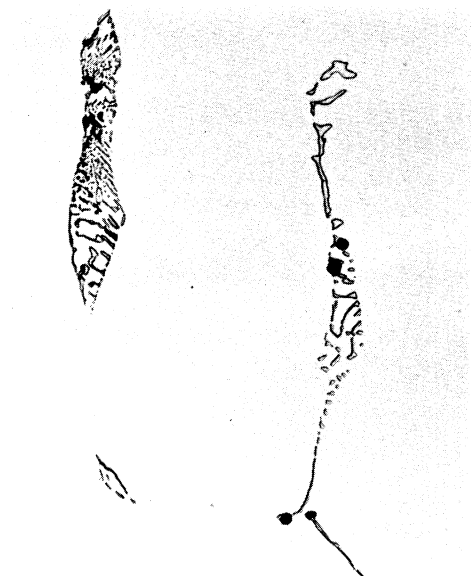
Figure 8. Microstructure of material as a function of exposure temperature showing the various stages of liquid formation. X500



(a) One minute at 2480°F, W.Q. The greyish structure is rich in Fe_2Cb .



(b) One minute at 2480°F, A.C. The dark grey structure is rich in Fe_2Cb .

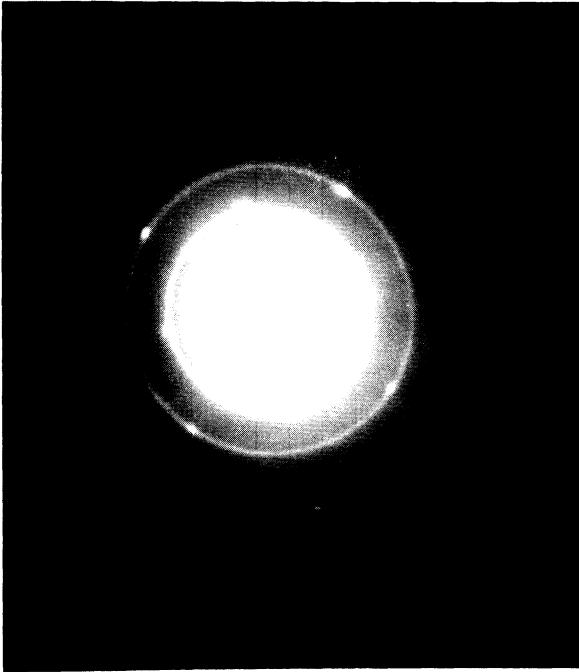


(c) One minute at 2480°F, furnace cooled to 2350°F, A.C. No Fe_2Cb evident.



(d) One minute at 2480°F, furnace cooled to 2350°F, held 10 minutes at 2350°F, A.C. Very coarse structure of CbC and austenite.

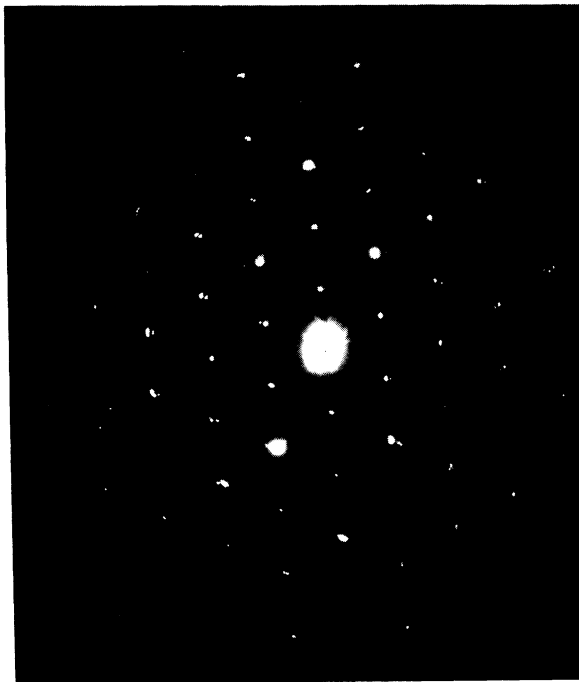
Figure 9. Influence of varying cooling conditions on microstructure of material held for one minute at a temperature above its liquation temperature. X500



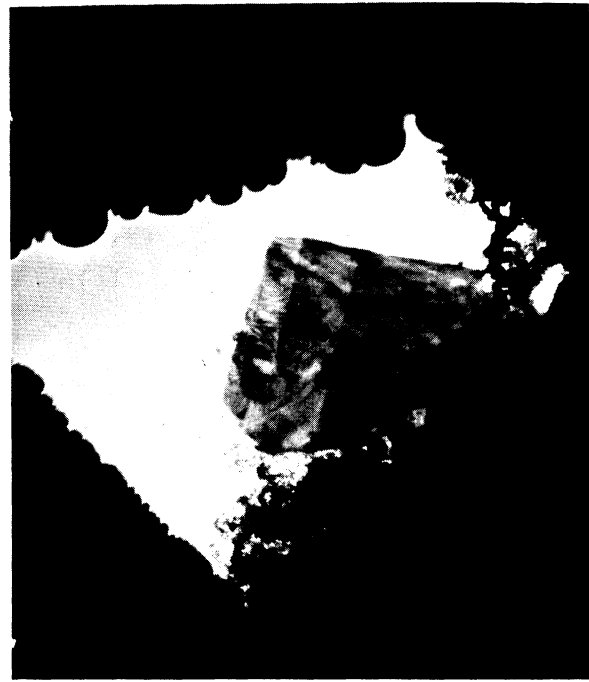
(a) Selected area diffraction pattern of CbC.



(b) Particles from which pattern at left was obtained. X10,000



(c) Selected area diffraction pattern of Fe₂Cb.



(d) Particle from which pattern at left was obtained. X10,000

Figure 10. Selected area diffraction patterns from CbC and Fe₂Cb particles.

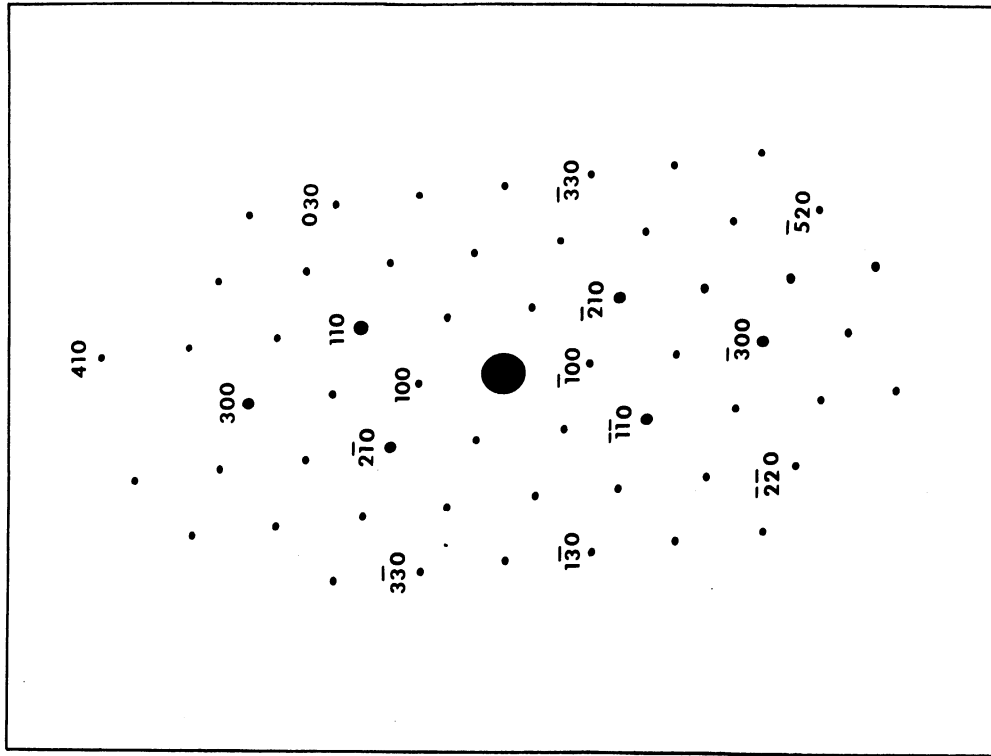
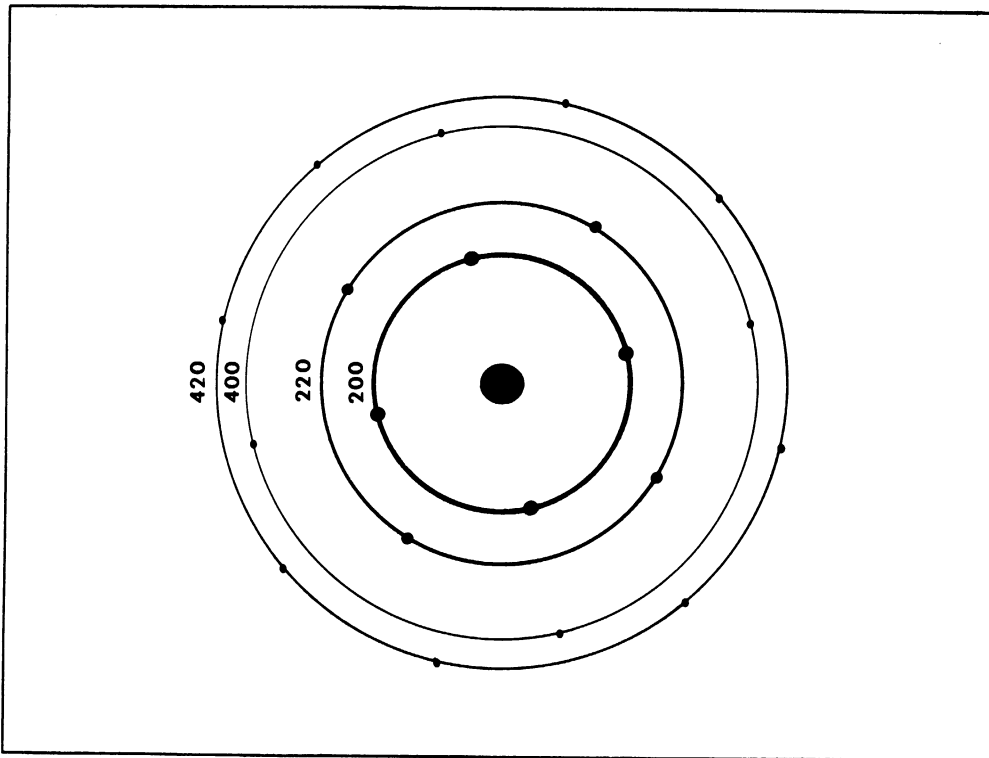
 **Fe_2Cb**  **CbC**

Figure 11. Indexed diagrams of electron diffraction patterns from CbC and Fe_2Cb particles.

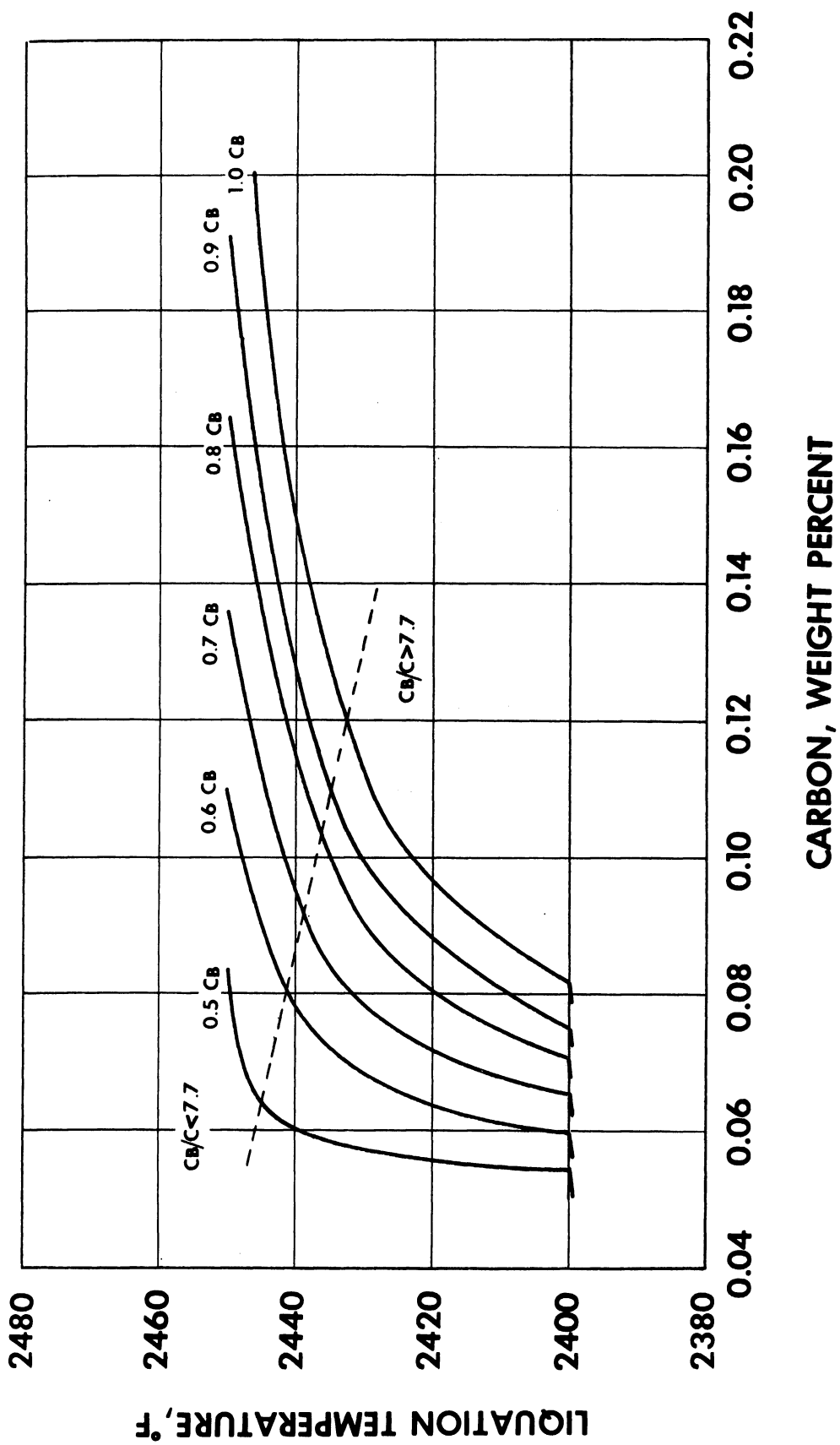


Figure 12. Liquation temperature as a function of carbon content for constant carbonium levels.

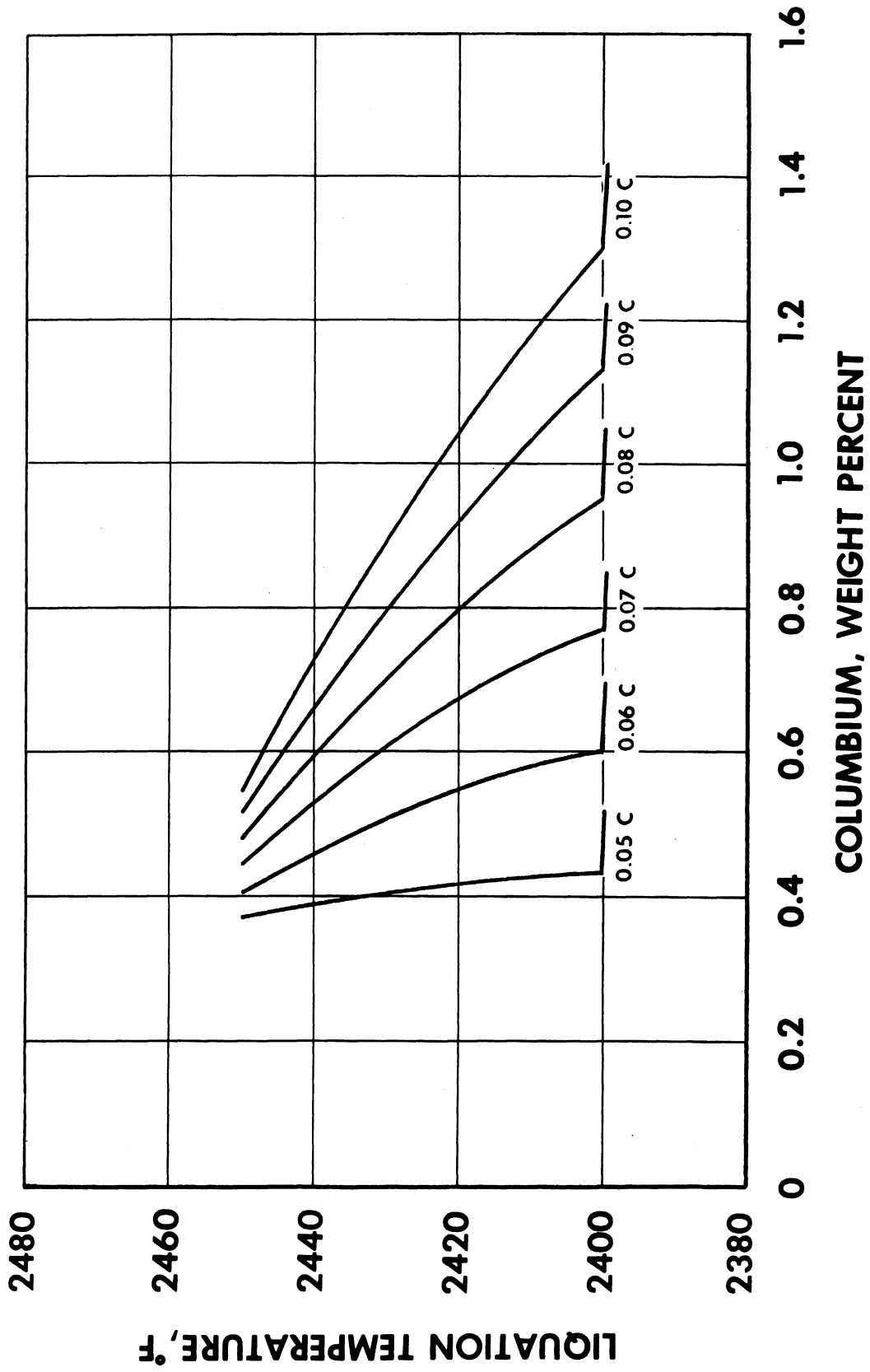
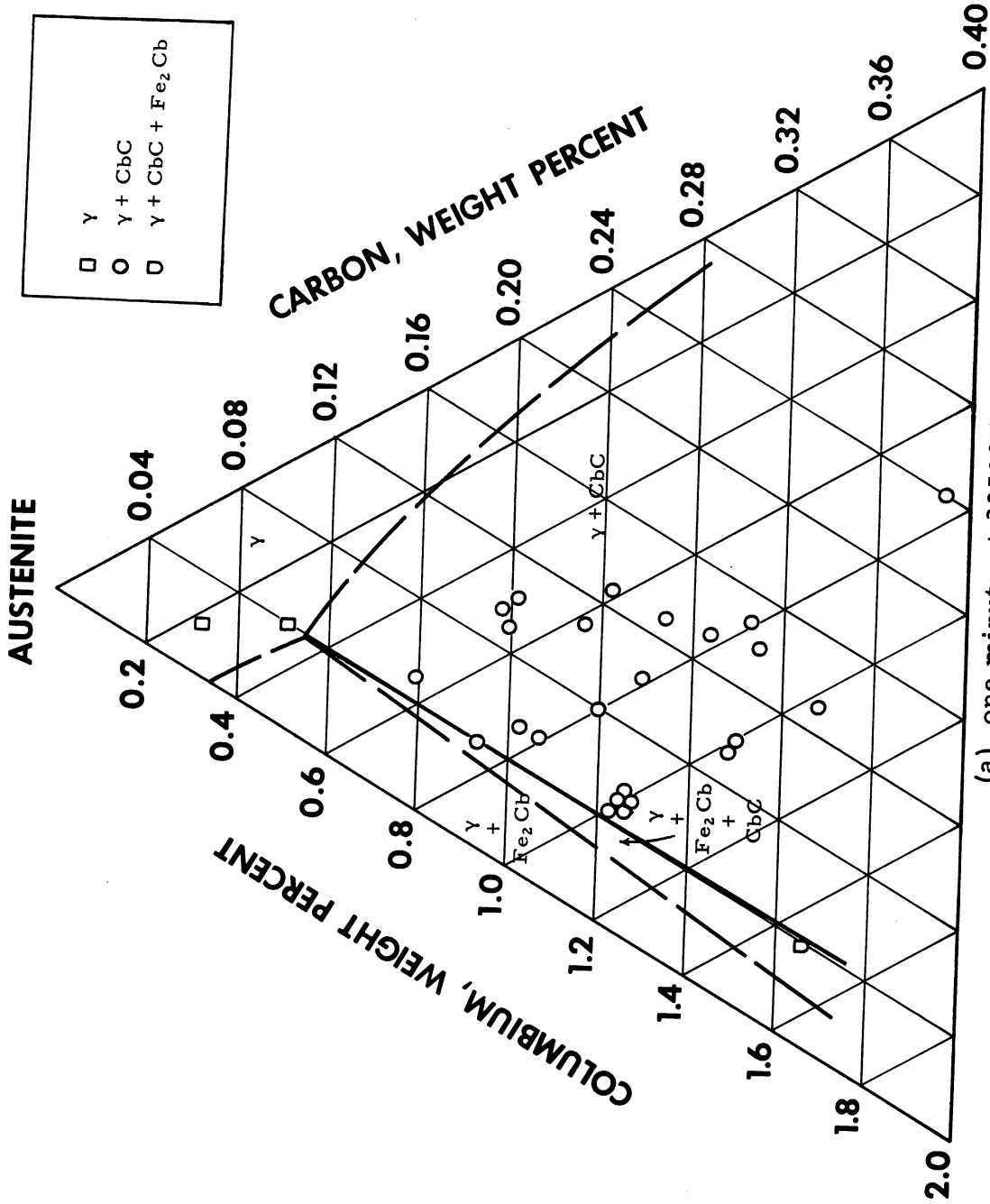
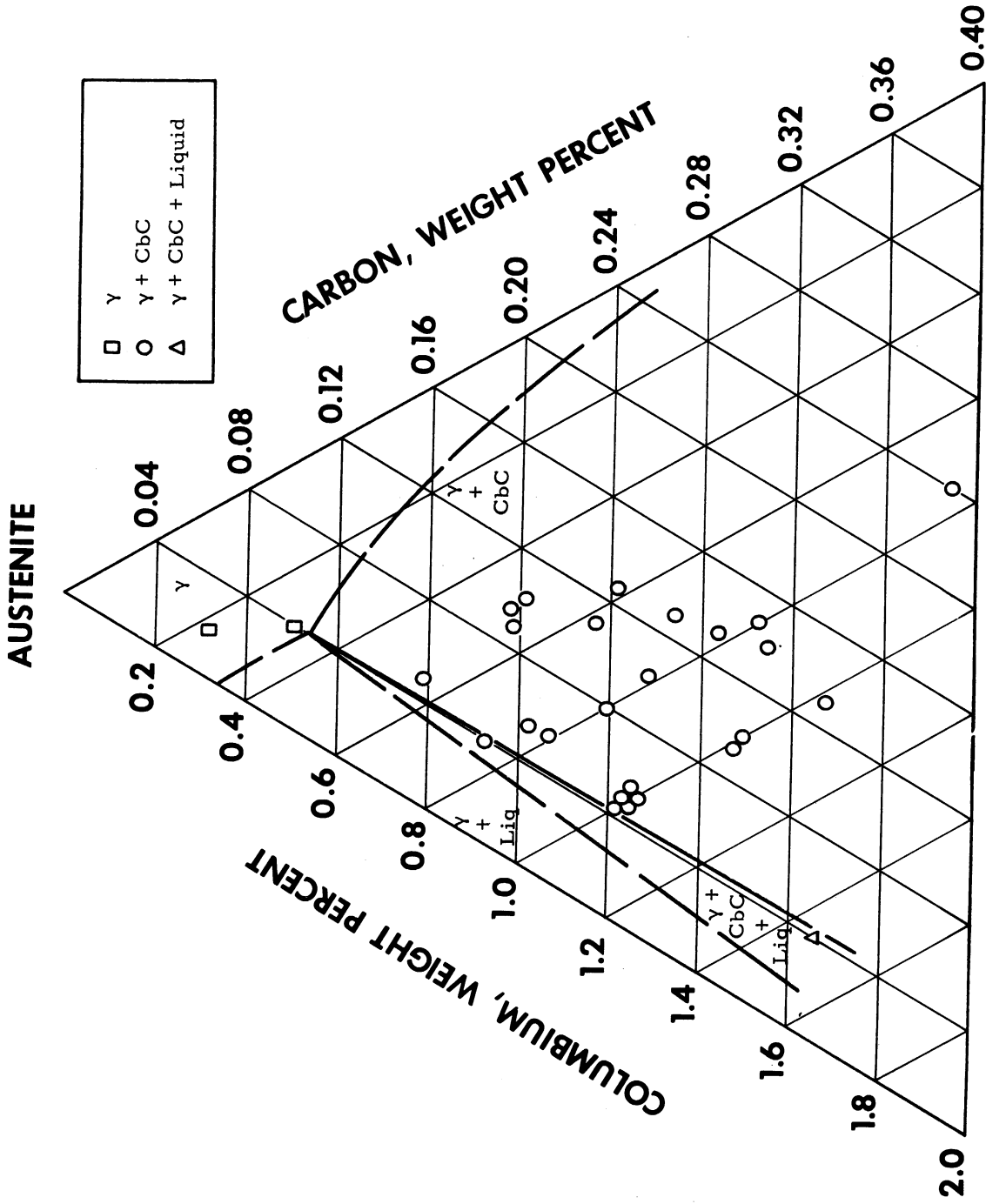


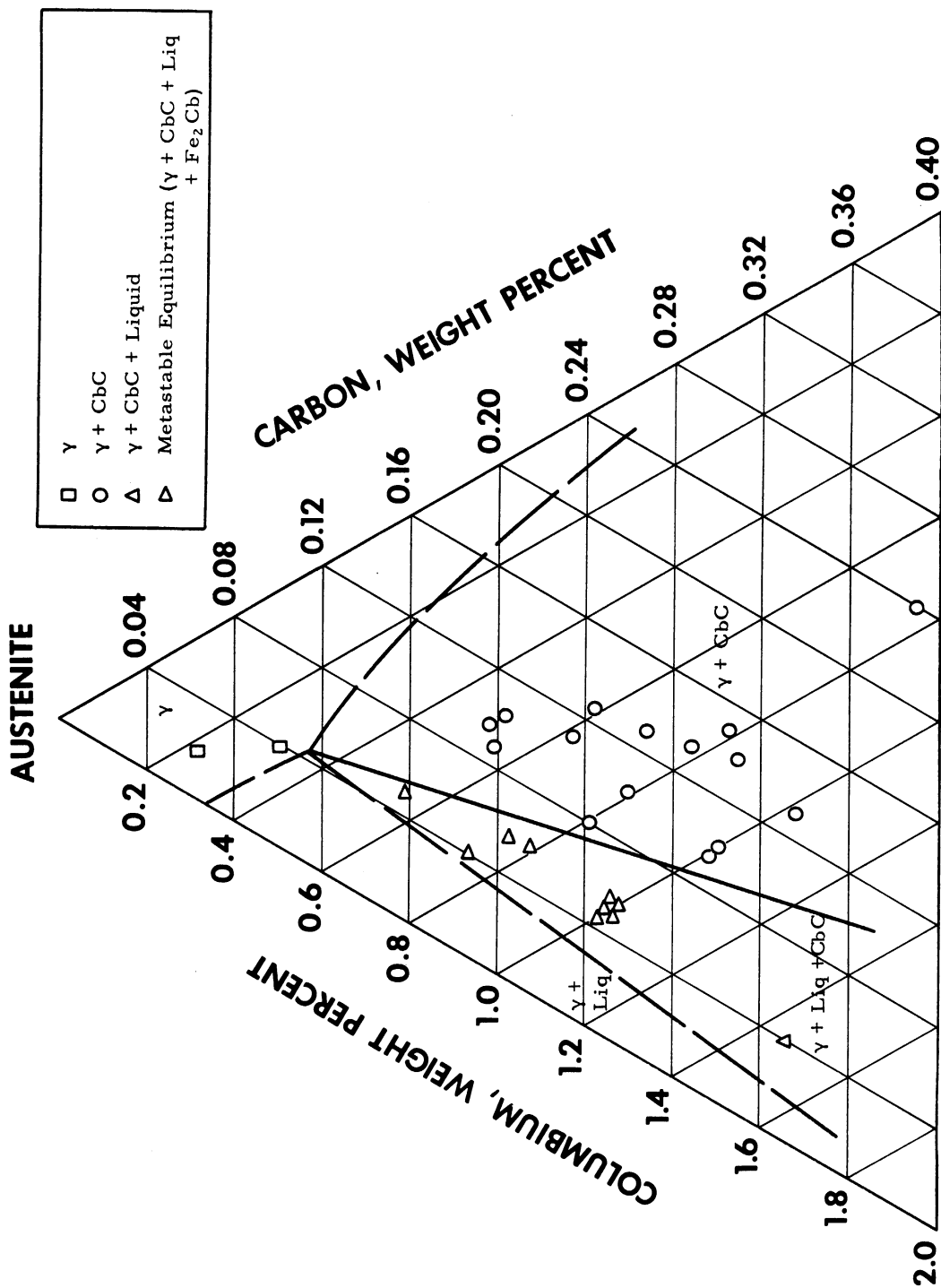
Figure 13. Liquidation temperature as a function of columbium content for constant carbon levels.



(a) one minute at 2350°F
 Figure 14. Isothermal section of the austenite corner of the austenite-carbon-columbium system.

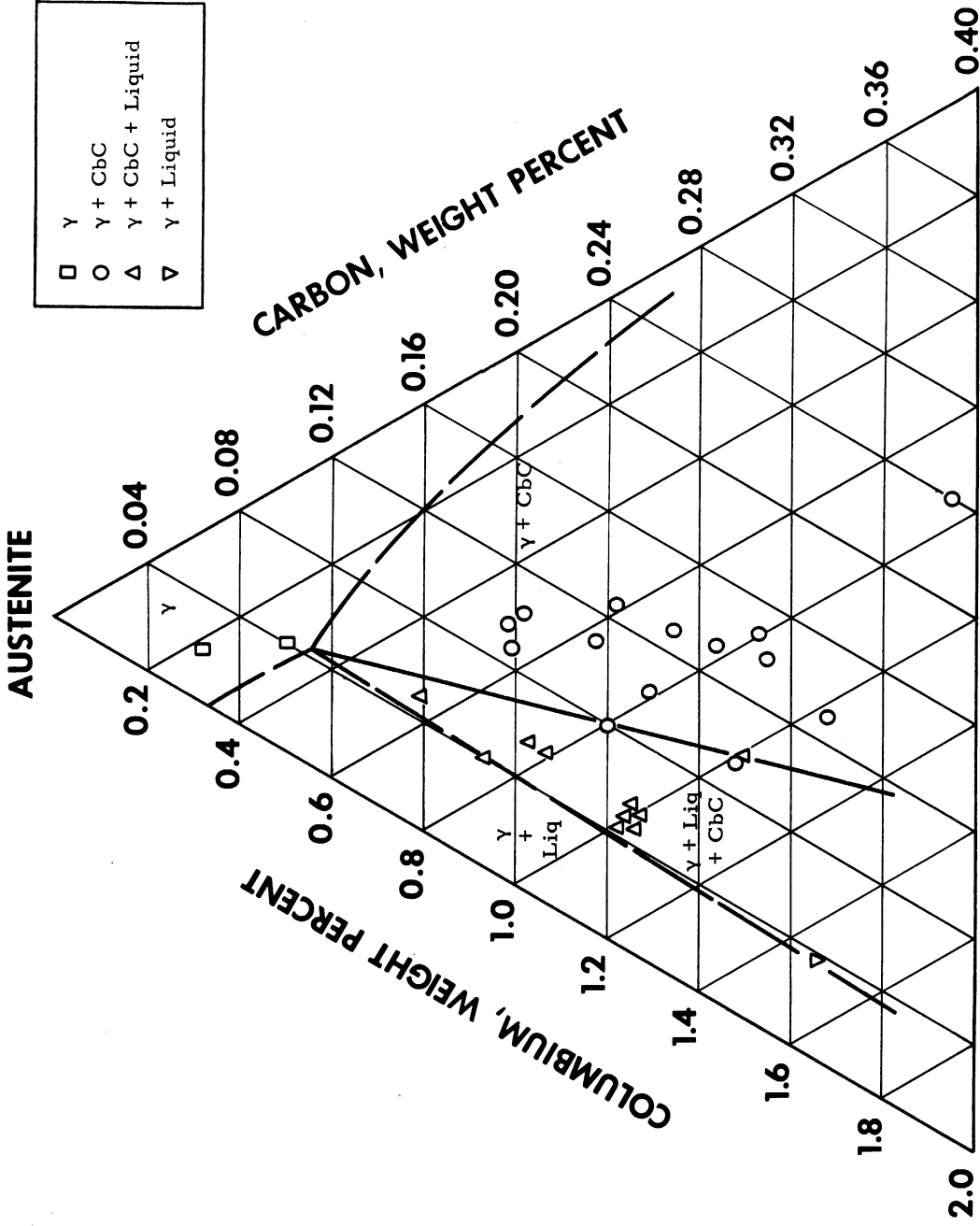


(b) one minute at 2380°F
 Figure 14 - continued. Isothermal section of the austenite corner of the austenite-carbon-columbium system.

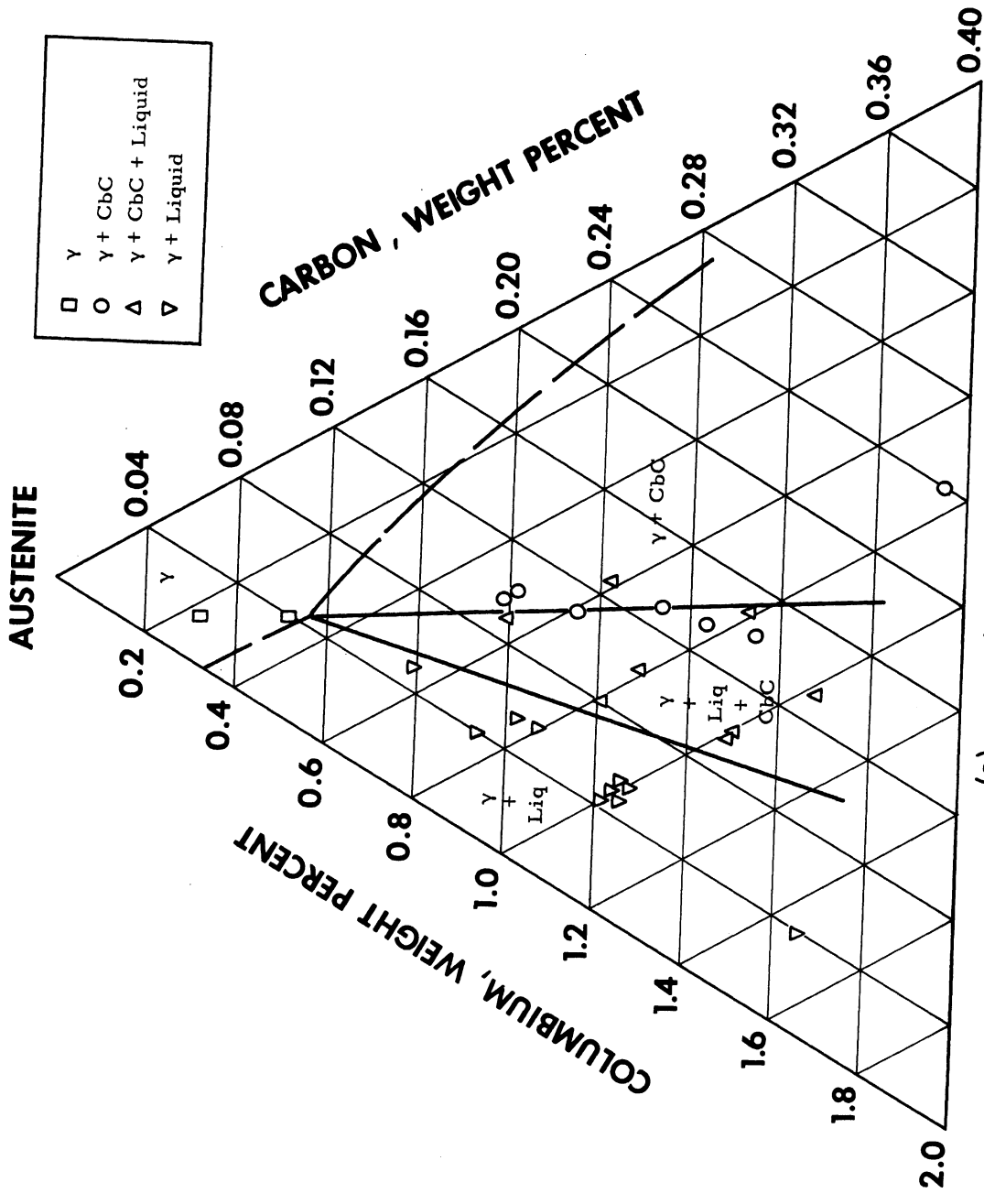


(c) one minute at 2400°F

Figure 14 - continued. Isothermal section of the austenite corner of the austenite-carbon-columbium system.



(d) one minute at 2420°F
 Figure 14 - continued. Isothermal section of the austenite corner of the austenite-carbon-columbium system.



(e) one minute at 2450°F
Figure 14 - concluded. Isothermal section of the austenite corner of the austenite-carbon-columbium system.

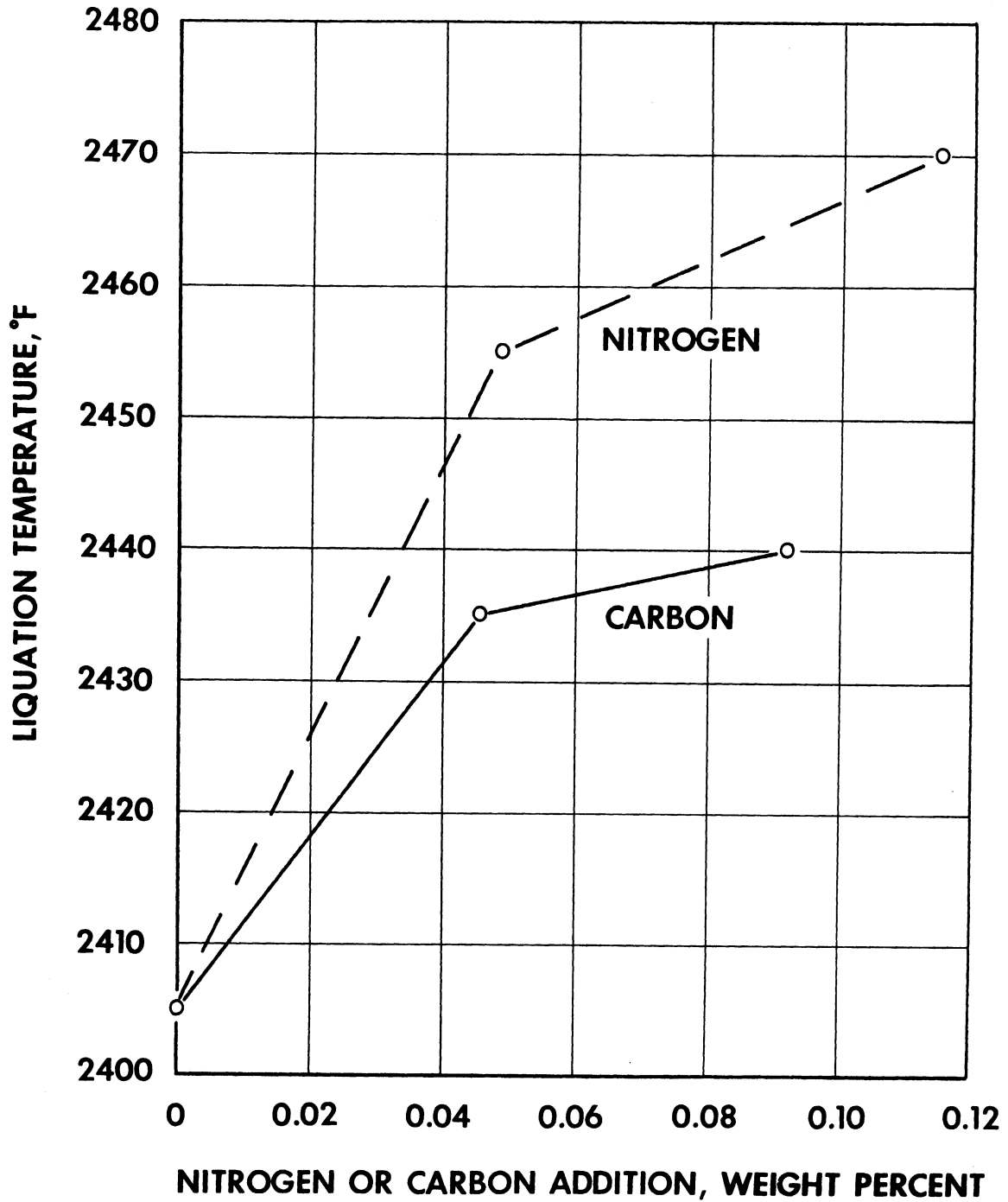


Figure 15. Effect of amount of nitrogen or carbon added on the liquation temperature of an alloy containing 0.055 C and 0.77 Cb.

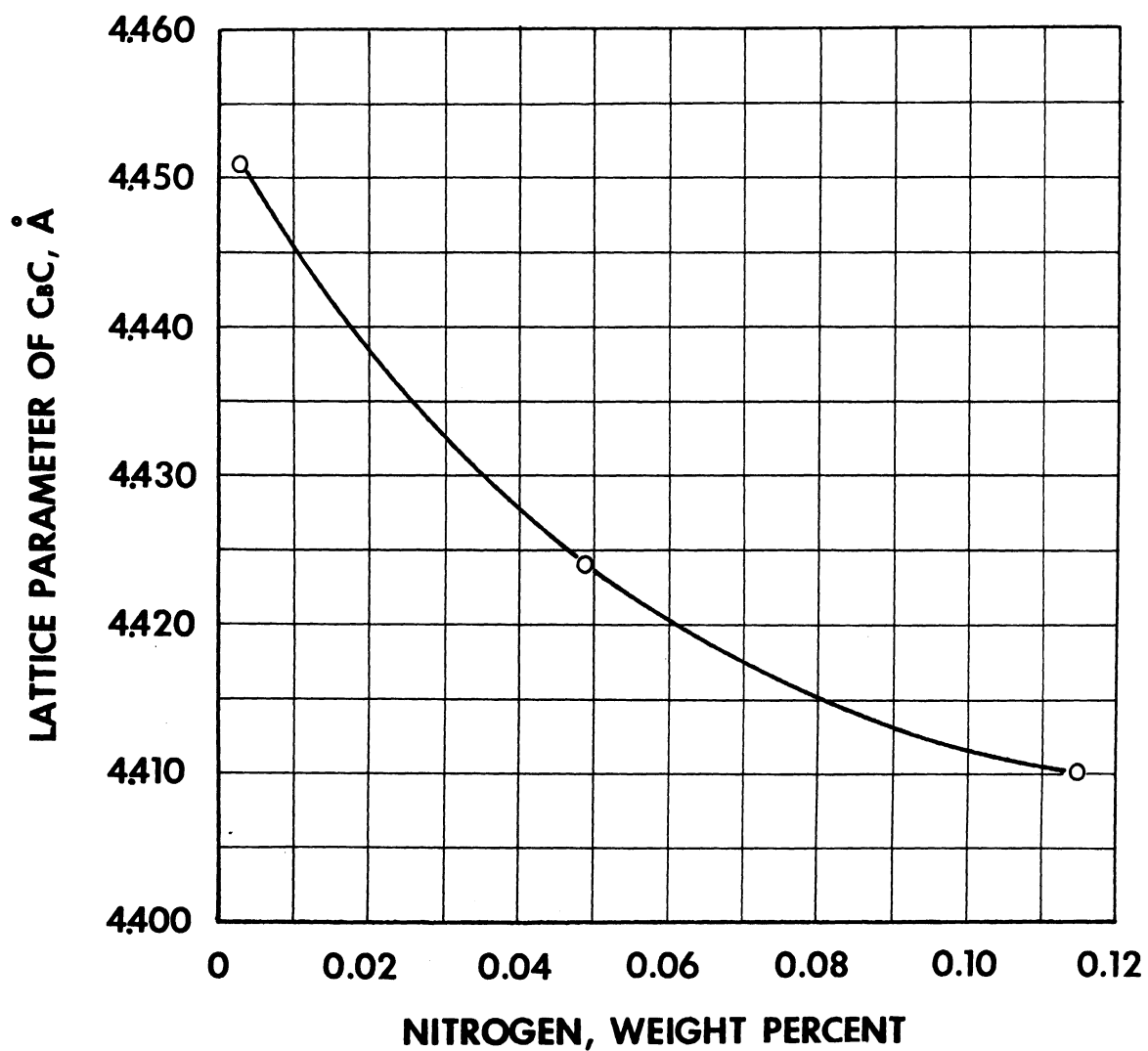


Figure 16. Lattice parameter of extracted phase as a function of nitrogen content of vacuum melted laboratory material.

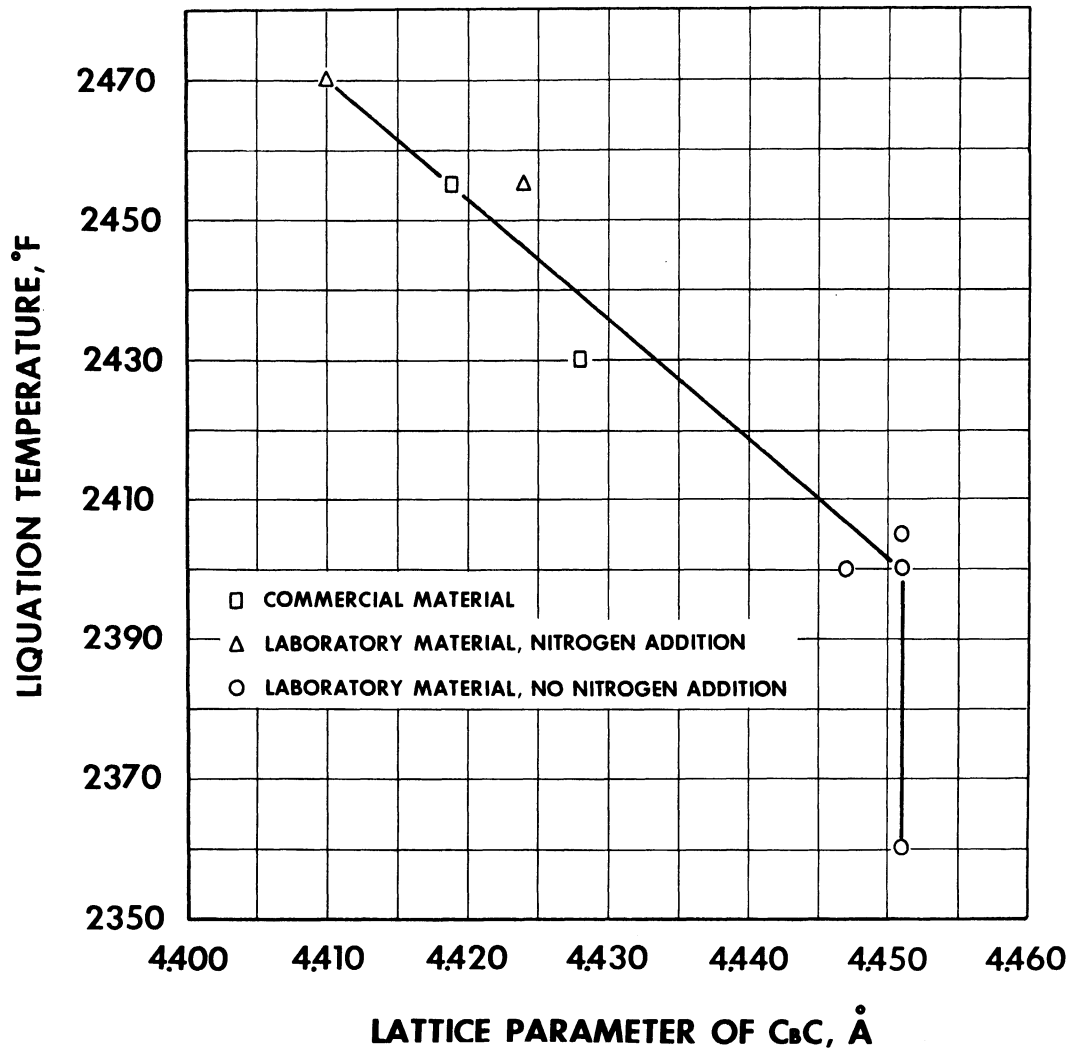


Figure 17. Liquation temperature as a function of lattice parameter of the extracted phases.

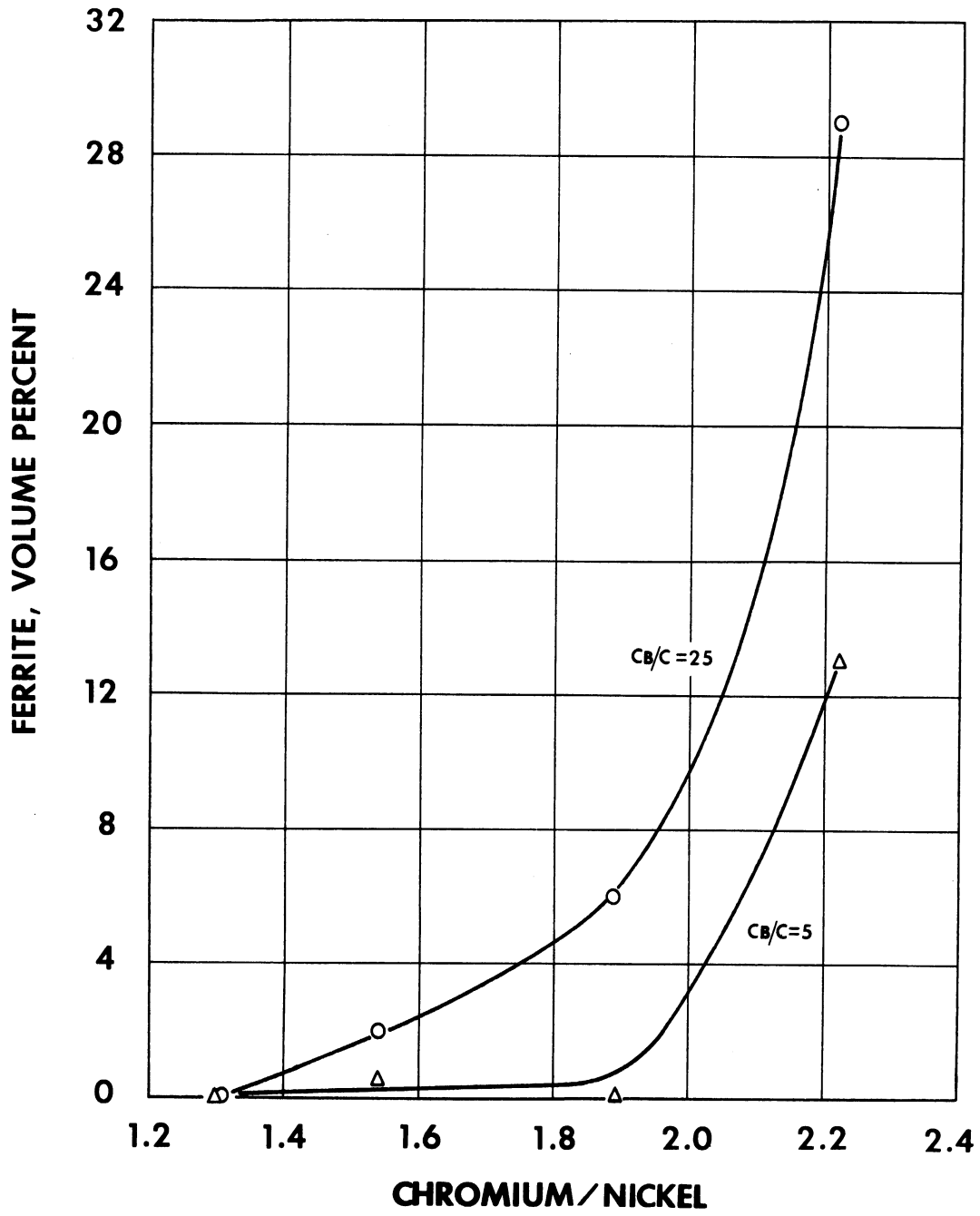


Figure 18. Dependence of the amount of ferrite on the ratio of chromium content to nickel content.

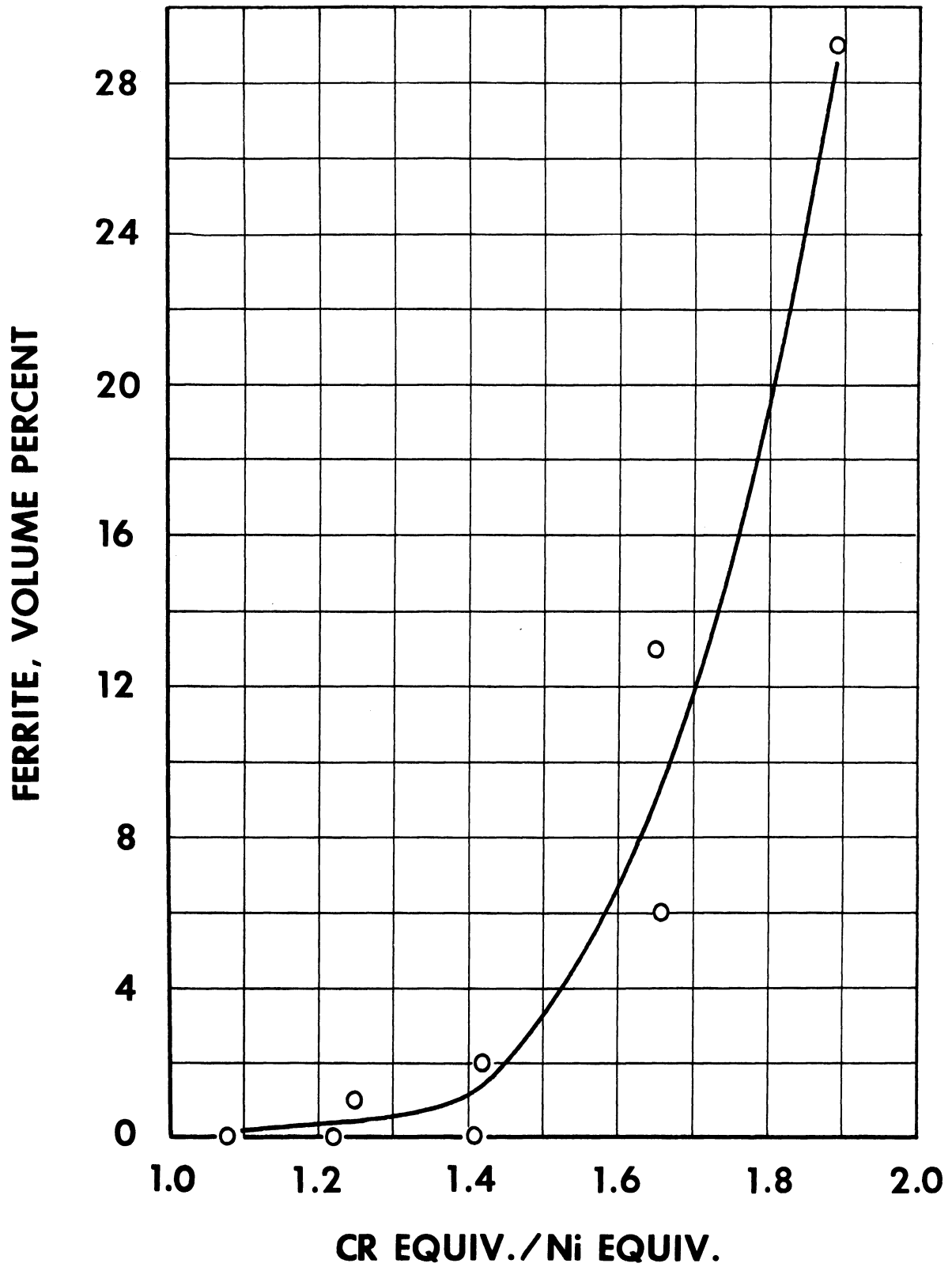
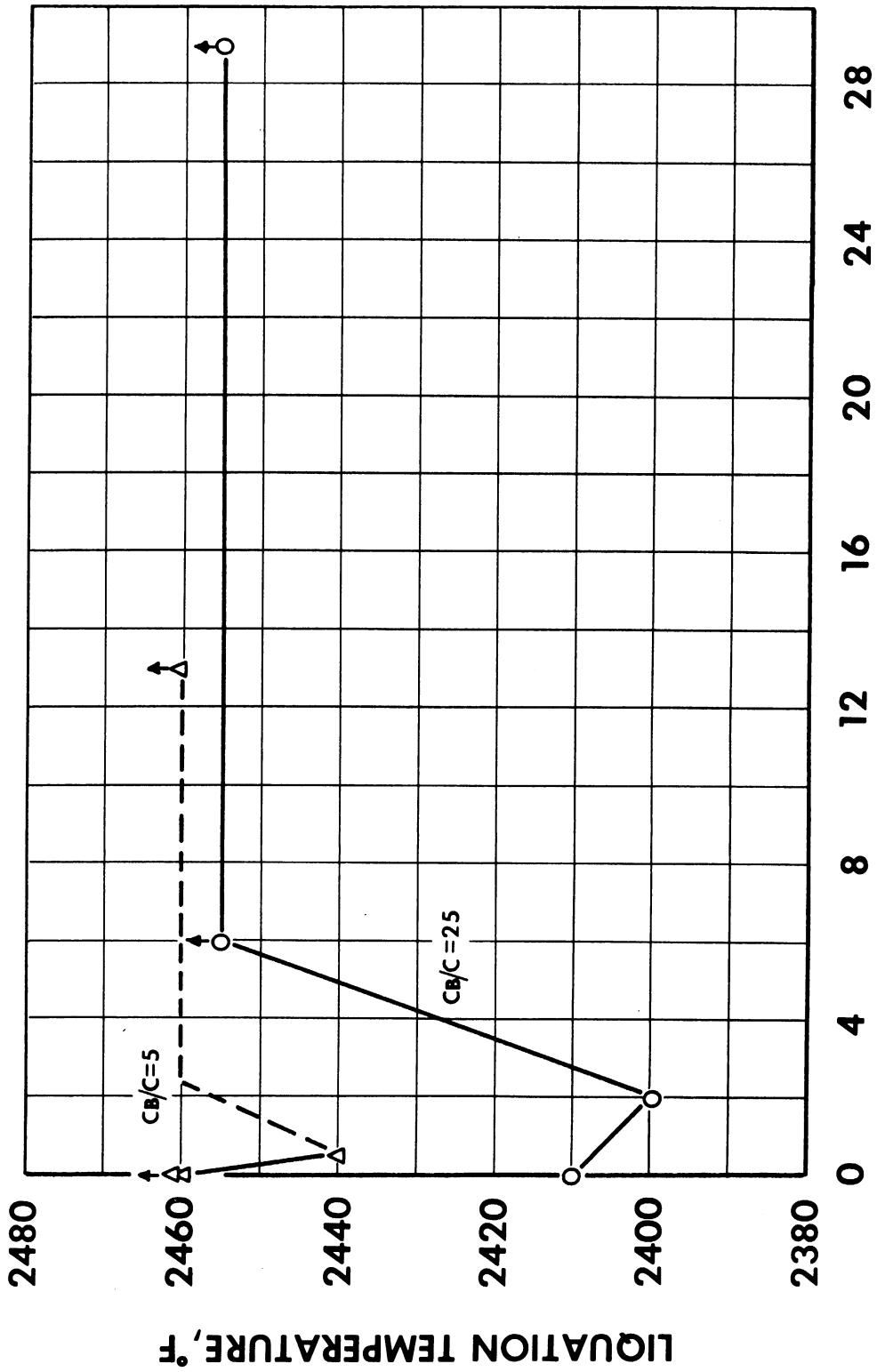


Figure 19. Dependence of the amount of ferrite on the ratio of chromium equivalent to nickel equivalent.



FERRITE, VOLUME PERCENT

Figure 20. Dependence of liquation temperature on the amount of ferrite present in a material.

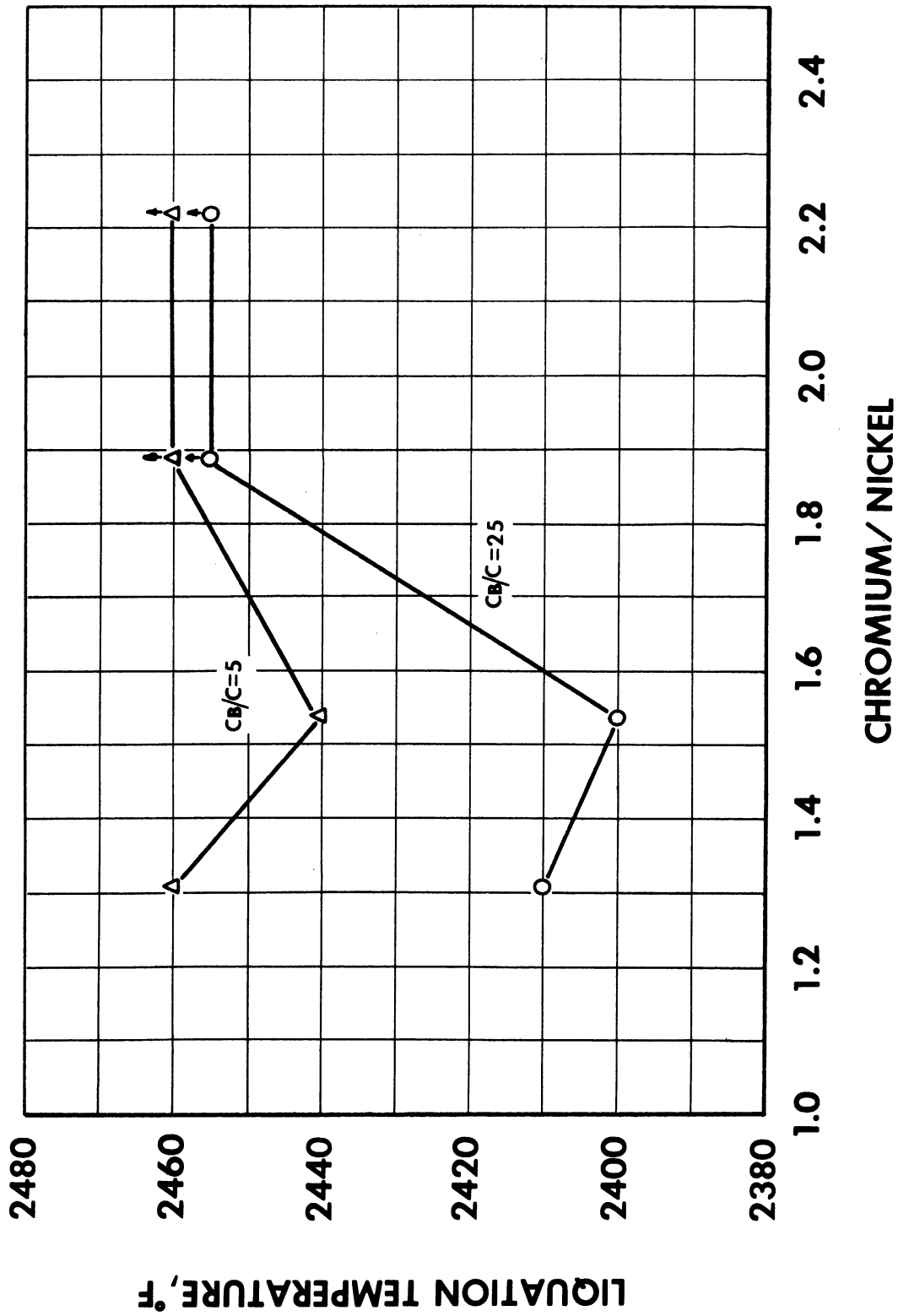


Figure 21. Liquidation temperature as a function of the ratio of chromium content to nickel content.

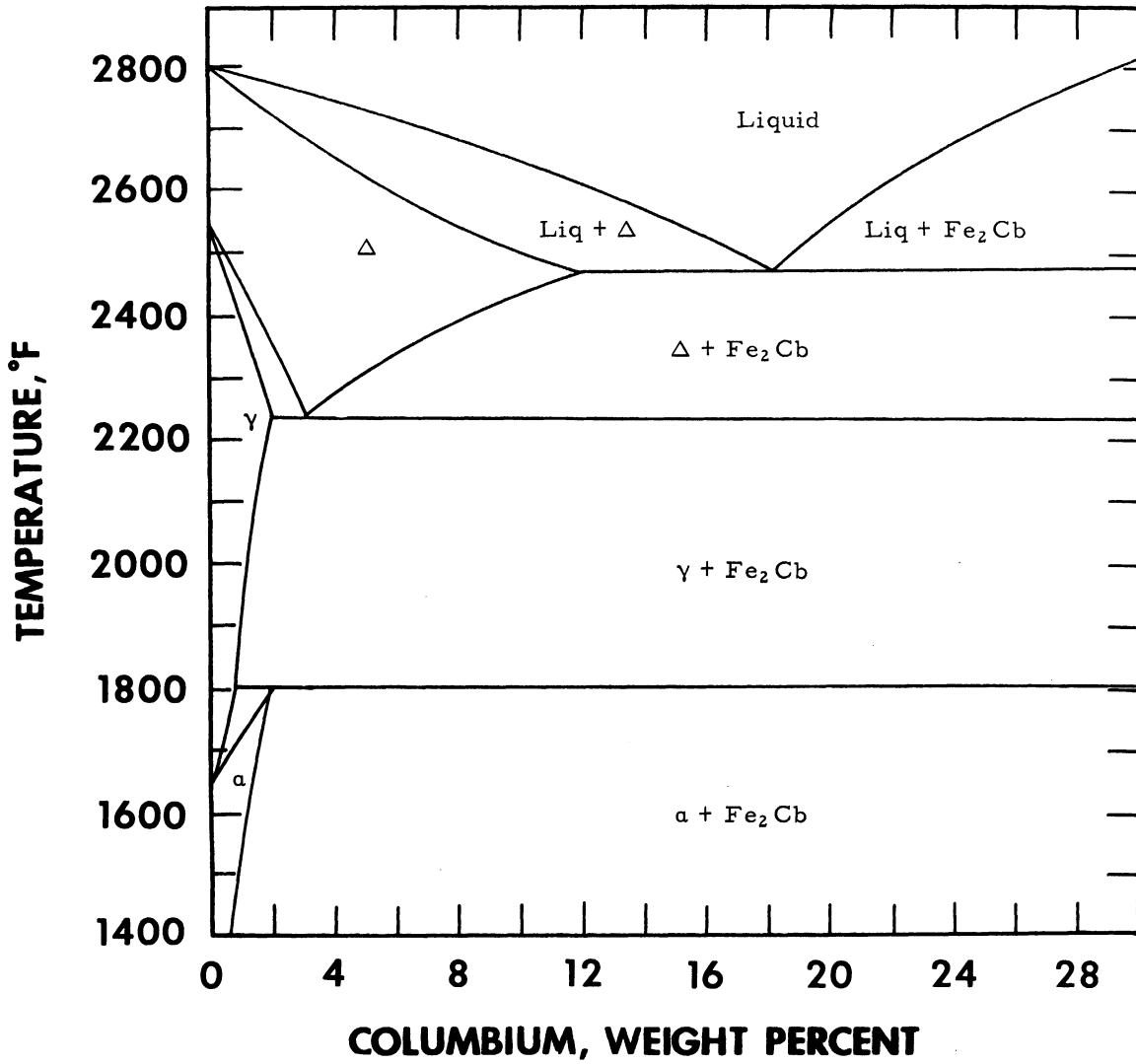
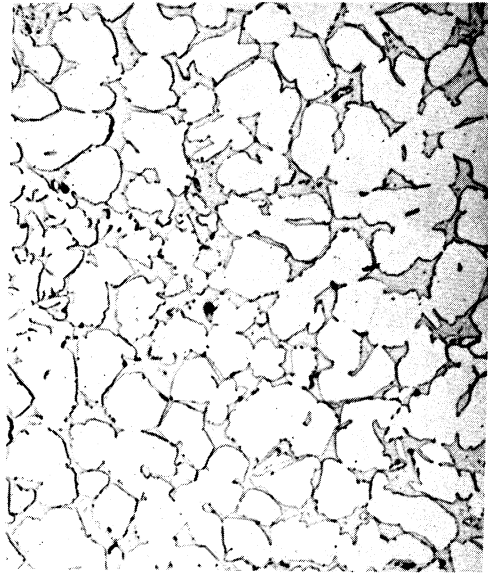


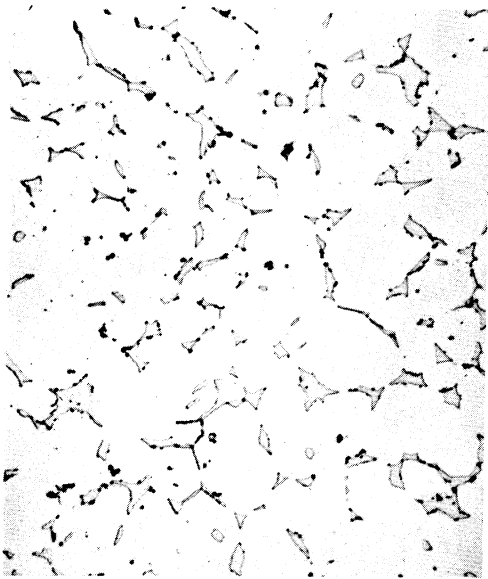
Figure 22. Iron-columbium phase diagram.



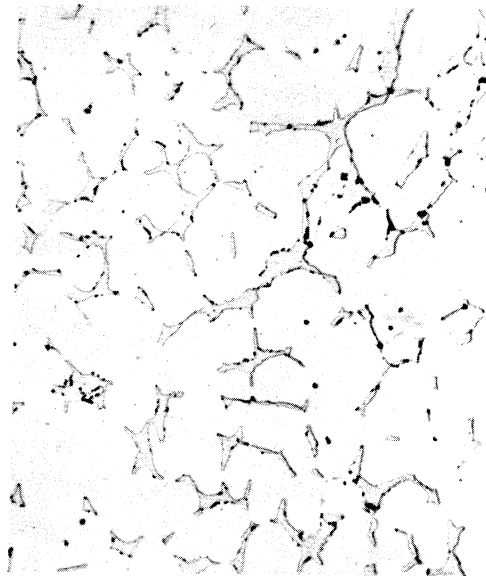
(a) Heat 1268



(b) Heat 1268



(c) Heat 1270



(d) Heat 1270

Figure 23. Microstructures of specimens showing considerable amounts of ferrite after high temperature exposure which do not exhibit the CbC phase. X500

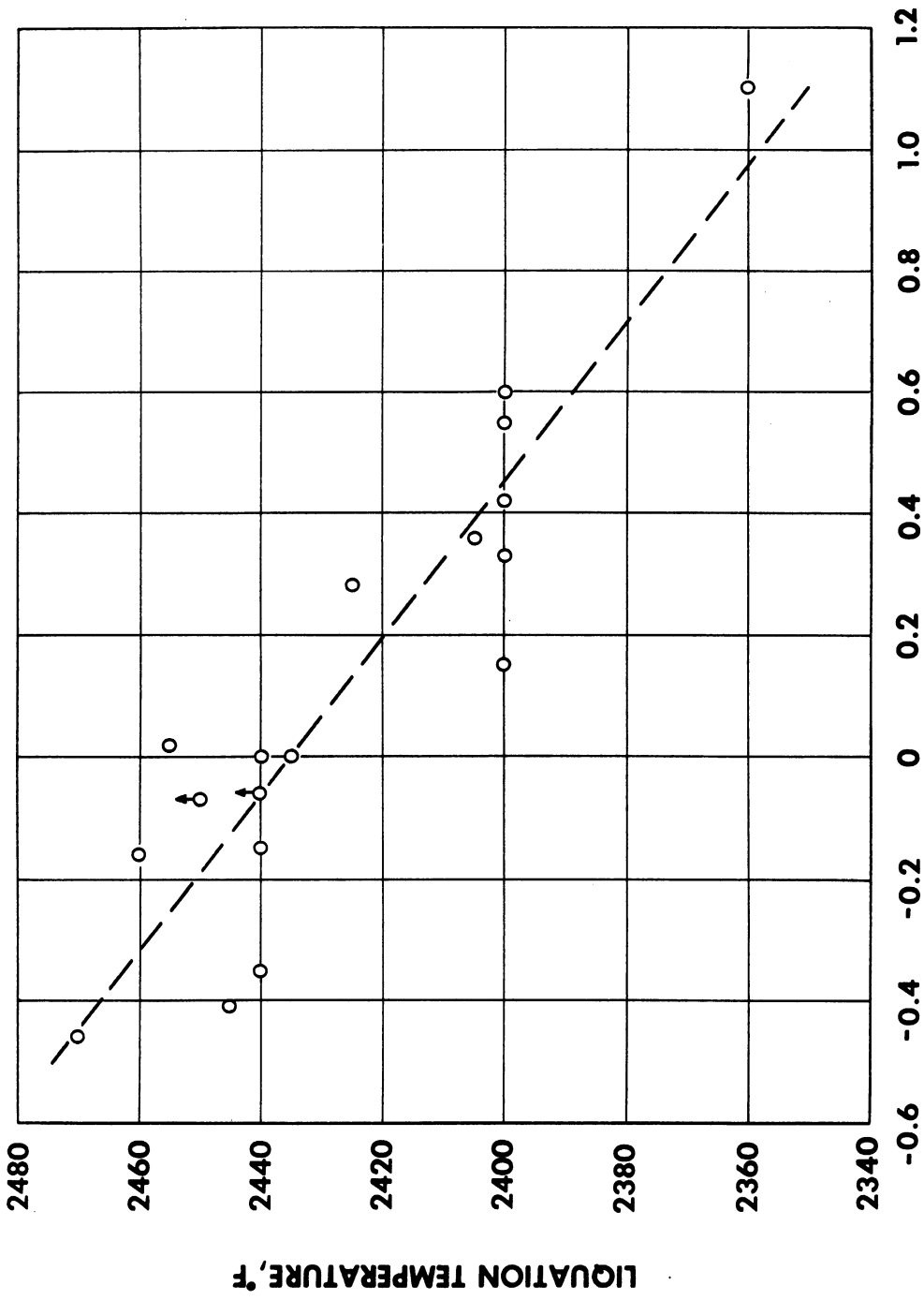


Figure 24. Liquation temperature as a function of amount of excess columbium.

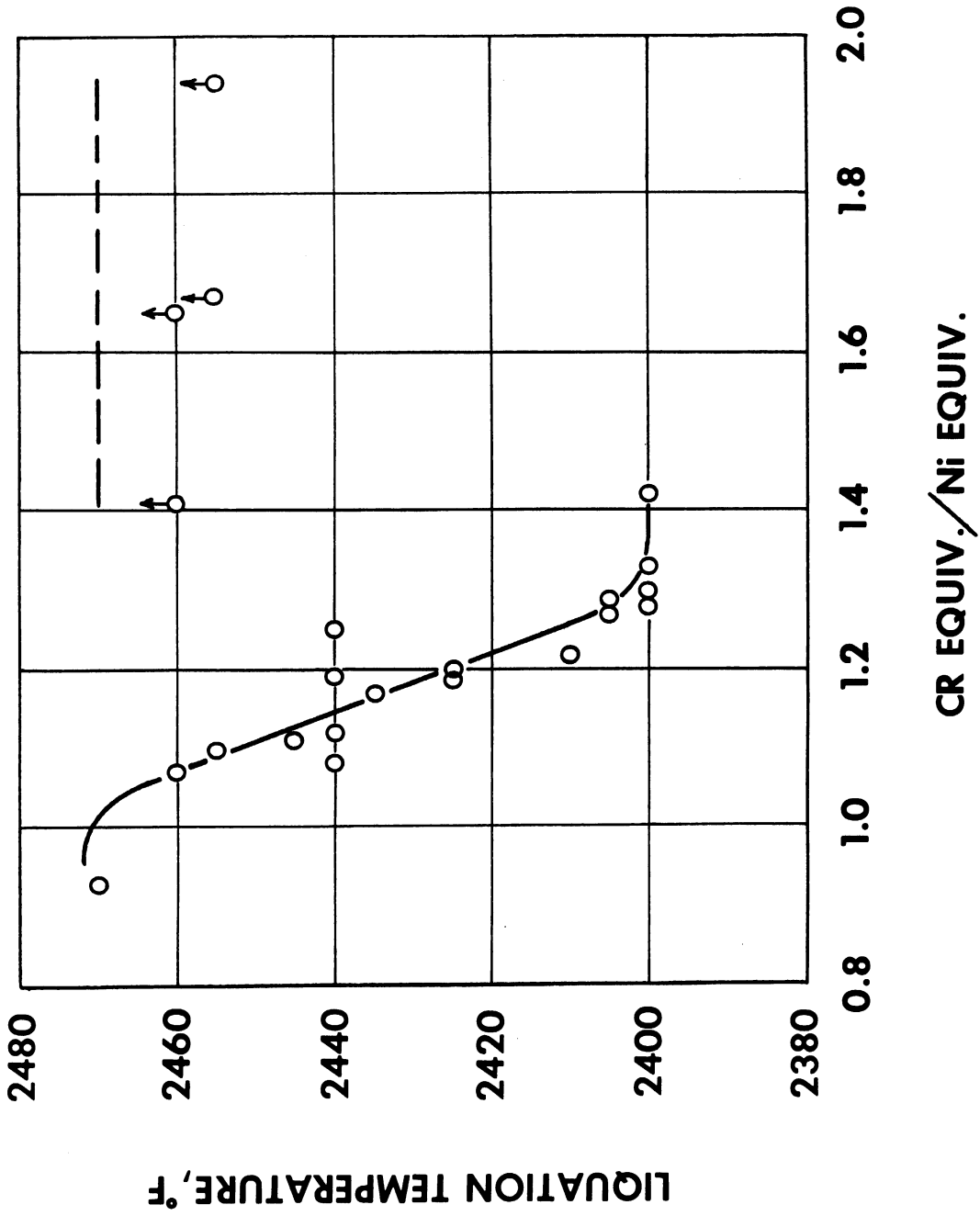


Figure 25. Liquation temperature as a function of the ratio of chromium equivalent to nickel equivalent.

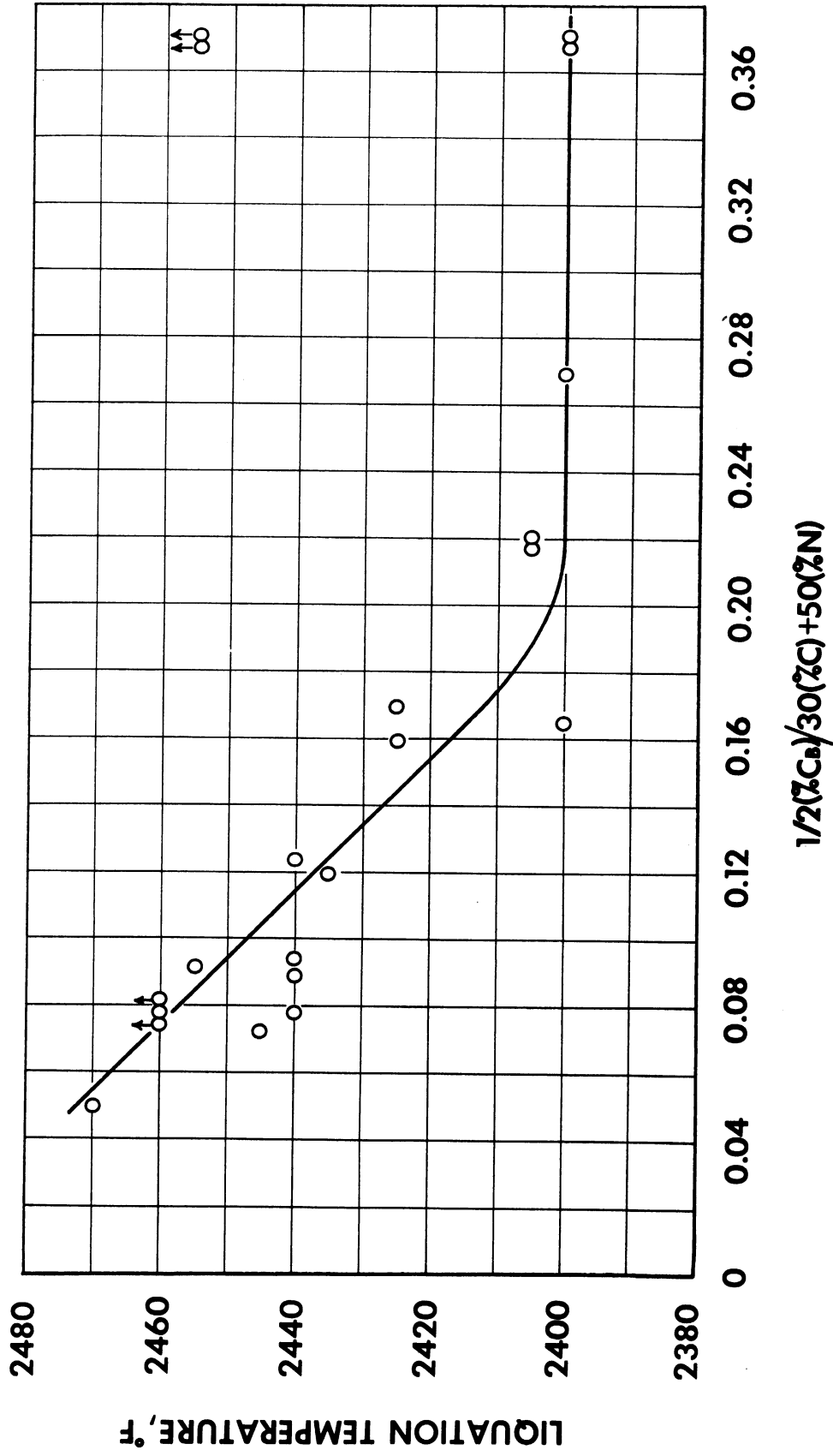
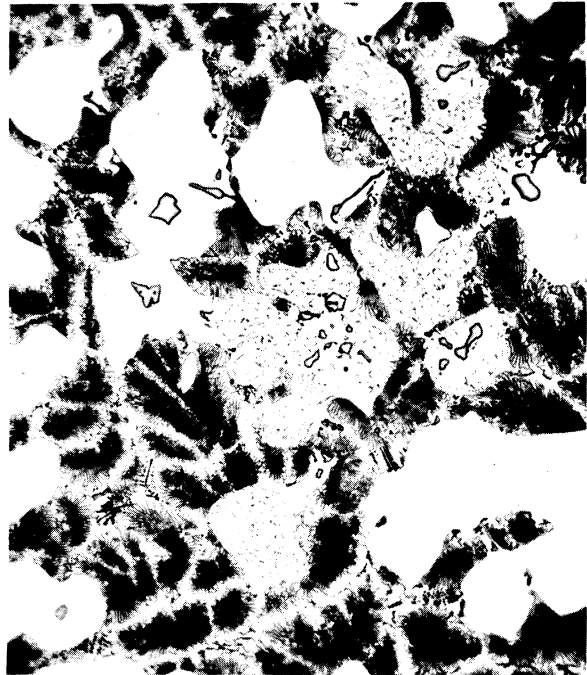


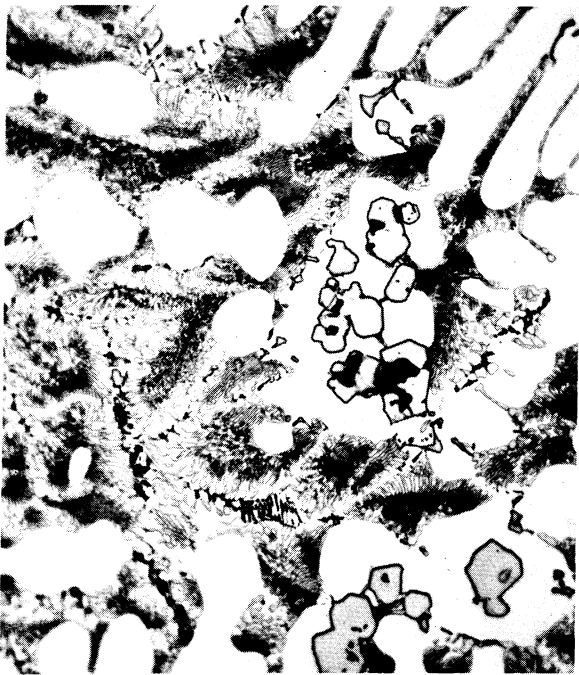
Figure 26. Liquation temperature as a function of a weighted ratio of columbium content to carbon content plus nitrogen content.

(a) H_3PO_4 etch

X37.5

(b) H_3PO_4

X500

(c) H_3PO_4 etch

X500

(d) H_3PO_4 etch + HF etch

X500

Figure 27. Micrographs of heat 1237 showing pronounced segregation in sample held for one hour at 2450°F after being hot worked 96 percent at 2100°F.

