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(54) Title: MICROTREATMENT AND MICROSTRUCTURE OF CARBIDE CONTAINING IRON-BASED ALLOY

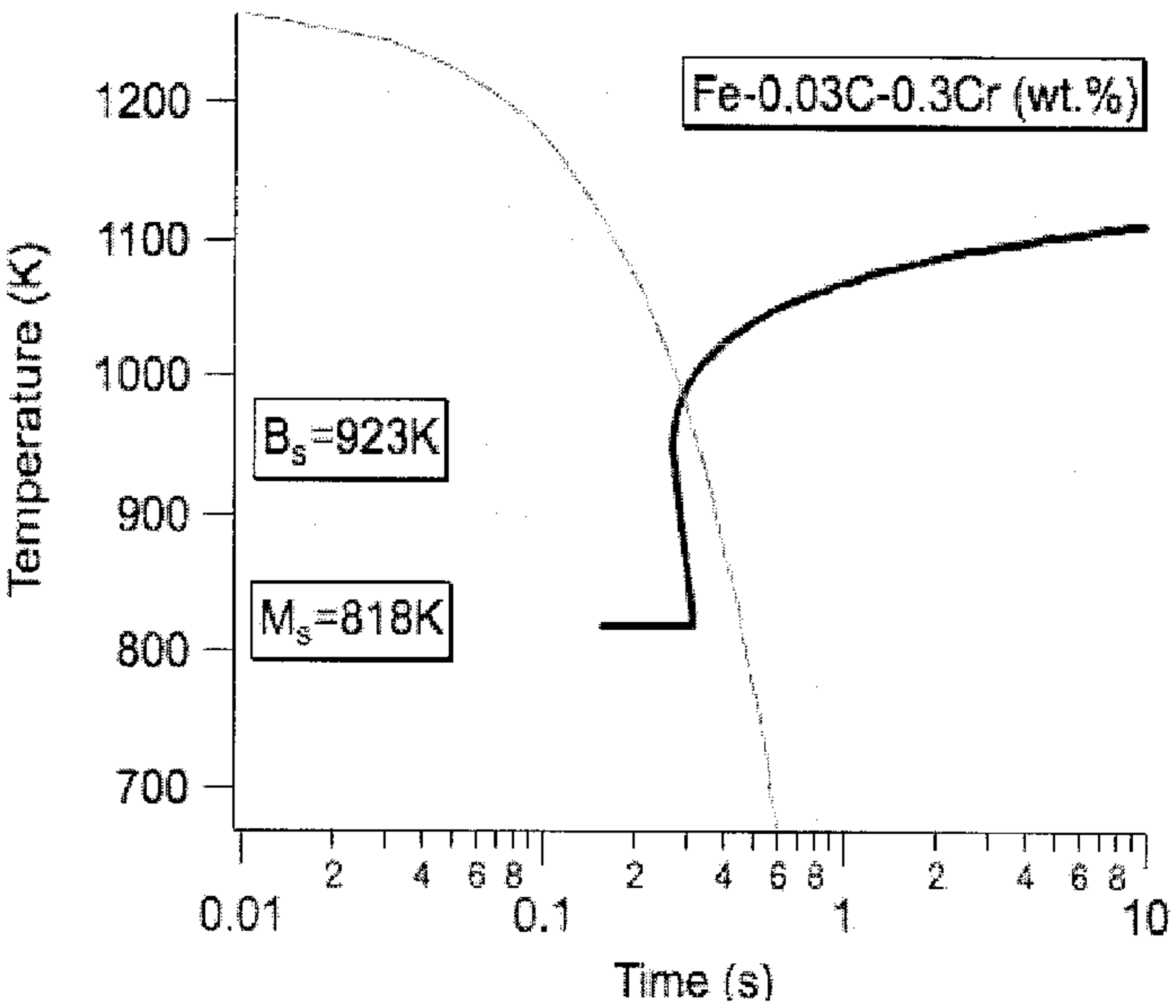

FIG. 11

(57) Abrégé/Abstract:
Processes and apparatuses for micro-treating iron-based alloys to transform and/or shape them and the resulting materials obtained by treating low, medium, and high carbon steel and other iron-based alloys to form at least a mixed microstructure that may contain martensite, bainite and un-dissolved carbides, and may also contain complex steel microstructures including portions of bainite, coalesced bainite, acicular ferrite, retained austenite and/or martensite along with combinations thereof by micro-treating said iron based alloy.

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**Declarations under Rule 4.17**:

— *as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))*

*[Continued on next page]*

# (54) **Title**: MICROTREATMENT AND MICROSTRUCTURE OF CARBIDE CONTAINING IRON-BASED ALLOY

(57) **Abstract**: Processes and apparatuses for micro-treating iron-based alloys to transform and/or shape them and the resulting materials obtained by treating low, medium, and high carbon steel and other iron-based alloys to form at least a mixed microstructure that may contain martensite, bainite and un-dissolved carbides, and may also contain complex steel microstructures including portions of bainite, coalesced bainite, acicular ferrite, retained austenite and/or martensite along with combinations thereof by micro-treating said iron based alloy.

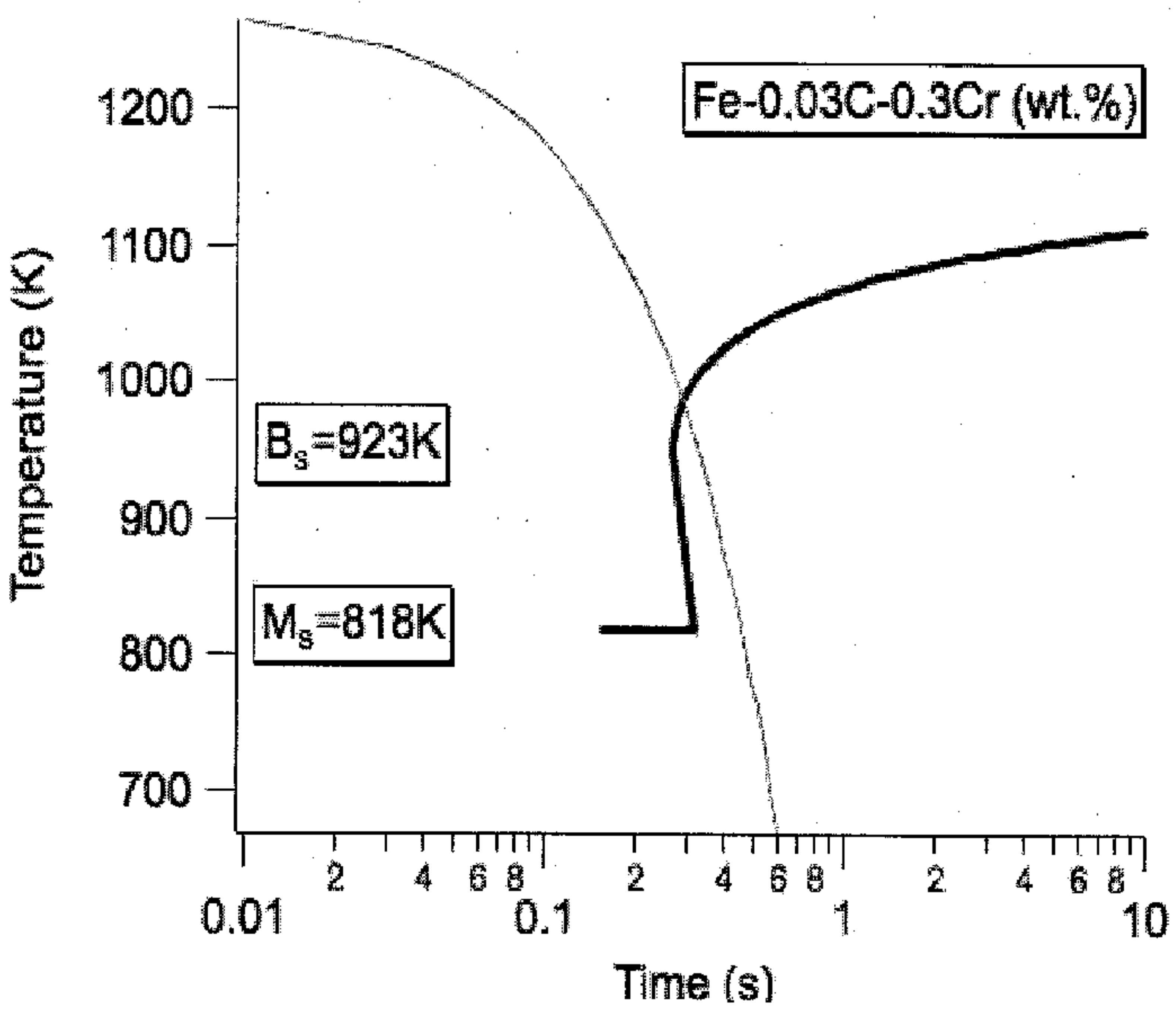

FIG. 11

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# MICROTREATMENT AND MICROSTRUCTURE OF CARBIDE CONTAINING IRON-BASED ALLOY

## CROSS REFERENCES TO RELATED APPLICATIONS

This application claims the benefit of U.S. Provisional Patent Application No. 61/651,992, and U.S. Utility Patent Application No. 12/485,785 which is incorporated herein by reference.

## TECHNICAL FIELD

This invention relates to treated iron-based alloys, and more particularly relate to processes for transforming and/or shaping the same and the various microstructure materials resulting therefrom obtained by treating low, medium, and high carbon steel with other metallic components and other iron-based alloys to at least a mixed microstructure that contains martensite, bainite and un-dissolved carbides, and may also contain complex steel microstructures including portions of bainite, coalesced bainite, pearlite, ferrite, acicular ferrite, retained austenite and/or martensite along with combinations thereof by micro-treating said iron based alloy.

## BACKGROUND OF THE INVENTION

Traditionally, metallurgists have wanted to take low quality metals, such as low carbon steel, and turn them into high quality steels and more desirable products through inexpensive treatments, including annealing, quenching, and tempering to name a few. Previous attempts have met with limited success in that they did not always produce a desirable product. Other attempts have failed on a large scale due to high processing costs or the need to ultimately incorporate excessive, expensive alloying.

Processing of high strength steel generally takes intense capital equipment, high expenditures, expensive and dangerous heated fluids, such as quenching oils and quenching salts, and tempering/annealing processes which include the use of furnaces, heated equipment, and residual heat from pouring molten steel. These quenching procedures are intended to raise the hardness of the steel to a desirable value. Bainite and martensite can be made by these processes and are very desirable materials for certain high strength applications as they generally have Rockwell C hardness of from about 20 and up. The increased hardness correlates to a comparable increase in tensile strength.

Typical advanced high strength steels have generally included bainitic and/or martensitic phases. Bainite is generally acicular steel structured of a combination of ferrite and carbide that exhibits considerable toughness while combining high strength with high ductility. Historically, although bainite has been commercially produced by austempering through lengthy austemper thermal cycling, bainite is a very desirable product. One practical advantage of bainitic steels is that relatively high strength levels can be obtained together with adequate ductility without further heat treatment, after the bainite transformation has taken place. Such steels, when made as a low carbon alloy, are readily weldable. Bainite has been found to be temper resistant and can form in the heat-affected zone adjacent to the weld metal, thereby reducing the incidence of cracking and providing for a less brittle weld seam. Furthermore, these steels having a lower carbon content tend to improve the weldability and reduce stresses arising from transformation. When austempered bainite is formed in medium and high carbon steels, weldability is reduced due to the higher carbon equivalence content.

The other conventional high strength steel constituent, martensite, is another acicular microstructure made of a hard, supersaturated solid solution of carbon in a body-centered tetragonal lattice of iron. It is generally a metastable transitional structure formed during a phase transformation called a martensitic transformation or shear transformation in which larger workpieces of austenized steel may be quenched to a temperature within the martensite transformation range and held at that temperature to attain equalized temperature throughout before cooling to room temperature. Martensite in thinner sections is often quenched in water. Since chemical processes accelerate at higher temperatures, martensite is easily tempered to a much lower strength by the application of heat. In some alloys, this effect is reduced by adding elements such as tungsten that interfere with cementite nucleation, but, more often than not, the phenomenon is exploited instead. Since quenching can be difficult to control, most steels are quenched to produce an overabundance of martensite, and then tempered to gradually reduce its strength until the right hardness/ductility structure for the intended application is achieved.

# SUMMARY OF THE INVENTION

In accordance with the present invention, low grade ferrous alloys in strips, sheets, bars, plates, wires, tubes, profiles, workpieces and the like are converted into multi-phase high strength steels with a minimum of cost, time and effort. Dual and more complex phase materials are achievable by practicing the present invention. Due to the short duration of the heating of the iron based alloy from the upper austenization temperature to the peak selected temperature, and the ability to rapidly achieve a partially bainitic microstructure, this method has become known as “Flash Bainite Processing”.

There are provided methods and apparatuses for extremely rapid micro-treating of low carbon iron-based alloys and articles made from and containing those alloys. The iron-based, or ferrous, alloys/articles start out having a first microstructure, containing carbides, prior to the micro-treating, and are converted into a second complex microstructure by rapid heating and rapid cooling into high strength steels on at least a portion of the alloy/article.

A method for rapidly micro-treating an iron-based alloy is disclosed for forming at least one phase of a high strength alloy, where the method comprises the steps of providing an iron-based alloy having a first micro-structure with an austenite conversion temperature. This first microstructure is capable of being transformed to an iron-based alloy having a second micro-structure including the above mentioned phases by rapidly heating at an extremely high rate, such as 300 °F/sec to 5000 °F/sec from below the austenitic conversion temperature to a selected temperature above the austenitic conversion temperature. This second microstructure is known to be heterogeneous due to the lack of time allowed above the upper austenization temperature for homogenization of alloying elements in the carbide containing iron based alloy. The traditional austenitic conversion temperatures are elevated for given alloys due to the short duration of the thermal cycle initiated by the rapid heating. This elevated austenization temperature is in part due to an averaging of austenization temperatures of the multiple alloy concentrations present within the steel in the individual austenite grains. Because different carbon concentrations have different upper austenization temperatures, the carbon concentration present in the majority of the prior austenite grains will have the greatest influence on the austenization temperature. An iron based alloy comprised primarily of ferrite, which contains very low carbon concentration, would have a relatively high upper austenization temperature closest to that of ferrite in pure iron.

This heating step involves nearly immediate heating of the iron-based alloy to a selected temperature above its austenite conversion temperature starting from a temperature below the upper austenization temperature. Then, the alloy is substantially immediately quenched once the peak selected temperature is reached, without any substantial holding period at the elevated temperature, most often at an extremely fast rate, i.e. 300°F/sec to 5,000°F/sec on at least a portion of the iron-based alloy in a quenching unit adjacent the heating unit. In some instances, slower or interrupted quenching is desired to enact continuous cooling transformation or time temperature transformation of the carbide containing iron based alloy. This procedure forms at least one phase of a high strength alloy in a desired area, depending upon where the treatment was performed. Extremely rapid quenching will form at least one phase of a high strength alloy, as described more fully herein below.

Quenching may be accomplished nearly instantaneously by various methods and apparatuses, including water baths, water sprays, chilled forming dies, air knives, open air convection, final operation chilled progressive dies, final stage chilled line dies, chilled roll forming dies, and quenching hydroforms among others. Slower or interrupted cooling is possible through the use of molten salts, oils, steam, heated gaseous solutions, chilled quenching rollers, and many other means known to those skilled in the art. Regardless of quenching method, initiation of quenching occurring substantially immediately after reaching the peak selected heating temperature is required to limit carbon migration, carbide dissolution, and alloy homogenization.

## BRIEF DESCRIPTION OF THE DRAWINGS

For a further understanding of the nature and advantages of the expected scope and various embodiments of the present invention, reference shall be made to the following detailed description, and when taken in conjunction with the accompanying drawings, in which like parts are given the same reference numerals, and wherein;

FIG 1A is a FEGSEM micrograph of bainite processed in accordance with the present invention;

FIG 1B is a FEGSEM micrograph of bainite processed in accordance with the present invention;

FIG 2A is a graph of typical temperature measurements at the inside wall of the processed tube;

FIG 2B is a cooling cycle time/temperature graph of the process in accordance with the present invention;

FIG 2C is the heating and cooling cycle simulating austenite grain development over time

FIG 3 is a transform analysis graph of temperature versus differential of temperature;

FIG 4A is a mechanical heterogeneity analysis of a raw material;

FIG 4B is a similar analysis of the flash processed material;

FIG 5 is a graph of elongation versus peak heating temperature;

FIG 6 is a stress versus strain graph of various examples of material;

FIG 7A is optical and SEM images of steel before and after Flash Bainite Processing;

FIG 7B is a transmission electron microscopy image of Flash Bainite Processed steel;

FIG 8 shows initial boundary conditions for simulation;

FIG 9A, 9B, 9C, and 9D are of cementite dissolution modeling at various heating rates;

FIG 10 is of the concentration gradients [C and Cr] at room temperature and at 1000°C; and

FIG 11 is a continuous cooling diagram of Fe-0.03C-0.3Cr wt % iron based alloy.

## DETAILED DESCRIPTION OF THE DRAWINGS

In accordance with the present invention, a new method of metal treatment is disclosed which results in transforming a low grade iron based alloy into a high strength steel with extremely rapidly heating of the metal followed immediately by rapidly quenching the material. The resulting steel is a heterogeneous composition of at least martensite, bainite, ferrite, and the other structures discussed in more detail hereinbelow.

In this regard, our experiments have shown that rapid quenching closely following rapid austenization has been shown to develop a dual hardness microstructure as illustrated in the attached drawings. Experimentation has shown that flash processing of materials with an AISI 4130 designation yields multiple hardness peaks of approximately 525 and 625 Vickers hardness. The combination of hardnesses has been verified by single sensor differential thermal analysis showing that two temperature ranges have transformation occurring during the single quenching operation. In AISI 4130, transformation occurs from 1202°F to 1022°F and again from 860°F to 680°F during water quenching.

While the phenomena for this double cooling transformation is not fully understood, multiple theories are present. The first is that the steel is rapidly heated and carbon leveling has not occurred. As such, multiple carbon and alloy concentrations exist at the individual grain size scale. The former ferritic regions contain minimal carbon while the former pearlitic and carbide containing regions have an abundance. The carbon enriched areas transform to martensite while carbon depleted areas transform to bainite. Prior carbides are often present nearly intact after Flash Bainite Processing has been completed

Another possible theory is that the upper transformation temperature occurs when austenite transforms to nano-scale platelets. The second transformation occurrence during cooling is the coalescing of the platelets into larger plates.

This double transformation notion leads us to another aspect of this invention. Since a double transformation is occurring, one could allow the first transformation to occur but halt the second. For example, rapidly heat the iron based alloy to a selected peak temperature, a few seconds later, quench the iron alloy in a quenching medium that is below the first transformation finish temperature but above the second transformation start temperature. The material would complete the first transformation but delay the second transformation.

This may cause for example, the first stage of Flash Bainite to form, for example, just the nano non-coalesced bainite phase, but then leave a significant amount of another phase, possibly retained austenite, or some other austenite daughter product. The material could then be brought down from the temperature between the first transformation finish temperature (i.e. 1022F) and the second transformation start temperature (i.e. 860°F). Note that the temperatures provided are from experimentation based on heterogeneity of 4130 chemistry steel. For other alloys of steel with differing chemistries, the first and second transformation start and finish temperature will differ and are well known to those skilled in the art.

Different alloys of steel are known to have different optimal peak heating temperatures to attain most ductile results. Lesser carbon steels will maintain highest ductility when the peak heating temperature is higher while steels with more carbon will maintain highest ductility when the peak heating temperatures are not as high. In the case of 1008 plain carbon steel at 0.035%wt carbon, A50 elongation of sheet metal is optimized at 8 to 10% when the peak heating temperature that the steel reaches is 2225-2275°F. In the case of 4140 chrome moly steel, at 0.41% wt carbon, A50 elongation of sheet metal is optimized when the peak heating temperature that the steel reaches is 1925-1975°F. For steels of carbon contents in between the two above examples, experimentation has found a nearly linear relationship of optimal peak temperature exists such that a 0.30%wt carbon steel attains best results when heated to 1950-2000°F. A steel with 0.20%wt carbon attains best results when heated to 2025-2075°F. A steel with 0.10%wt carbon attains best results when heated to 2125-2175°F. Through linear interpolation, preferred ductility peak heating temperatures can be determined. As such, a 0.15%wt carbon steel would thus have a preferred peak heating temperature of 2075F-2125°F. These optimal peak temperatures apply when working with steels that are in the pearlite/ferrite condition or in the spheroidized state. Steels that have been cold rolled and not subsequently, fully normalized/annealed, thus remaining work hardened, have stored energy residing in them due to the stresses imparted to them. In such cases the optimal peak heating temperatures can be reduced by as much as 100-200°F from the above mentioned prescribed peak heating temperature.

The addition of alloying elements known to be strong carbide formers has been found to be beneficial to the final microstructure's mechanical properties. Such alloying elements include, but are not limited to, chromium, molybdenum, vanadium, silicon, aluminum, boron, tungsten, and titanium. Two plates of 1020 based plain carbon were Flash Bainite processed. The only significant difference in the steel chemistry was that one had 0.33% weight chromium added. The steels were rapidly heated to 2050°F in a few seconds. Upon reaching peak 2050F, the steels were quenched in water spray to room temperature. The modified 1020 with 0.33%wt chromium tested at 1500-1600MPa at 9 to 10% A50 elongation. The plain carbon 1020 steel (without chromium) tested at 1350-1450MPa at 7.5 to 8.5% A50 elongation. Given that the only experimental difference was the 0.33% weight chromium in the modified-1020 chemistry, the improvement in mechanical properties can be attributed to the presence of the chromium and molybdenum carbides due to the chromium addition to the 1020 alloy. Similarly 1050 plain carbon steels were compared to 6150 chrome vanadium alloyed steel. After Flash Processing to

1900°F, the 6150 steel had approximately 1 to 2% percentage points higher elongation than the plain carbon 1050 did. The strength of the Flash Processed 6150 was also 100MPa higher yield and 150MPa higher ultimate tensile strength than the Flash Processed 1050. It has been found typical that commercially available plain carbon steels have 7.5 to 9.5% total elongation once Flash Bainite processed. Steels containing carbide forming alloys trend in excess of 9-11% or more total elongation. Flash Bainite Processed 4140 steel resulted in 1600MPa yield strength, 2100MPa tensile strength and 10% total A50 elongation. Testing of 4130, when using a full 1/2" width A50 specimen at 1/4" thick has resulted in 11-12% total A50 elongation at 1500MPa yield and 1900MPa ultimate tensile strength.

It was also found that spheroidization of the prior microstructure was beneficial to enhancing the mechanical properties of the Flash Bainite processed steel. It is believed that spheroidization further limits carbon migration by organizing the carbon into spheres which are known to be the geometrically most efficient manner of volumetric storage with respect to surface area. By limiting carbon migration through speroidization, the percentage of bainite can be controlled. Other methods of developing texture in the steel to control prior austenite grain size and interaction with elemental migration has shown to be beneficial. For instance, in cases of 4130 steel, hot banded 4130 was found to have 10-15% lower ballistic resistance than 75% spheroidized 4130 against armor piercing and other small arms projectiles.

Before Flash Bainite Processing, the control of initial microstructure was needed to achieve these unique microstructures. The above-mentioned hypothesis was evaluated using computational thermodynamic and kinetic models. In this model, a system containing ferrite (a) and cementite (M3C) was considered. Assuming a linear heating rate of 1, 10 and 100Ks$^{-1}$, the austenite growth kinetics was calculated. The calculations show that, in case of Fe-C system, the rapid dissolution of $Fe_3C$ occurred at 10Ks$^{-I}$. In comparison, the dissolution rate of $M_3C$ (enriched in Cr) was sluggish even at I Ks$^{-1}$. The above results support the proposed mechanism for microstructure evolution during Flash Bainite Processing.

It is a first aspect of the present invention to provide an inexpensive, quick and easy way to produce a low, medium, or high carbon iron-based alloy containing an appreciable percentage of nano-sized platelet bainite while having some of the desirable mechanical properties of nano-sized laths of martensite. While other thermo-mechanical processing techniques require lengthy thermal processing to obtain a complex bainitic-martensitic microstructure, Flash Bainite Processing can do so with a single, rapid quenching operation which can take less than 10 seconds from above the lower austenitic temperature to below the lower martensitic temperature. Other longer duration methods explained herein can provide other desirable metallurgical results provided that the first quenching step to below the bainitic finish temperature occurs substantially immediately after reaching peak heating temperature.

It is a second aspect of the present invention to provide a method and apparatus for micro-treating low, medium, or high carbon iron-based alloys to contain a desirable quantity of flash bainite processed complex microstructural material with bainite and martensite interspersed within the same prior austenitic grains. The micro-treated low, medium, or high carbon iron-based alloy may have varying thicknesses for different applications and may be readily weldable while having high tensile strength, along with the ability to minimize material and reduce weight. One aspect of the present invention for the elevated quench interruption temperature is to use a quench medium at this temperature that could be molten salts, super heated gases, or heated oils, among others. This aspect causes the first iron based alloy transformation that is caused by molten salt yet the temperature is above the second transformation start temperature so that the second transformation is slowed by molten salt's temperature. After initially slowing, all other iron alloy transformations are intentionally occurring in molten salt through either continuous cooling transformation or time temperature transformation. From this temp, below 1022°F in the case of 4130 steel, the steel could be cooled in a manner in which the remaining austenite is brought down to ambient temperature with either minimal further transformation occurring or transformation to some other desirable austenite daughter phases.

Another aspect of this invention has to do with the heating and quenching apparatus. Other previously filed patent applications for apparatus employ single or multiple heating and quenching heads to cool the material. The present method employs a single heating unit to heat multiple pieces of material. For example, a rectangular induction coil could have material passing by it and heated both inside and outside of the coil. If the coil were appropriately sized, a rectangular tube could be heated inside the coil while other pieces, such as pieces of bar stock could be heated on the outside of the induction heating coil simultaneously.

Another aspect of this invention has to do with heating interrupted pieces of material. For example, a strip could have multiple cutouts removed from its shape. These pieces could be manufactured in the soft state and then Flash Bainite Processed to their final hardness state. Sometimes, when such a strip is heated, the edges near the cutouts will concentrate heat and melt the corners. The present aspect of this invention will allow plugs of similar material to be held in place of the interruptions to absorb the heat. This will thus prevent the melted corners. Even when plugs are not employed, since the heating and quenching is so rapid, the corners of the shaped iron based alloy are not melted.

The concept of rapid heating, quenching, reheating, and quenching was discussed in my previous patent application filed on June 16, 2008, which is incorporated herein by reference, referring to an iron based alloy component. The method could be applied as well to a rolling strip of metal. A similar thermal technique known as quench and partitioning has been used. Quench and partitioning technology austenizes steel over many minutes to level carbon, dissolve carbides, and homogenize alloy distribution in the steel. quench and partitioning then quenches to below the martensite start temperature, either holds at that sub-Ms temperature or reheats just above the martensitic start temperature and then quenches to ambient. The reason for such a hold is the partitioning of carbon to attain a desirable quantity of retained austenite in the final product. Another aspect of Quench and Partitioning technology austenizes steel over many minutes, quenches to below the martensite start temperature, reheats above martensitic start temperature and bainite finish temperature and then quenches to ambient after a desired amount of transformation has occurred. The present innovation is a new technique of Quench/Partition technology. For the Flash quench and partitioning, all aspects are the same as conventional quench and partitioning with the exception of employing the rapidity of the Flash heating cycle. As soon as the peak austenization temperature is reached, rapidly heating at an extremely high rate, such as 300 °F/sec to 5000 °F/sec, quenching is initiated. The novelty over traditional quench and partitioning is that a heterogeneous, non-homogenized, austenized steel is being quenched. As before with an iron based alloy part, strip, or section, the heater will rapidly austenize the steel, quench the material to enact a transformation above the martensitic finish temperature, hold or reheat with the second heater, or heated quenching medium, to a subaustenitic temperature to stabilize or transform the existing microstructure, and then quench to room temp with the second quench. Such methods are known to provide desirable quantities of retained austenite.

The resulting high strength steel may include at least one portion of the resulting high strength material made of coalesced bainite, upper bainite, lower bainite, martensite, ferrite, retained austenite, pearlite, ferrite, acicular ferrite, and/or dual or complex phase combinations thereof, depending on the placement of the treatments described and claimed herein below.

Complex phase materials can be made, such as martensite and bainite located next to ferrite and pearlite. These highly desired complex phase materials are achievable in the same workpiece by quenching only in various patterns so that a pattern of high strength steel can be manufactured in desired areas across the surface and/or cross section of an article after it has been heated. By only quenching certain areas, various material phases are possible in various locations where desired.

Looking first with combined reference to Figures 1A and 1B, there can be seen that the flash bainite includes a bi-modal distribution of bainitic platelets or plates which exhibit highly desirable combinations of strength, ductility and toughness. The flash processing of the present invention can create almost distortion free flat sheets, bars, plates and straight tubing. As can be seen in these figures, the microstructure produces a fine grain structure within the bi-modal distribution of microstructures which yields the surprising strength and ductility.

With reference to FIG 2A, a graph is shown charting temperature in degrees C. versus time in seconds to illustrate the cooling cycle as processed at the inside wall of one of the test tubes. Typical temperature measurements of this inside wall are showing that there is a very low temperature-time history ratio. In this particular example, utilizing AISI 4130 sheet metal tubing has a lower temperature to time history ratio.

Looking now to FIG 2B, there is shown a graph of temperature versus time showing the flash processing temperature to time history ratio in addition to the conventional continuous annealing temperature to time history. Clearly, the temperature to time history ratio for the continuous annealing is much greater than that ratio for the flash processing.

FIG 2C illustrates the austenite growth during the Flash Bainite Processing thermal cycle. Region I shows prior austenite grains. Region II shows austenite growth. Region III shows heterogeneous austenite grains. Region IV shows a complex mixture of bainite and martensite within the same prior austenite grains.

FIG 3 illustrates an analysis of temperature in degrees centigrade versus the change in temperature also in degrees centigrade. This analysis shows transformations at between 1022 and 1202 degrees F. and 680 to 860 degrees F during cooling. This analysis suggests that we have two different transformation conditions leading to very localized microstructural heterogeneity, although experiencing homogeneity on a macro scale.

Looking now to Figures 4A and 4B collectively, there can be seen two mechanical heterogeneity analyses showing that there are two distinct regions of microstructure between the raw material and the flash processed material in accordance with the present invention. These findings are consistent with the previous analyses showing two separate transformations during the flash processing procedure. Both FIG A and FIG B are graphs of normalized frequencies versus hardness, which illustrate the distribution of hardness. FIG 4A shows the base metal hardness distribution as very slight, while the material that has proceeded through flash processing illustrates both a high hardness zone as well as a low hardness zone over a broader distribution of hardness.

Looking now to FIG 5, yet another aspect of the invention is illustrated with fully strengthened with AISI 1010 material that has been flash processed. This graph shows elongation versus peak flash temperatures, to show that the highest elongation occurs at the peak flash temperature, 1180 degrees C. having an A50 elongation of 7.9%. At a peak flash temperature of 1010 degrees C., the elongation percentage is 5.6. Temperatures higher than 1180 C. have lower elongation than 7.9%. Optimum elongation is found at medium to larger grain sizes which is counter-intuitive to the thought of grain refinement. The chemistry of this material in percent by weight is 0.10 C, 0.31 Mn, less than 0.01 Si, sulfur, phosphorus, and 99.41 iron.

Looking at FIG 6, which is a graph of tensile strength in KSI versus tensile strain in percentage. With an example of Flash Bainite Processed AISI 1020 modified to include 0.32%wt chromium after tempering to various temperatures in a range from 400 to 700 degrees C., 8 examples are shown with varying widths in inches. This experiment shows that even after 300 seconds of tempering at 932 degrees F., flash processed AISI 1020+Cr will retain 79% of its "as quenched" tensile strength. Furthermore, the elongation does not drop to + or – 5% with less than 5 seconds of tempering.

In FIG 7A, microstructures of both initial (ferrite and carbides) and final flash processed (lath morphology and carbides) samples are provided. In order to validate the mechanism and observed microstructure from a theoretical standpoint, diffusion controlled growth modelling was performed. In FIG. 7A are microstructure images from optical and backscatter electron imaging before and after flash processing. The rectangles mark the location of the scanning electron microscopy images. In FIG 7B, transmission electron microscopy revealed bainitic sheaves growing from a prior austenite grain boundary that confirmed the hypothesis above.

## RE-AUSTENIZATION KINETIC MODELING

DICTRA software, commercially available from Thermo-Calc Software, Inc. of McMurray, PA was used to simulate re-austenization kinetics during rapid heating conditions. The software predicts the interface velocity during phase transformation using critically evaluated thermo-dynamic and kinetic data.

Two conditions were used to evaluate the re-austenization conditions. In the first condition, the dissolution of cementite ($Fe_3C$) in a Fe-C system was considered.

In the second condition, the dissolution of Cr-enriched cementite ($M_3C$) is considered in a Fe-C-Cr system. The initial compositions of the ferrite and cementite were calculated at 1292°F (spheroidization temperature) based on bulk Cr and C concentration (0.3 wt.%C and 0.88 wt.%Cr) for a typical 4130 steel. Boundary conditions for the simulations are shown schematically in FIG. 8. The simulations were performed for heating from 1292°F to 1832°F at rates of 1, 10, and $100°Ks^{-1}$. Austenite was allowed to form at the ($\alpha/M_3C$) interface and grow into both cementite and ferrite.

### Dissolution Kinetics of $Fe_3C$:

The first two simulations, with heating rates of 1 and 10 $Ks^{-1}$, showed the full dissolution of cementite into a-ferrite, even before the nucleation and growth of austenite into the ferrite (FIG. 9A and 9B). When heated at a rate of 100 $Ks^{-1}$, the cementite does not have enough time to fully dissolve into ferrite (FIG. 9C). As result, the austenite forms at the cementite-austenite interface and grows into both the cementite and ferrite. Interestingly, even in this condition, the cementite is fully dissolved well before the ferrite is consumed by the austenite. These situations allow for more time for complete carbon homogenization of the austenite.

**Dissolution Kinetics of $M_3C$:**

Similar DICTRA simulations were performed in a Fe-Cr-C system. In these calculations, sluggish dissolution was seen for all heating rates including 1 $Ks^{-1}$. Similar sluggish dissolution with enriched-Cr has also been reported by those skilled in the art. Details of the results from $1Ks^{-1}$ are presented in FIG 9D. FIG 9D shows minimal dissolution of the cementite and nucleation of austenite at the ferrite cementite interface. However, even after reaching 1000°C, the dissolution of cementite is incomplete. The concentration gradients [C and Cr] at room temperature and at 1000°C are compared in FIG. 10. As the temperature is increased slowly, austenite consumes the ferrite slowly. At these conditions, a large peak in Cr concentration develops at the interface and within the newly formed austenite. When analyzing the carbon concentration profile, it is clear that carbon diffusion is indeed controlled by the Cr diffusion and interface. This would give rise to a situation with low carbon austenite potentially Cr-enriched austenite.

During an intermediate step during flash processing, in accordance with this invention, carbon migration and carbide dissolution yield many different co-existing compositions of steel. These co-existing compositions can exist due to localized heating gradients occurring at the atomic level throughout the bulk of the material being treated. These compositions are somewhat predictable by using alloys with from about 0.01 to about 0.05 wt. Percent of carbon, and from about 0.2 to about 0.5 wt. Percent chromium. For example, if using a steel such as 4140, which contains 0.40 wt percent carbon, and 0.90 wt. Percent chromium, it is controllable and likely that you can attain 0.02 wt. Percent carbon and 0.3 wt percent chromium in the high multiplicity of heterogeneous chemistry on the localized austenite grain scale. Further, it is anticipated, for example, that utilization of a 1002 steel with 0.02 wt % carbon and 0.3 wt% chromium would result in nearly 100% bainitic microstructure after prolonged austenitization and homogenization followed by rapid quenching at a rate of between 200°C/sec. and 3000°C/sec.

This combination of using 0.01 to 0.05 wt% carbon and 0.2 to 0.5 wt% chromium in a carbide containing iron based alloy precursor material and a quenching rate of between

200°C/sec. and 3000°C/sec. results in a heterogeneous microstructure which includes at least bainite. Quenching is preferably performed with water.

Using mass balance criteria, the composition of the bulk austenite, would contain between 0.01-0.03 wt.% C and 0.33 wt.% Cr after quenching with a cooling rate of 1000°C/sec. The resultant CCT diagram (Fig. 11) for this austenite is calculated using the model developed by Dr. Harry Bhadeshia at Cambridge University in the UK. When the calculations were overlaid with a cooling rate from flash processing (1000°C$s^{-1}$), the formation of bainite was shown to be possible. Meanwhile, bulk regions that have Cr and C enriched areas regions close to the carbide interface should be able to transform to martensite, since the $T_0$ temperature (temperature at which the free energy of ferrite of the same composition is equal to austenite) of this region is 730°C. These results support the feasibility of obtaining a mixed microstructure of bainite, martensite, and carbides during flash processing of spheroidized steels or other steels with carbides present. It is important to note, further evaluation of different initial microstructural conditions (i.e. pearlite, paraequilibrium cementite, and additional alloying elements) must be considered and the possibility of differing results exists practicing Flash Bainite Processing methodology.

## INDUSTRIAL APPLICABILITY

The present invention finds applicability in the metal treatment industry and finds particular utility in steel treatment applications for the processing and manufacture of high strength steels in high volume processing.

The foregoing description of a preferred aspect of the invention has been presented for purposes of illustration and description. It is not intended to be exhaustive or to limit the invention to the precise form disclosed. Obvious modifications or variations are possible in light of the above teachings with regards to the specific aspects. The aspect was chosen and described in order to best illustrate the principles of the invention and its practical applications to thereby enable one of ordinary skill in the art to best utilize the invention in various aspects and with various modifications as are suited to the particular use contemplated. It is intended that the scope of the invention be defined by the claims which are appended hereto.

# IN THE CLAIMS

What is claimed is:

1. A metal treatment process for transforming an carbide containing iron based alloy into a high strength steel, comprising:

rapidly heating the alloy to at least about 1000 degrees C. at a rate of 300 °F/sec to 5000 °F/sec from below the austenitic conversion temperature to a selected temperature above the austenitic conversion temperature,

substantially immediately quenching the alloy at a rate of from about 200 to 5,000 degrees F/s.,

whereby multiple transformations to multiple austenite daughter phases occur and at least a mixed microstructure results that may contain martensite, bainite and un-dissolved carbides, and may also contain complex steel microstructures including portions of bainite, coalesced bainite, acicular ferrite, retained austenite and/or martensite along with combinations thereof by micro-treating said iron based alloy.

2. A microstructure of carbide containing iron based alloy, comprising:
a mixed heterogeneous microstructure of a carbide containing iron based alloy having at least one austenite daughter phase containing at least one of martensite, bainite, un-dissolved carbides, coalesced bainite, acicular ferrite, retained austenite, or combinations thereof.

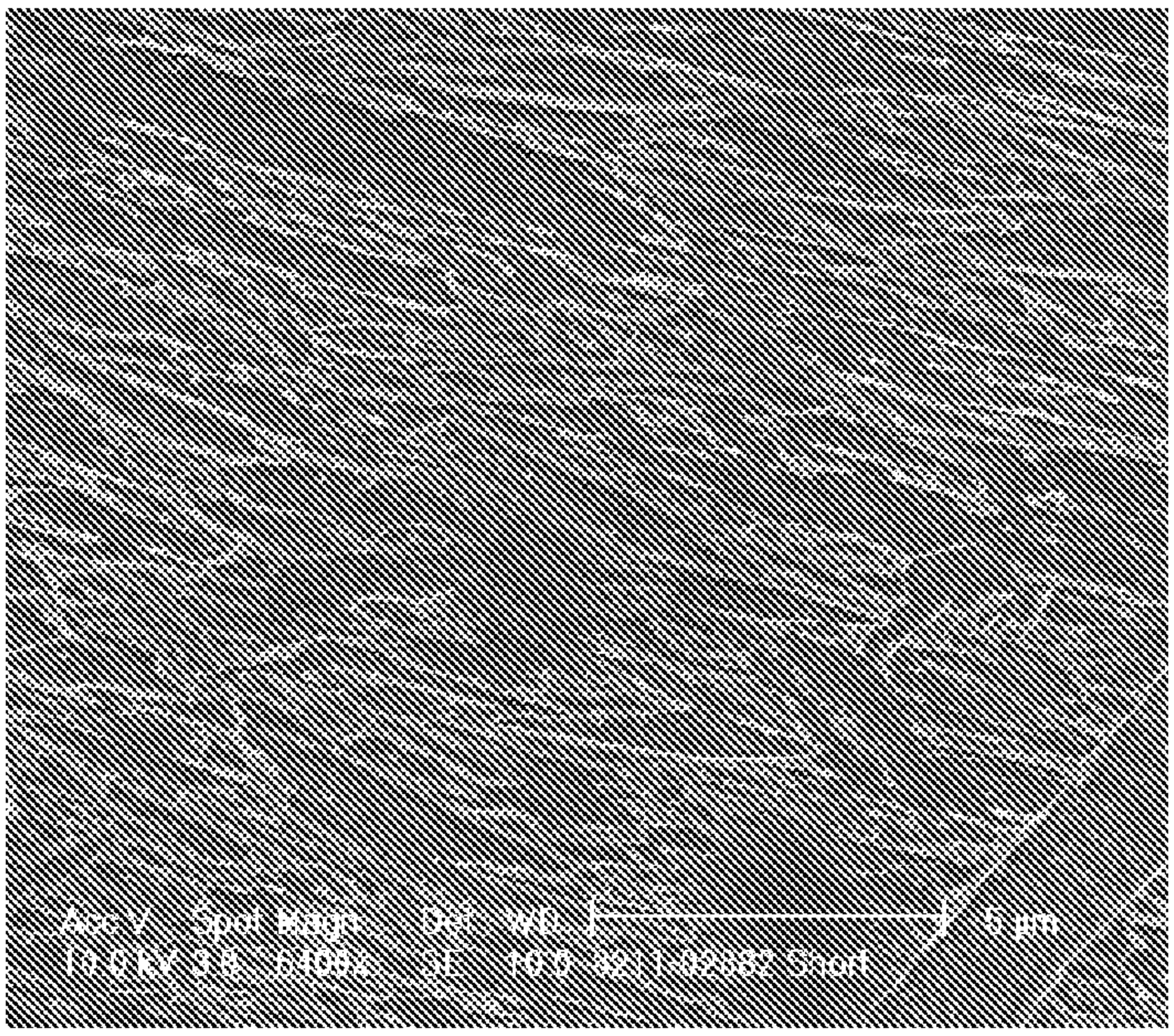

Acc.V Spot Magn Det WD
5 µm
10.0 kV 3.0 6400x SE 10.0 4211-02882 Short

FIG. 1A

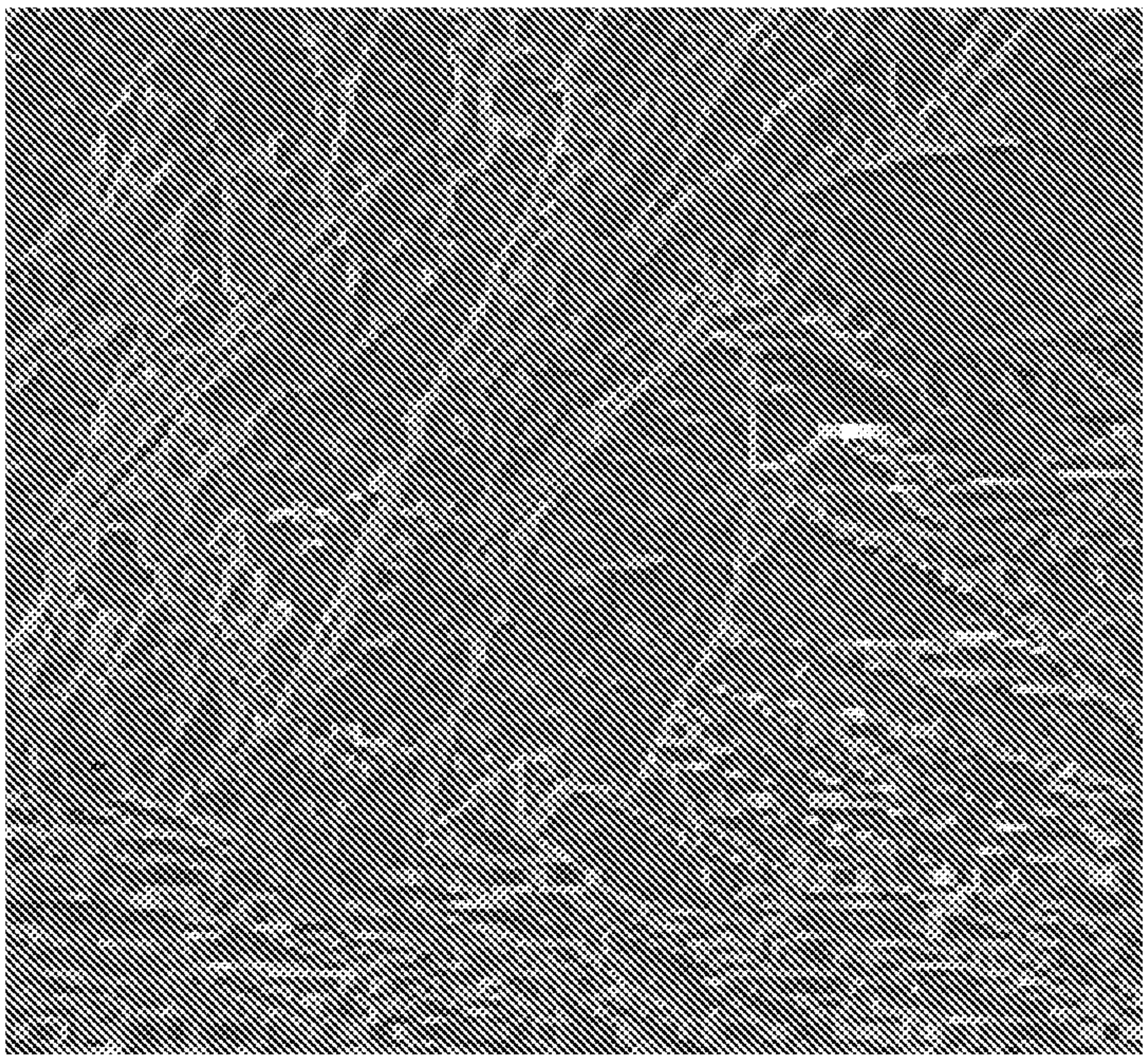


FIG. 1B

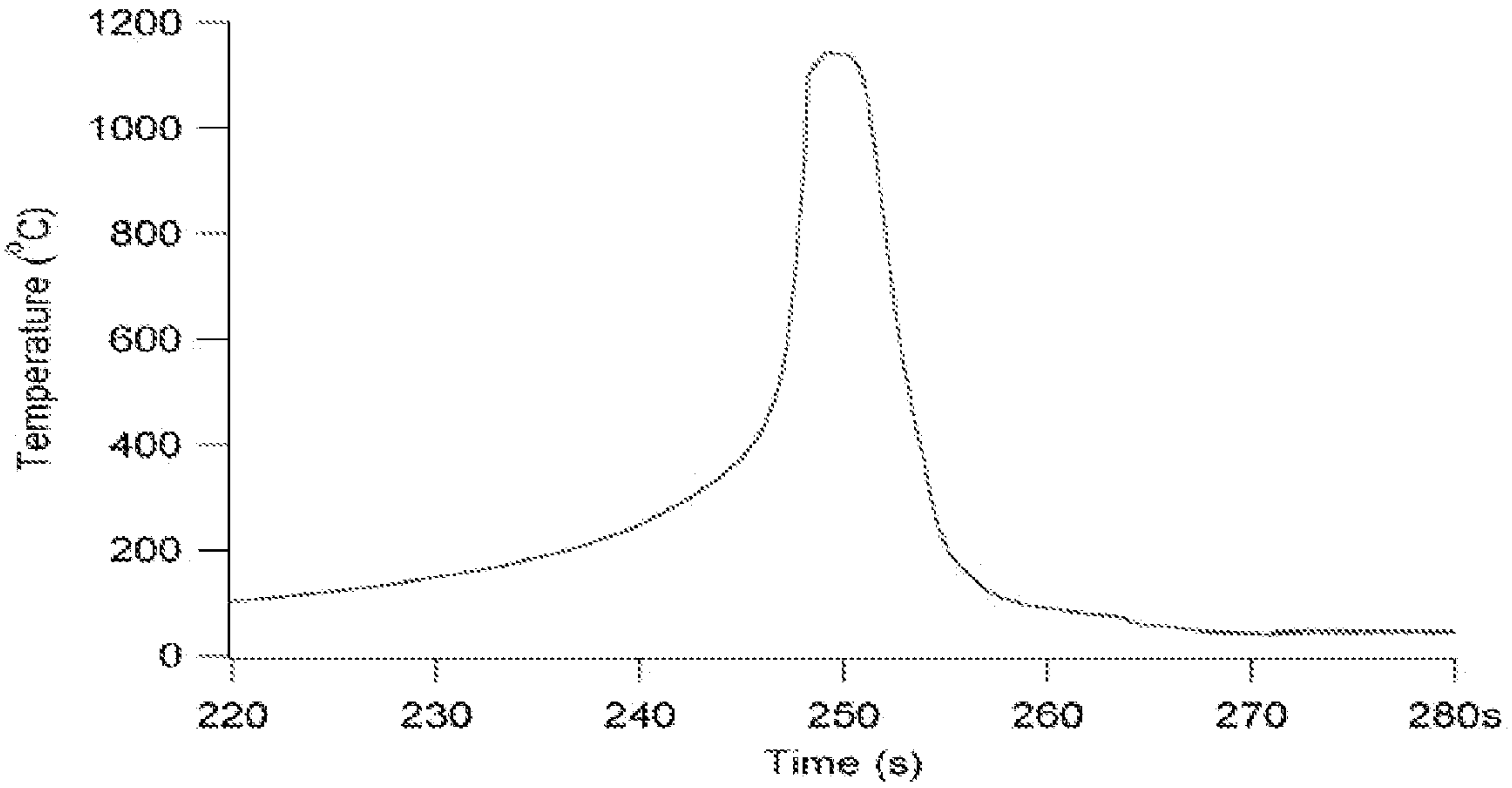

1200
1000
800
600
400
200
0
Temperature (°C)
220
230
240
250
260
270
280s
Time (s)

FIG. 2A

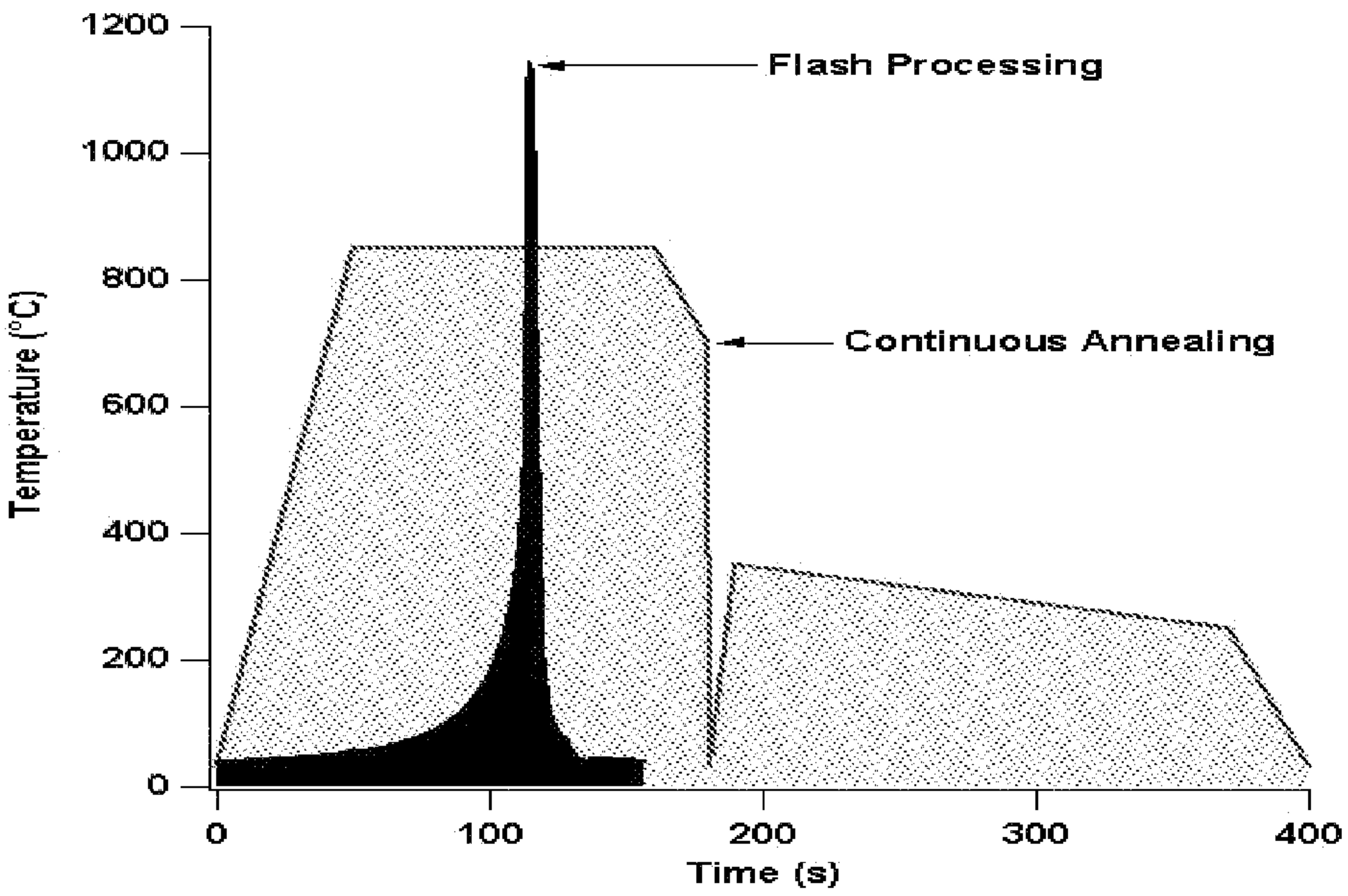

1200
1000
800
600
400
200
0
Temperature (°C)
Flash Processing
Continuous Annealing
0
100
200
300
400
Time (s)

FIG. 2B

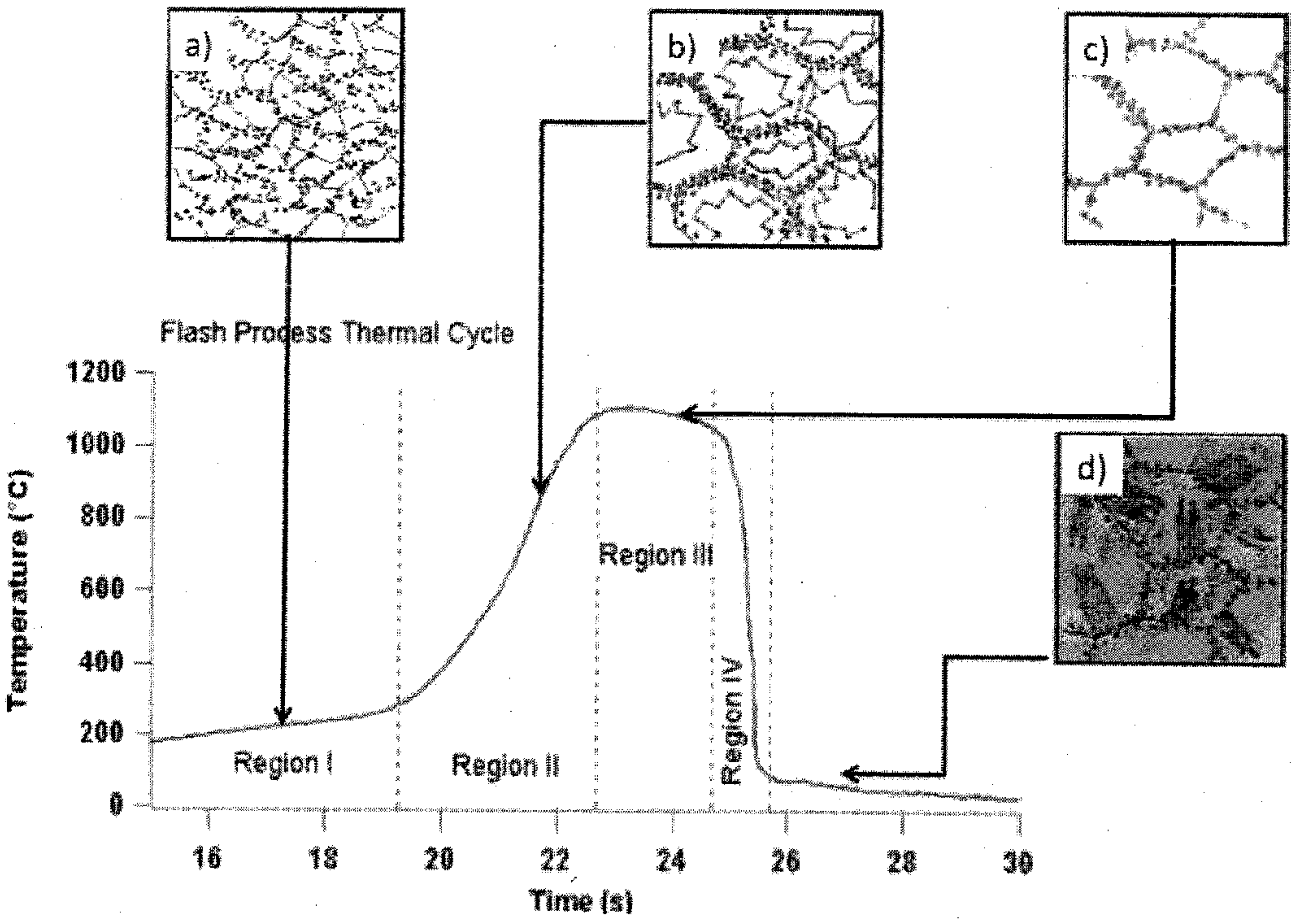

a)
b)
c)
d)
Flash Process Thermal Cycle
1200
1000
800
600
400
200
0
Temperature (°C)
Region I
Region II
Region III
Region IV
16
18
20
22
24
26
28
30
Time (s)

FIG. 2C

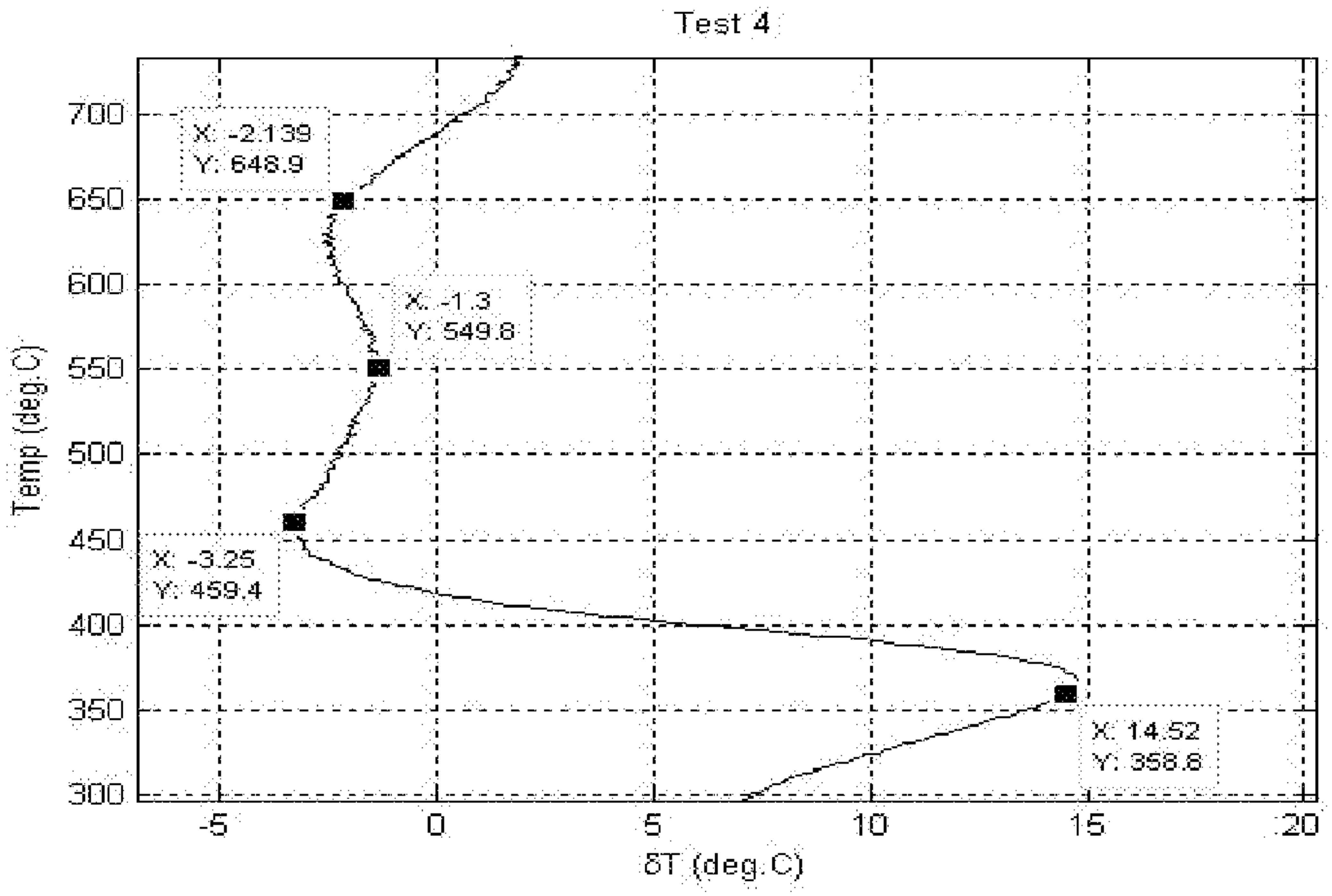

Test 4
700
650
600
550
500
450
400
350
300
Temp (deg.C)
X: -2.139
Y: 648.9
X: -1.3
Y: 549.8
X: -3.25
Y: 459.4
X: 14.52
Y: 358.8
-5
0
5
10
15
20
δT (deg.C)

FIG. 3

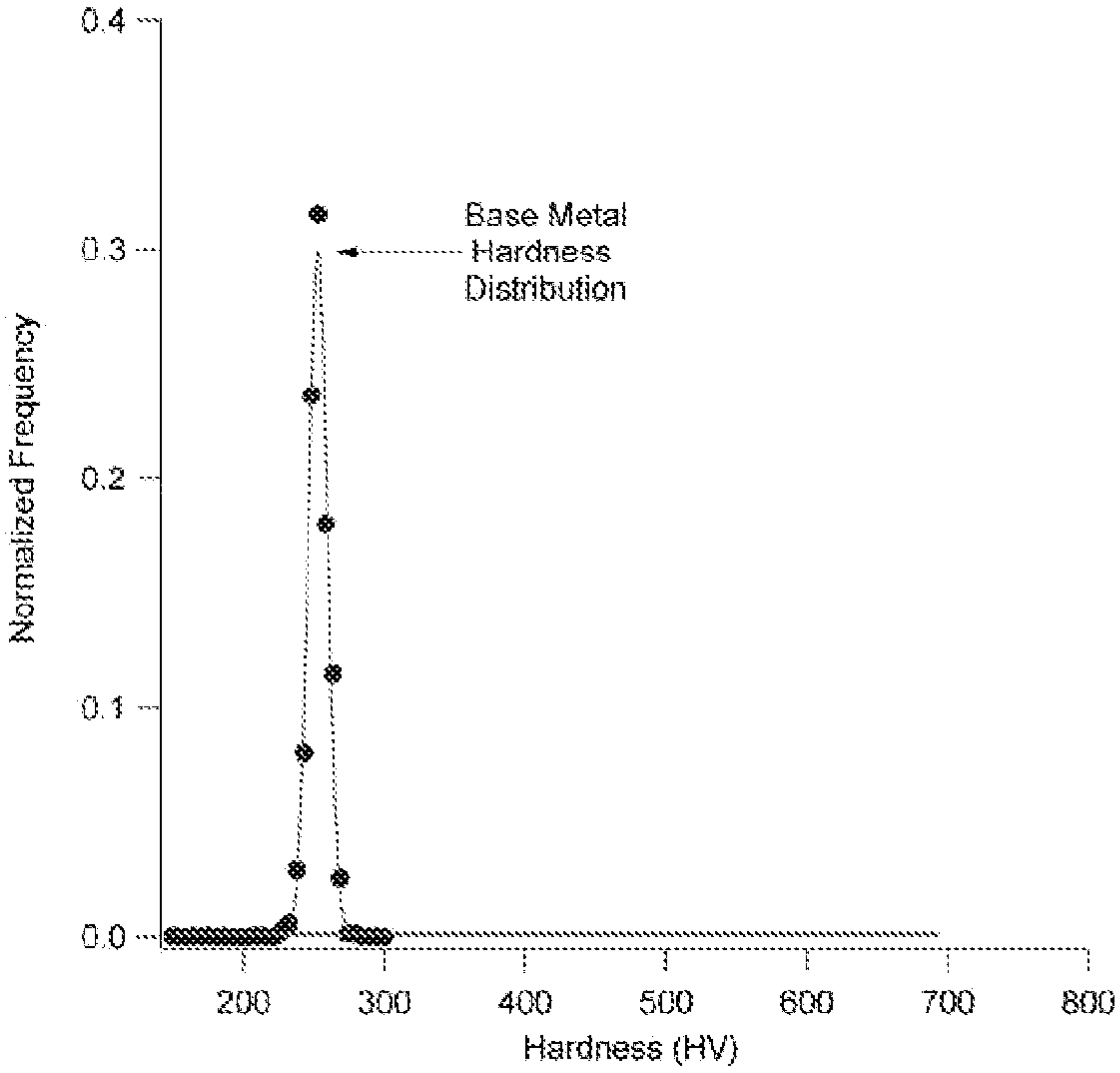

0.4
0.3
0.2
0.1
0.0
Normalized Frequency
Base Metal
Hardness
Distribution
200
300
400
500
600
700
800
Hardness (HV)

FIG. 4A

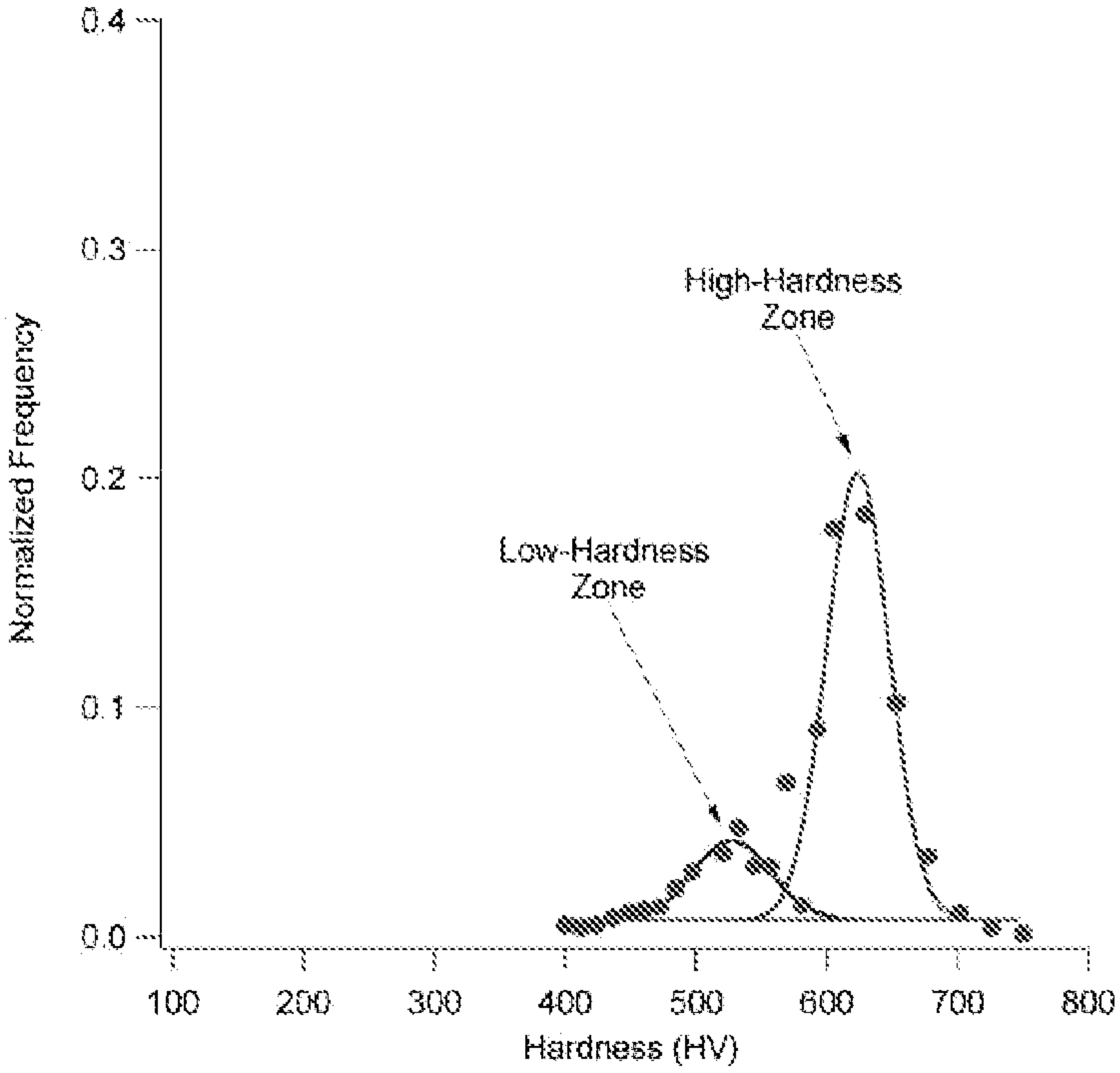

0.4
0.3
0.2
0.1
0.0
Normalized Frequency
High-Hardness
Zone
Low-Hardness
Zone
100
200
300
400
500
600
700
800
Hardness (HV)

FIG. 4B

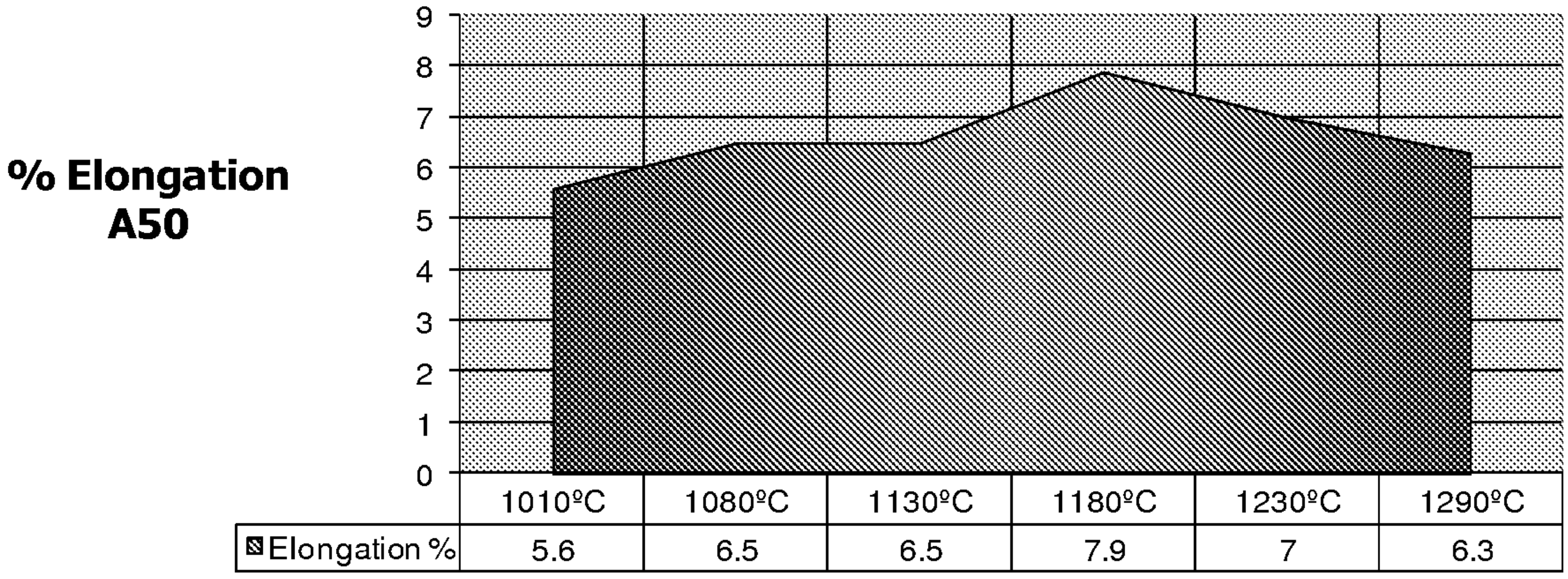


FIG. 5

| | Width (in) | Thickness (in) | .2% Offset Yield (ksi) | YPE (%) | Tensile Strength (ksi) | Elongation (%) | n-Value (10-20%) () | r-Value @ 15% () | rm () | Specimen Label |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 0.504 | 0.122 | 177.7 | ----- | 226.2 | 8.1 | ----- | ----- | 0.000 | AQA |
| 2 | 0.500 | 0.122 | 174.8 | ----- | 199.4 | 5.3 | ----- | ----- | 0.000 | 400A |
| 3 | 0.508 | 0.122 | 168.6 | ----- | 187.1 | 4.8 | ----- | ----- | 0.000 | 450B |
| 4 | 0.509 | 0.122 | 164.7 | ----- | 177.9 | 5.0 | ----- | ----- | 0.000 | 500A |
| 5 | 0.502 | 0.122 | 147.2 | ----- | 155.5 | 5.3 | ----- | ----- | 0.000 | 550B |
| 6 | 0.507 | 0.122 | 130.4 | ----- | 137.0 | 7.2 | ----- | ----- | 0.000 | 600B |
| 7 | 0.510 | 0.122 | 125.8 | ----- | 133.8 | 9.0 | ----- | ----- | 0.000 | 650B |
| 8 | 0.500 | 0.122 | 123.8 | 1.2 | 132.5 | 10.3 | ----- | ----- | 0.000 | 700B |

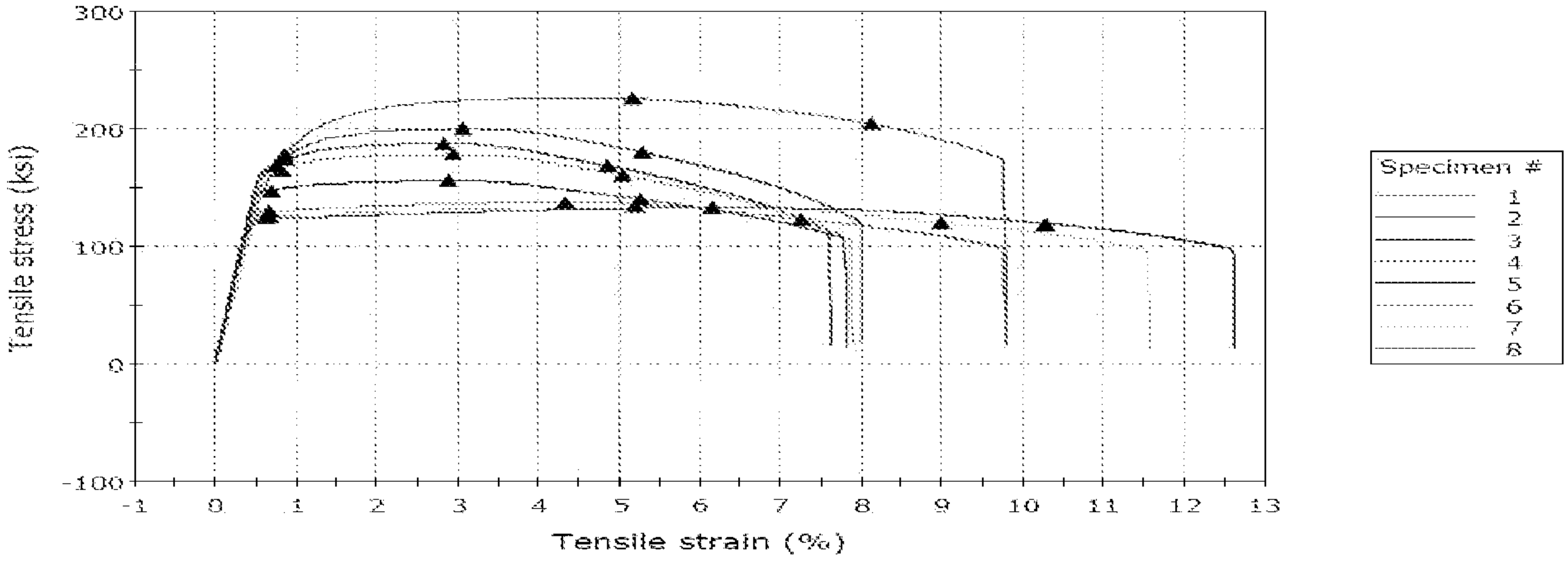
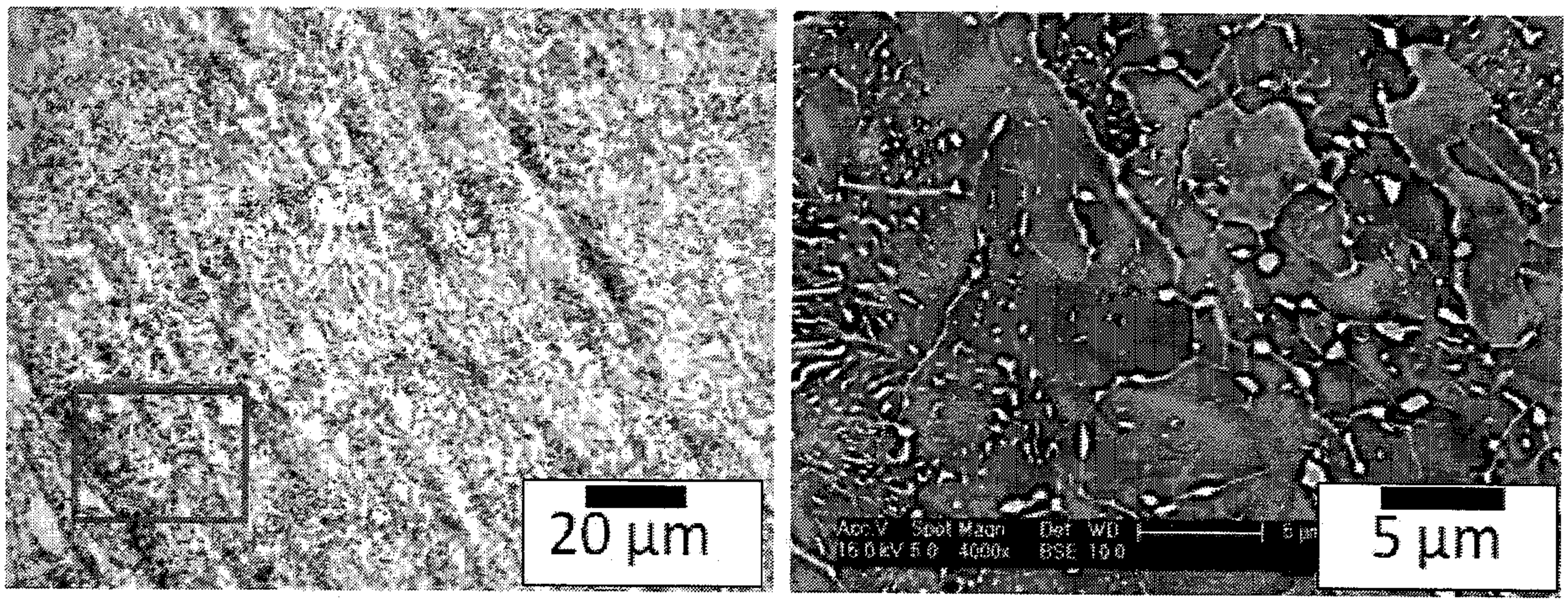


FIG. 6

Before Flash Processing



After Flash Processing

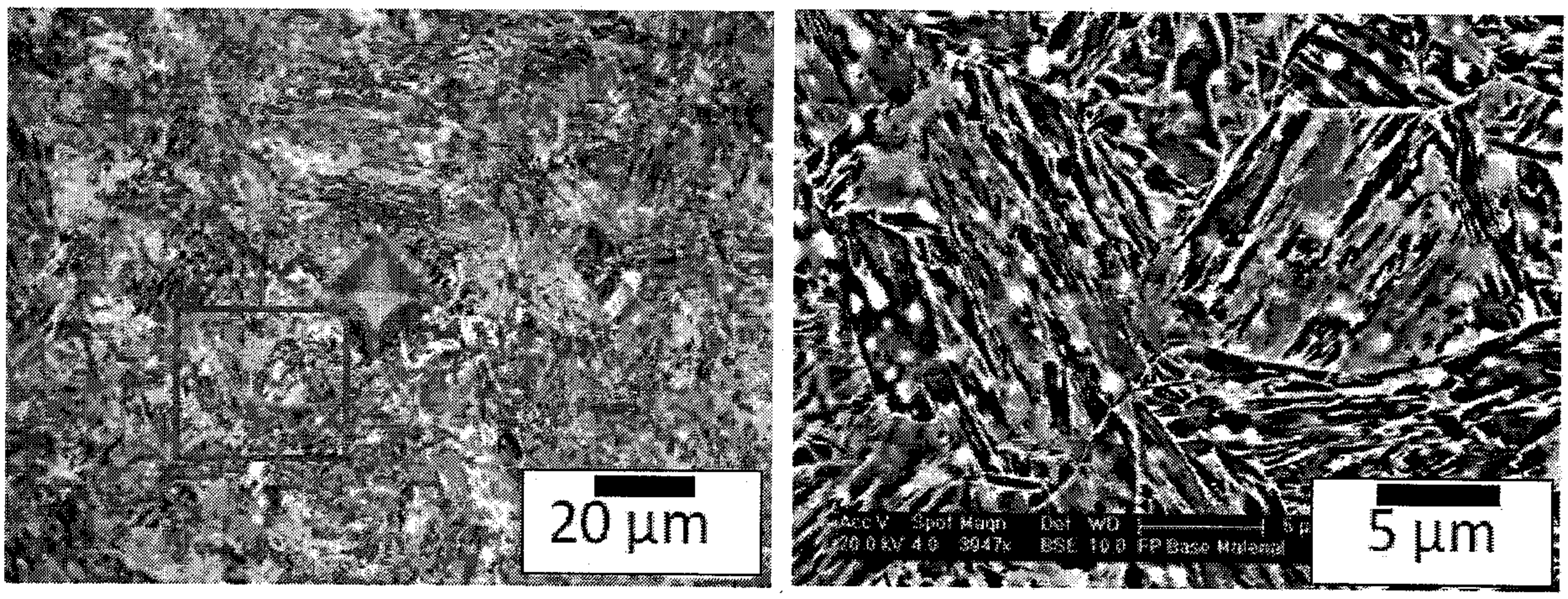


FIG. 7A

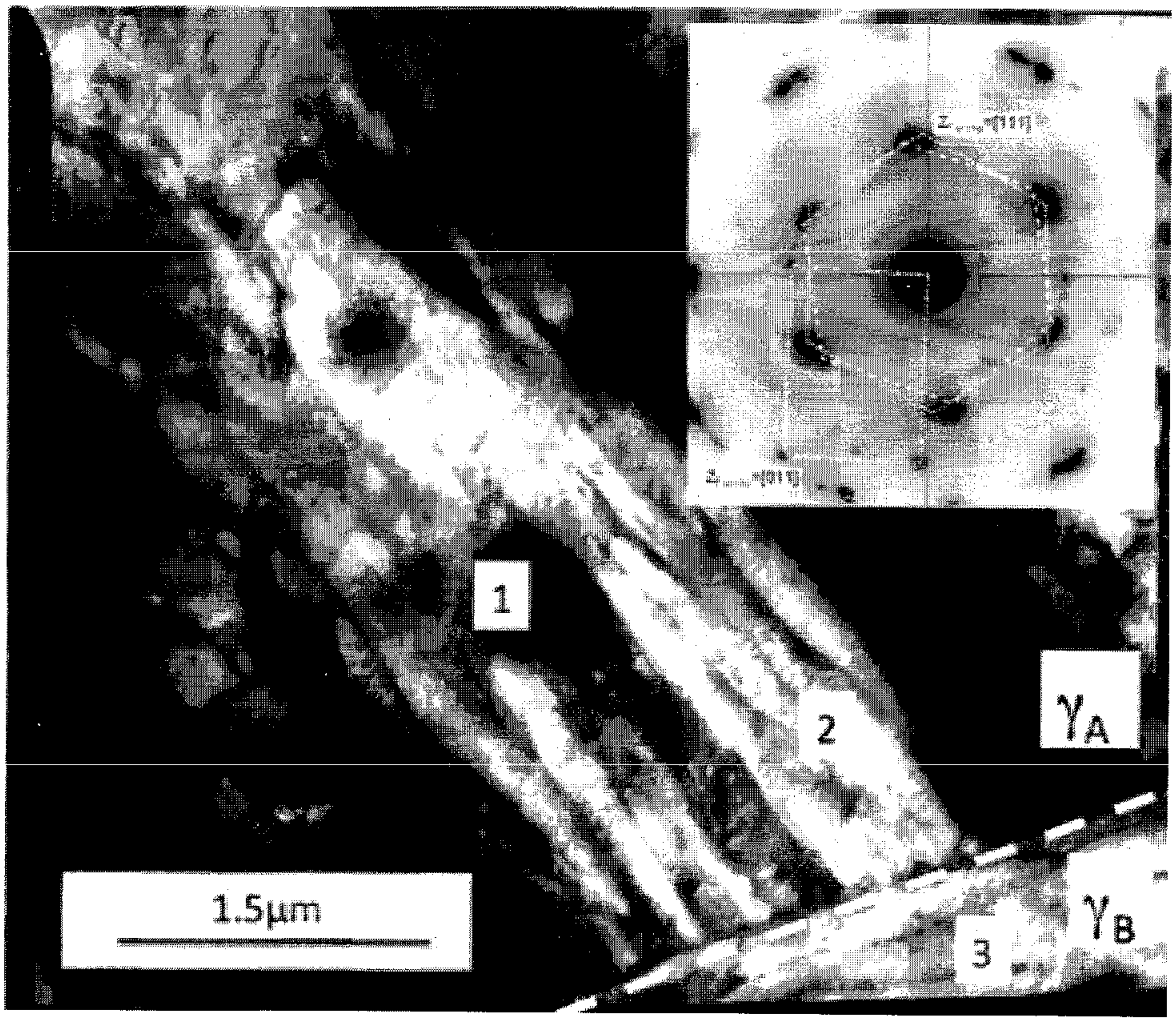

1
2
3
γA
γB
1.5μm

FIG. 7B

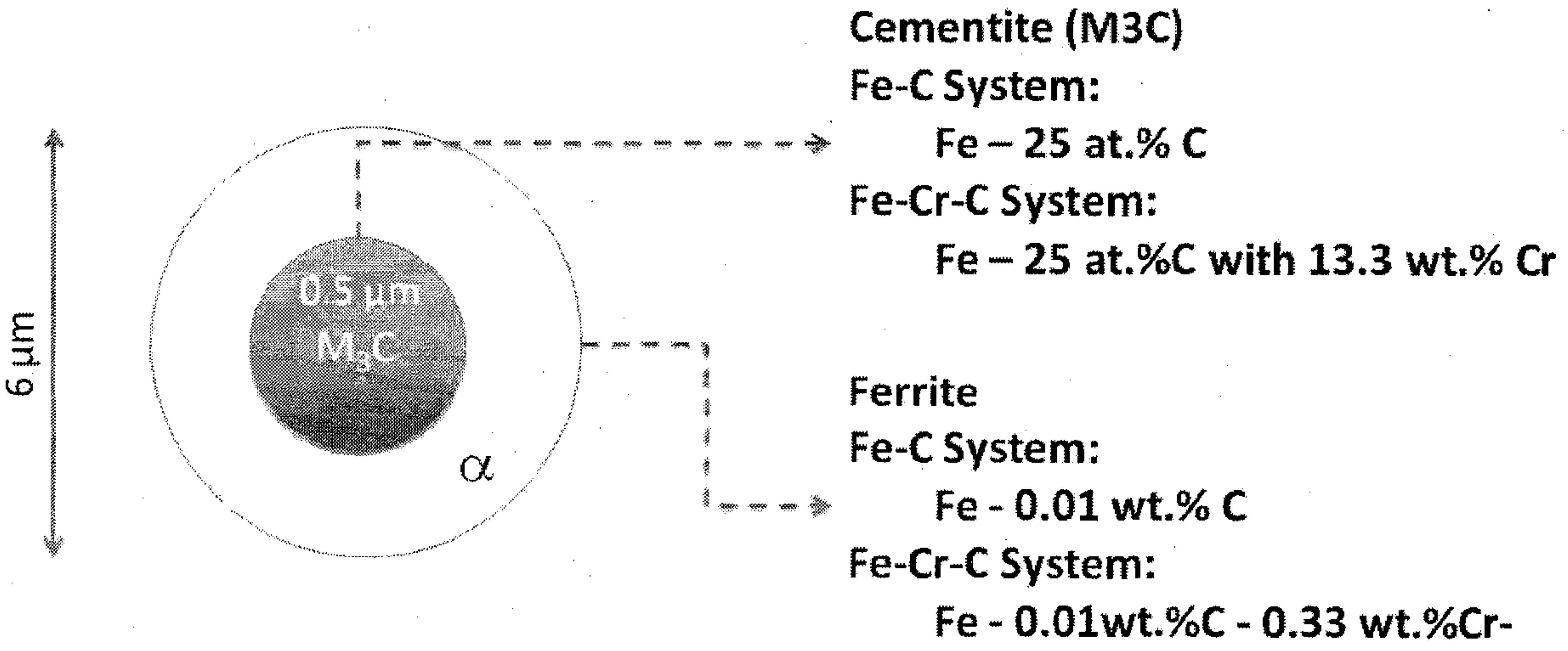

Cementite (M3C)
Fe-C System:
Fe – 25 at.% C
Fe-Cr-C System:
Fe – 25 at.%C with 13.3 wt.% Cr
0.5 μm
M3C
α
6 μm
Ferrite
Fe-C System:
Fe - 0.01 wt.% C
Fe-Cr-C System:
Fe - 0.01wt.%C - 0.33 wt.%Cr-

FIG. 8

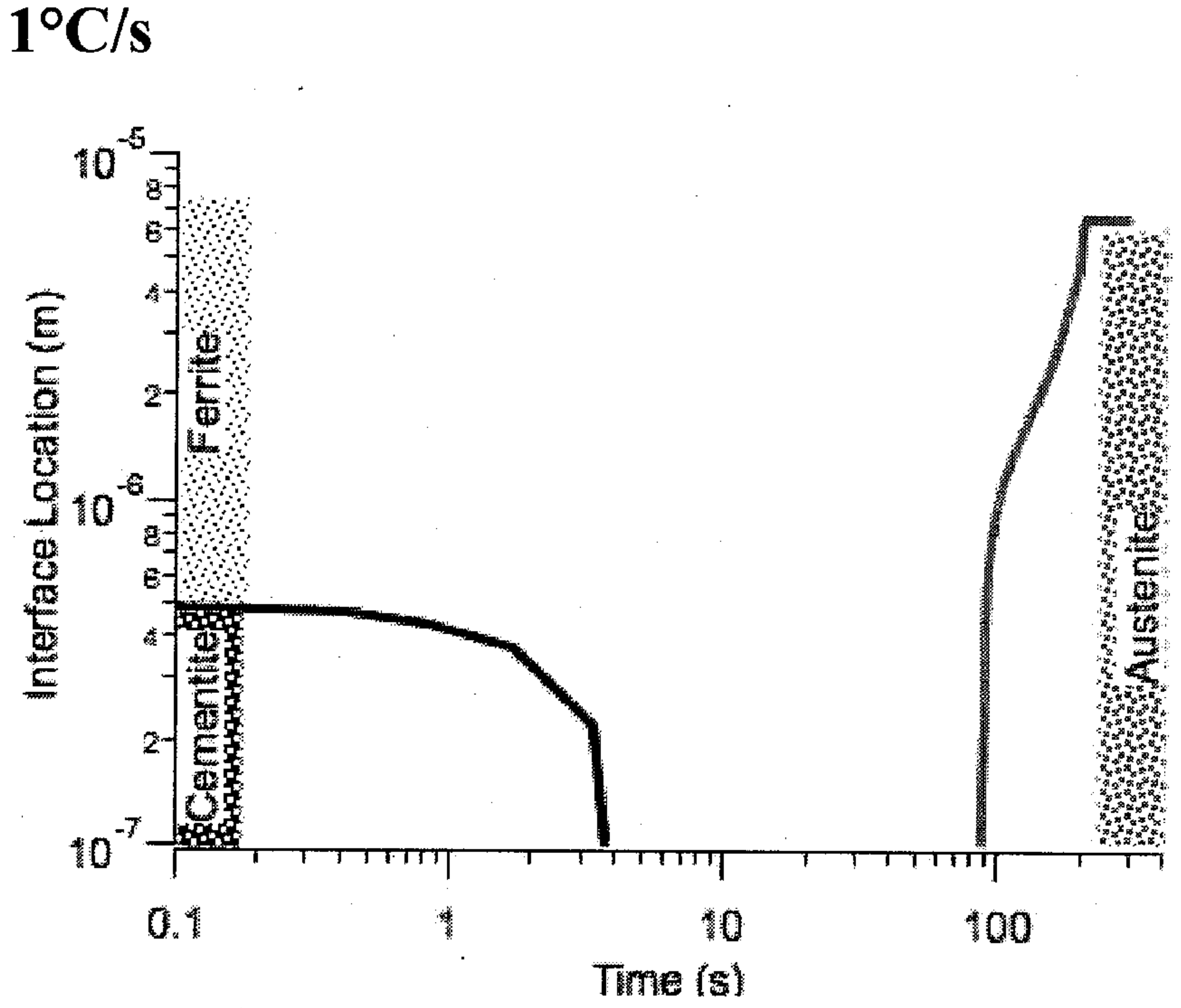

1°C/s
Interface Location (m)
$10^{-5}$
8
6
4
2
$10^{-6}$
8
6
4
2
$10^{-7}$
Ferrite
Cementite
Austenite
0.1
1
10
100
Time (s)

FIG. 9A

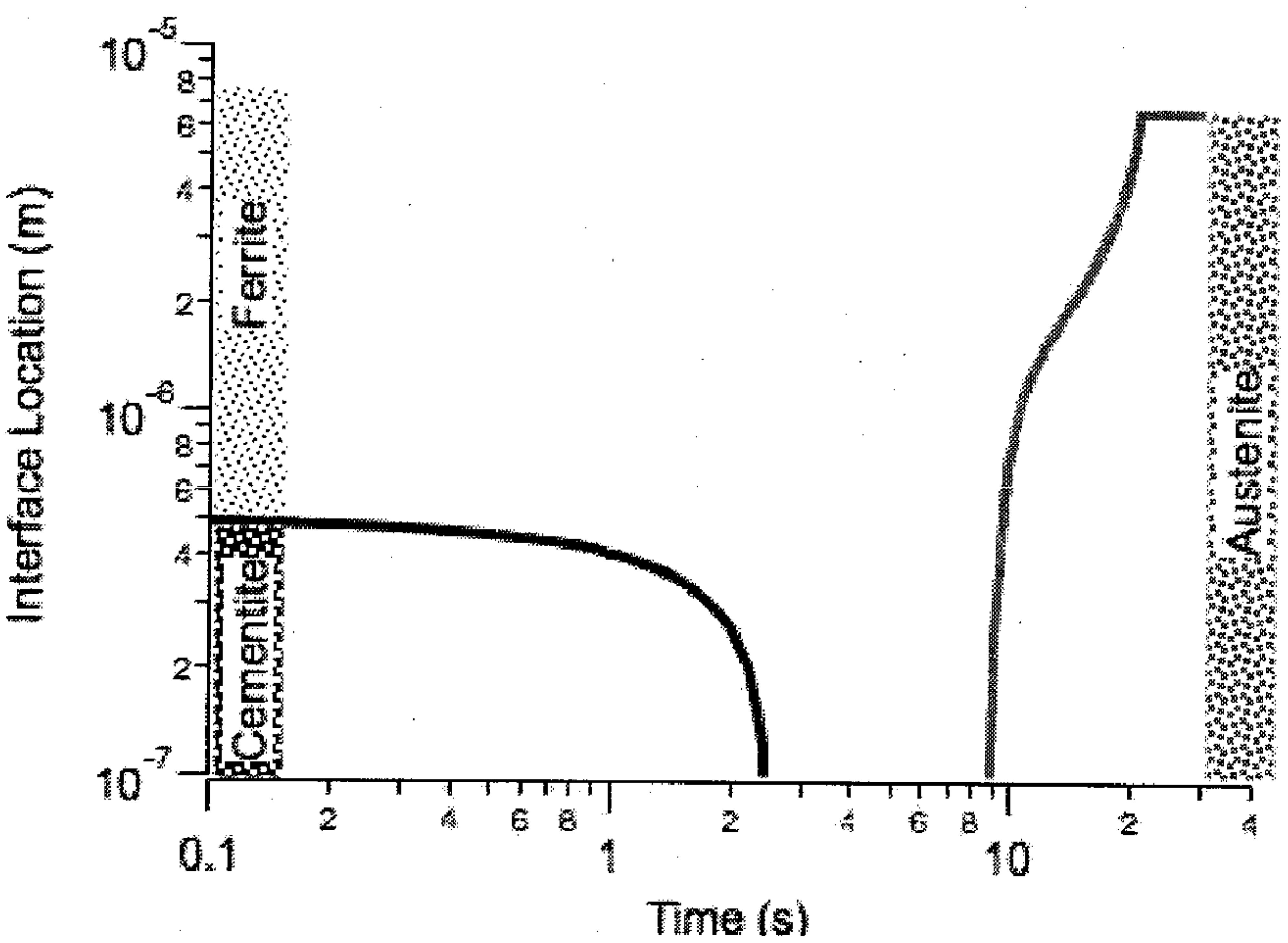

Interface Location (m)
$10^{-5}$
8
6
4
2
$10^{-6}$
8
6
4
2
$10^{-7}$
Ferrite
Cementite
Austenite
0.1
2
4
6
8
1
2
4
6
8
10
2
4
Time (s)

FIG. 9B

**100°C/s**

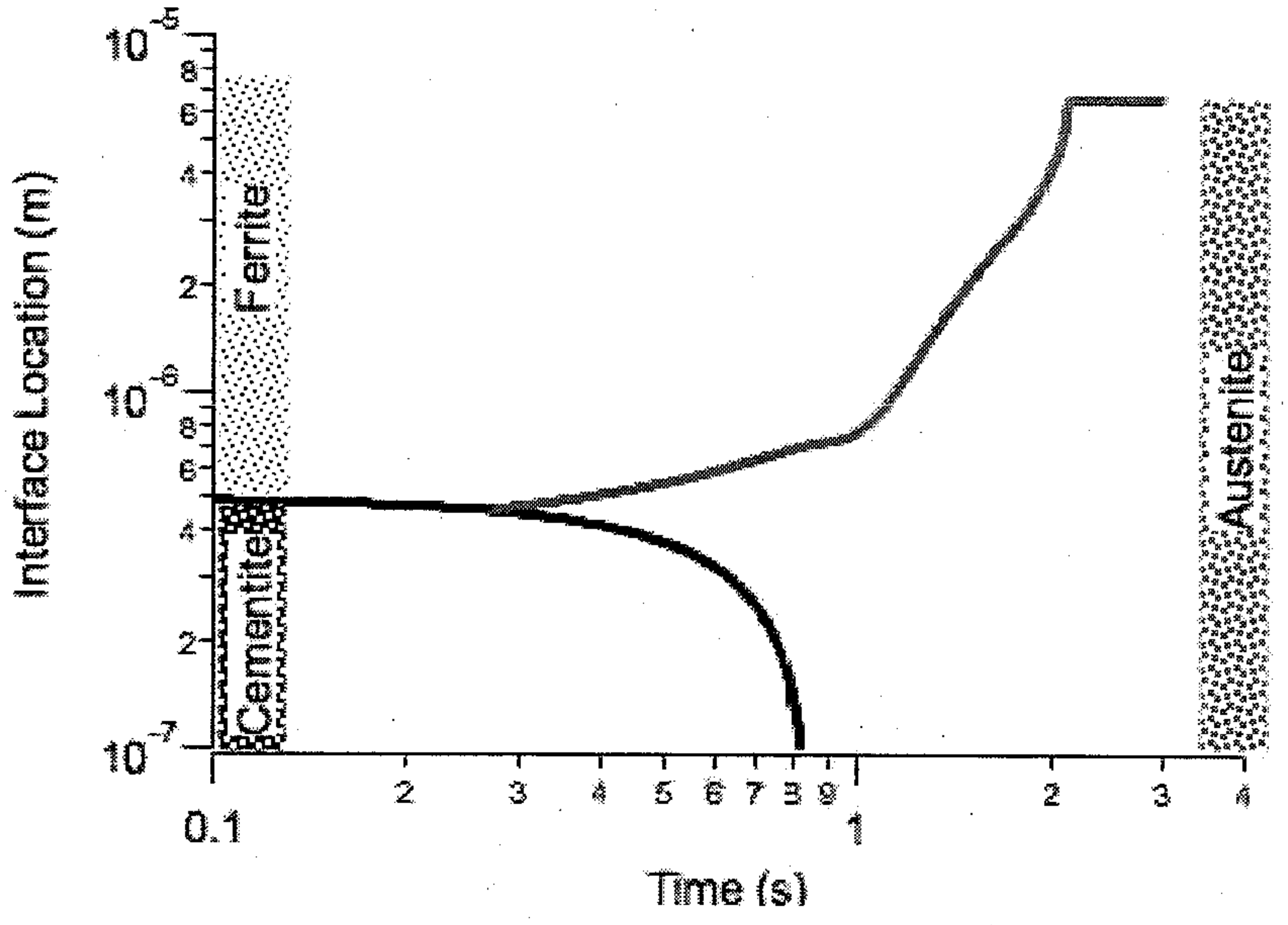


FIG. 9C

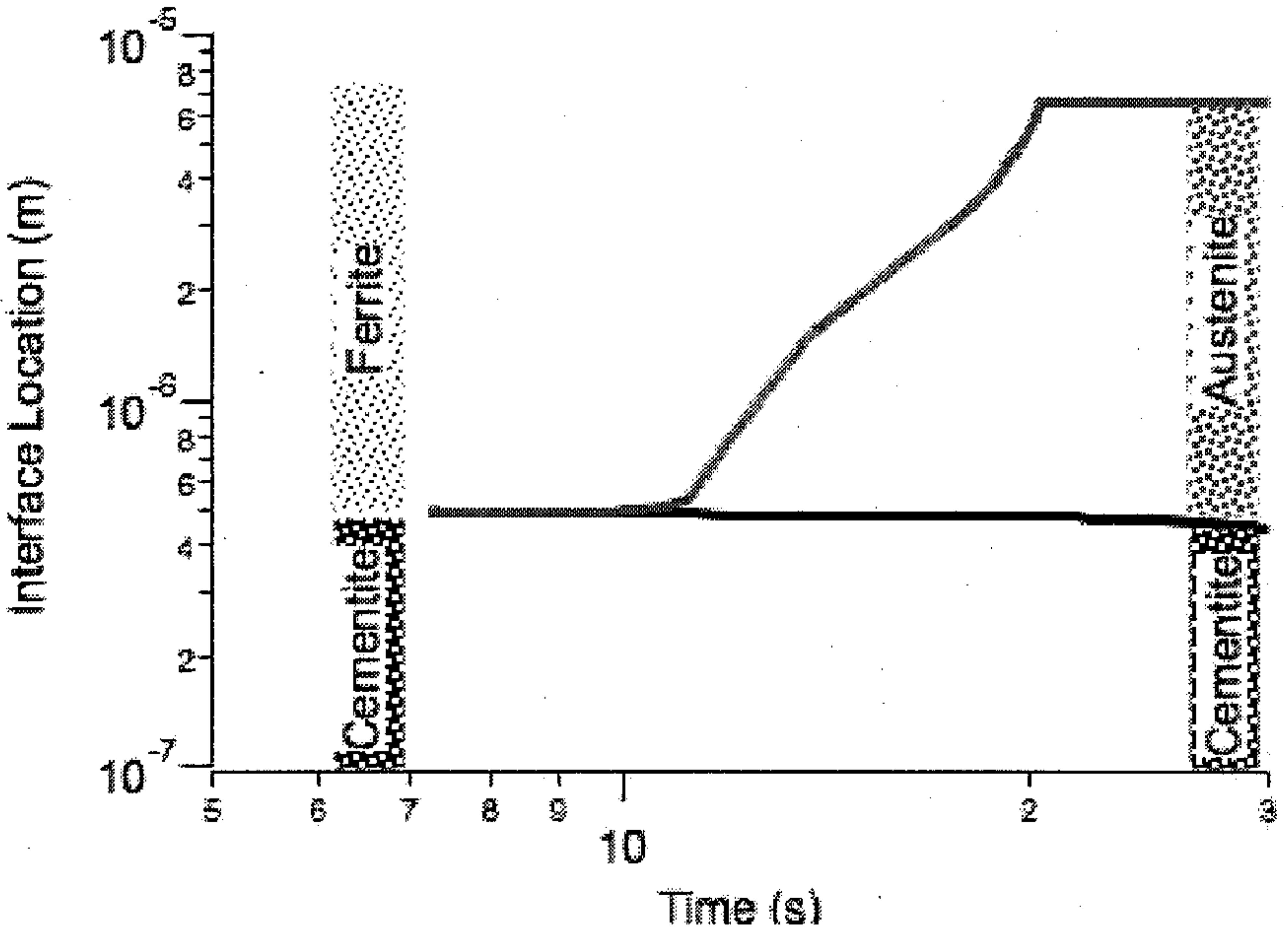


FIG. 9D

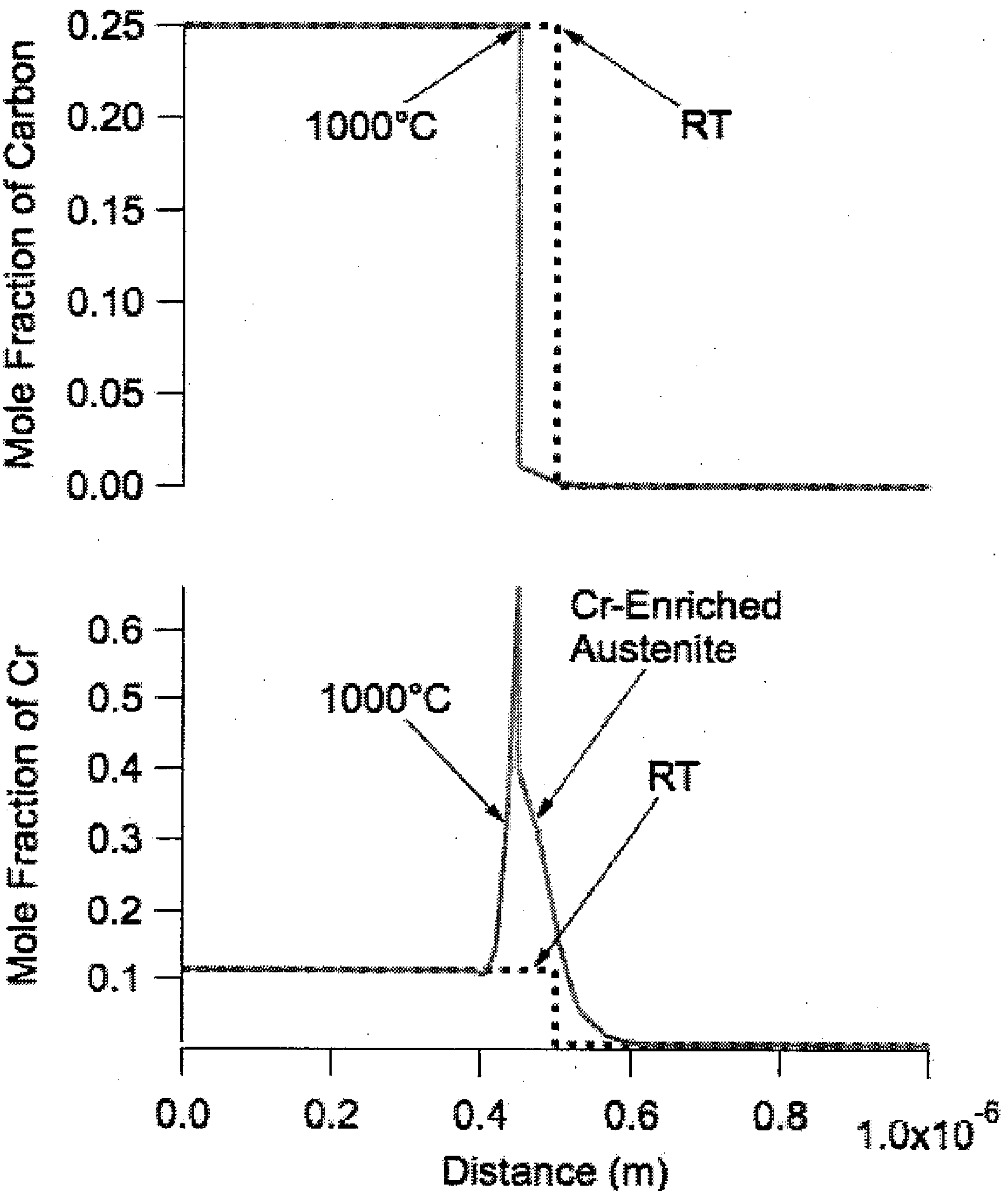

0.25
0.20
0.15
0.10
0.05
0.00
Mole Fraction of Carbon
1000°C
RT
0.6
0.5
0.4
0.3
0.2
0.1
Mole Fraction of Cr
1000°C
Cr-Enriched
Austenite
RT
0.0
0.2
0.4
0.6
0.8
$1.0x10^{-6}$
Distance (m)

FIG. 10

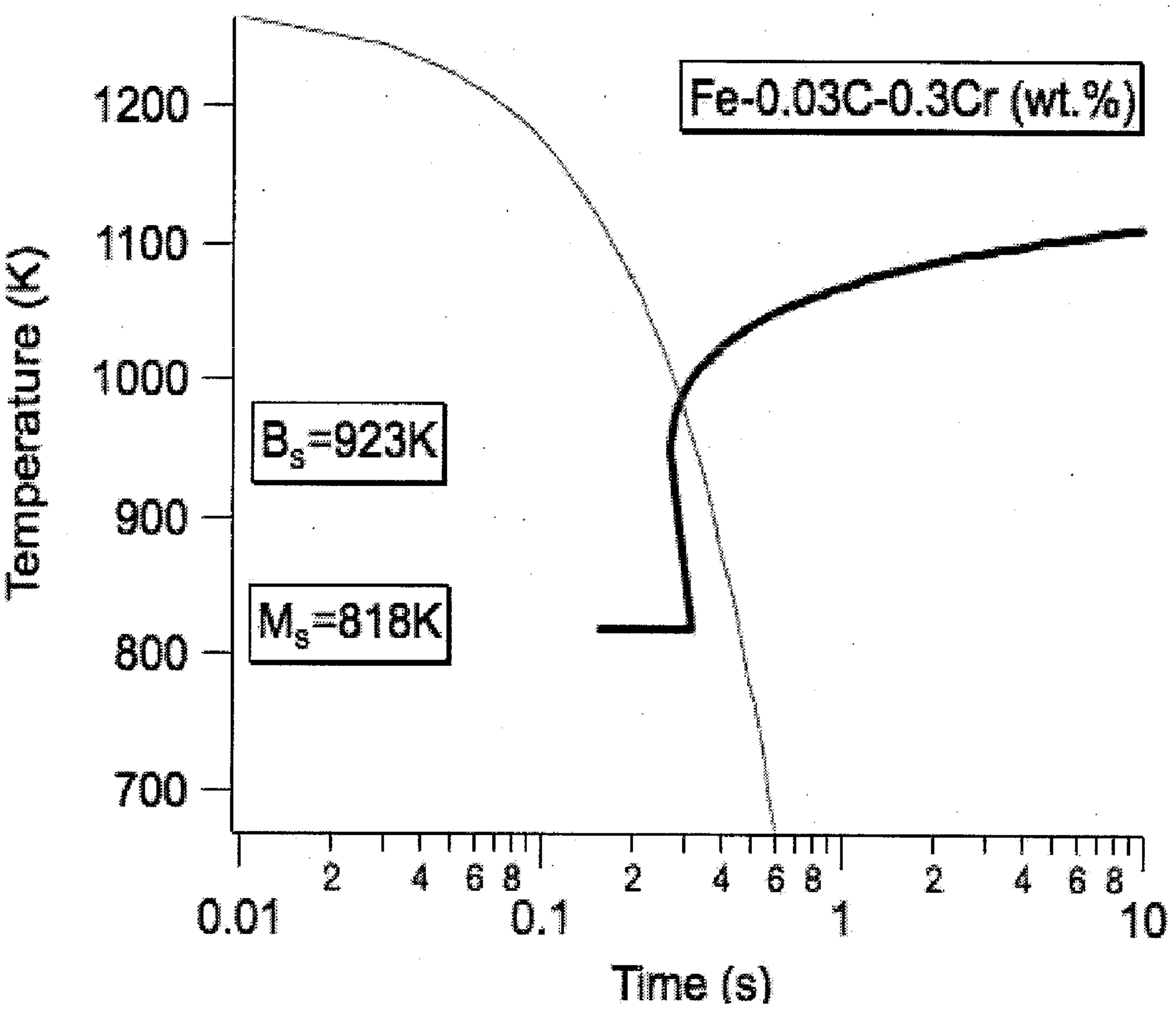

Fe-0.03C-0.3Cr (wt.%)
B$_s$=923K
M$_s$=818K
Temperature (K)
1200
1100
1000
900
800
700
0.01
2
4
6
8
0.1
2
4
6
8
1
2
4
6
8
10
Time (s)

FIG. 11

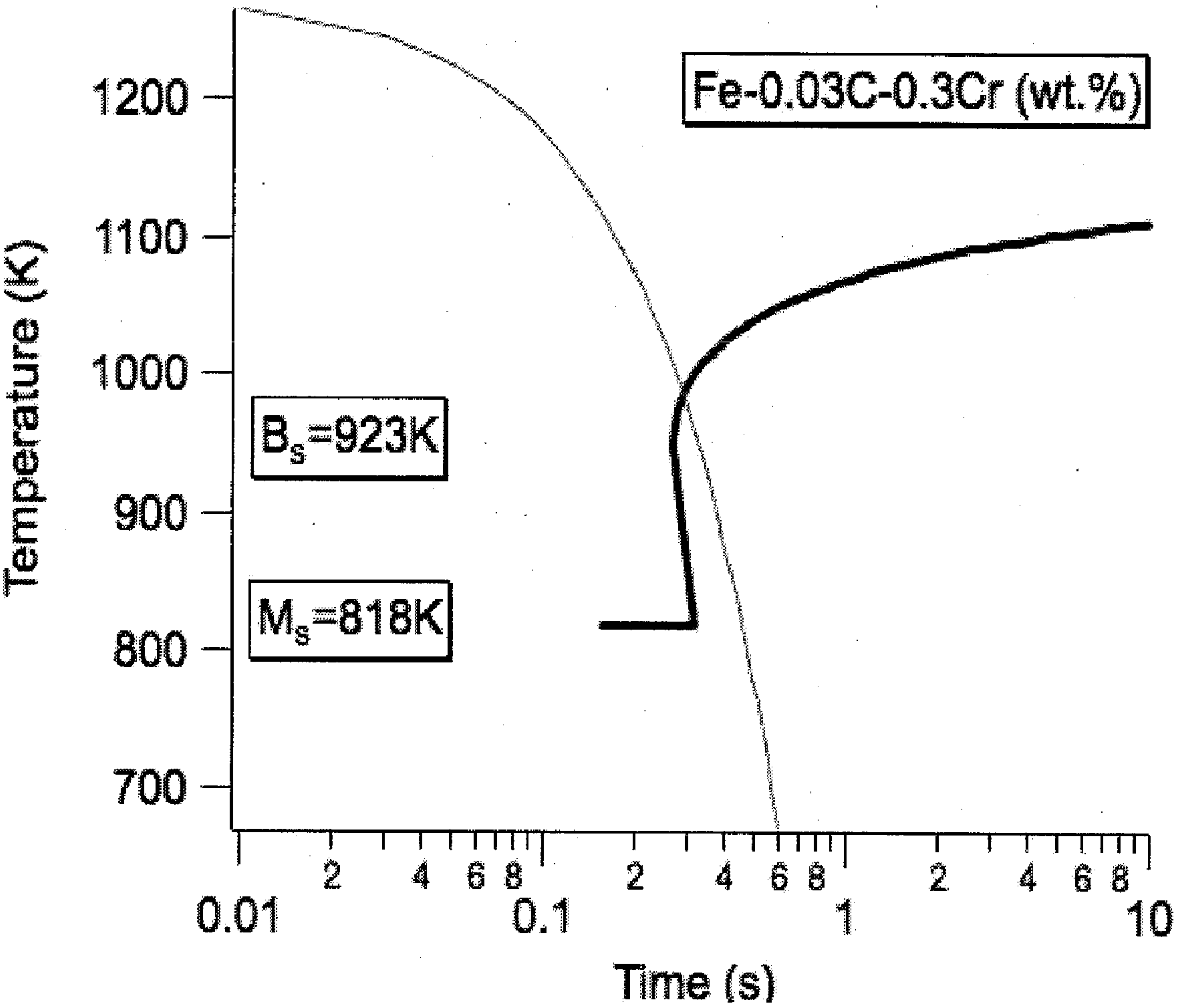

Fe-0.03C-0.3Cr (wt.%)
$B_s$=923K
$M_s$=818K
Temperature (K)
1200
1100
1000
900
800
700
0.01
2
4
6
8
0.1
2
4
6
8
1
2
4
6
8
10
Time (s)

FIG. 11