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R. M. Horn, E. R. Parker, and
V. F. Zackay

Yearly Report for Period
October 1, 1976 to September 30, 1977

Prepared for the U. S. Department of Energy
under Contract W-7405-ENG-48

LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA BERKELEY

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Prepared for
The United States Department of Energy

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FOREWORD

This report covers work performed under contract 4733 for the period October 1, 1976 through September 30, 1977, with emphasis on the work performed for the period July 1 through September 30, 1977. This work was administered by the Fossil Energy Division of ERDA with Dr. T. B. Cox as the Project Manager. The report was prepared by Dr. R. M. Horn of the Materials Science and Mineral Engineering Department of the University of California, Berkeley, formerly with the Materials and Molecular Research Division of the Lawrence Berkeley Laboratory.

The research studies for the report were performed under the direction of Professors E. R. Parker and V. F. Zackay of the Materials Science and Mineral Engineering Department of the University of California, Berkeley. They were assisted by the following personnel:

Project Leader:	R. M. Horn
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ABSTRACT

This report represents a summary of progress during the first year of a program to modify current ferrous alloys and develop new low-alloy steels that can be field-fabricated into large-diameter, thick-walled pressure vessels for commercial coal gasifiers. The report emphasizes work performed in the fourth quarter. Determination of design criteria for the pressure vessel steels has been completed, incorporating information gained through review of the literature and gained through interaction with industry, national laboratory personnel, and research contractors. Work has been performed to verify that simulation techniques lead to good reproducibility. This work has required evaluating commercially-produced material and small ingot material. Primary program effort has been placed on carrying out studies in modified commercial alloy systems to direct scaled-up investigations during the second year. Transformation behavior, microstructural characterization and mechanical property assessment have been determined for several modified alloys. Emphasis has been placed on Mn-Mo-Ni steels, A533-types, and Cr-Mo steels, A-542-type during the first year. Initial compositions for complete thick-section characterization have been determined. Larger, 150-lb developmental ingots have been ordered for the second year study. Work on the third system, Ni-Cr-Mo steels (A543-type) has focused on embrittlement susceptibility, with composition modifications having been selected for studying this phenomenon. Finally, work on eutectoid steels has been undertaken on an associated fundamental studies program. These studies, which will address thick-section problems during the second year, have been aimed at identifying useful alloy systems.

1. OBJECTIVE AND SCOPE

The objective of this program is to adapt or develop low-alloy steels that can be field-fabricated into large-diameter, thick-wall pressure vessels for coal gasification/liquefaction systems. The program will use thick-section simulation methods to guide the modification of current ferrous alloys and to develop new low-alloy steels that will meet these needs. The program is divided into five tasks which are as follows:

1. Alloy Design Criteria Study
2. Thick-plate Simulation
3. Evaluation of Commercially-Available Materials
4. Modification of Current Alloys
5. Alloy Design

These five tasks will necessarily overlap with task 1, 2 and 3 serving as the basis for the alloy design work done in tasks 4 and 5.

Each task has goals that help define the work for the succeeding task. The completion of task 1 will lead to the determination of defined material properties that will meet coal gasifier needs. This task will also assess the limitations imposed by steel-making practice and vessel fabrication methods. It will also document the properties of present-day code-acceptable materials in thicknesses forecast.

Task 2 will establish the limits of usefulness of laboratory methods for developing thick-section steels from small lots of material. The task will be coupled with work defined in task 3, the evaluation of thick-section properties of current code-acceptable material.

The information gathered in task 3 will be used in the selection of alloy modifications explored in task 4. Task 5 will use developmental approaches to design alloy steels in order to satisfy the material needs for gasifier pressure vessels developed in Task 1.

2. PROGRESS SUMMARY

The program is on schedule with the guidelines presented in Table I. Work on task 1 has been completed. The highlights of the topical report are incorporated into this report. Task 2 has also been carried far enough to lend confidence that simulation methods are valid. Tasks 3 and 4, being performed concurrently, have generated the information necessary to start the thorough investigations of the second year.

2.1 TASK 1 - DESIGN CRITERIA STUDY

Over the first year interactions with steel manufacturers, pressure vessel fabricators, A/E firms, national laboratory personnel, and other ERDA-NASA-EPRI contractors have been used to determine appropriate design criteria for thick-section pressure vessel steels. The design criteria have been used to direct the first year's research program. In particular, specific criteria for commercial pressure vessel steels have been used as the basis for composition modifications for improved properties.

2.2 TASK 2 - THICK PLATE SIMULATION

Progress on the task has centered around three tasks in the first year. These tasks were (1) constructing a facility to perform programmable heat treatments, (2) determining appropriate cooling rates for slab thicknesses and cooling processes of interest, and (3) evaluating simulation techniques in commercial material to verify reproducibility of properties. These three tasks have been completed, allowing research on alloy development to be conducted with assurance that results are representative of thick plate material made commercially.

2.3 TASK 3 - EVALUATION OF COMMERCIAL MATERIALS

Work, coupled with task 2, has been aimed at property determination of current steels. Characterization of A533B, A542, and A543 steels has been performed. Both commercially and laboratory heat-treated material has been examined. This work also serves as the basis for alloy modification studies.

2.4 TASK 4 - MODIFICATION OF CURRENT ALLOYS

Several composition modifications of A533B and A542-type steels have been made. These alloys have been designed to meet the criteria established in task 1. Characterization of transformation behavior, microstructure, and mechanical properties have been performed in small laboratory lots of material. These evaluations have served as the basis for thorough studies beginning early the second year.

2.5 TASK 5 - DESIGN ALLOYS

Work on this task has been initiated as part of another basic research program. The study, centered around V-Ni eutectoid steels, has been directed toward characterization of transformation behavior and microstructure with only limited work on mechanical properties. Second year research will be directed toward thick-section application of several eutectoid steels using the preliminary results for critical heat treatment selection.

TECHNICAL PROGRESS

3.1 TASK 1 - ALLOY DESIGN CRITERIA

During the first year, concurrent with the initiation of work on alloy reserach, efforts have been made to determine design criteria for steels to be used in thick wall pressure vessels for coal gasification. The development of these criteria has centered around interactions with industry, national laboratory personnel, and ERDA-NASA-EPRI contractors. Review of the literature has also been incorporated. The information gathered has been condensed into a topical report which will be reviewed in the following sections.

The area of investigation needed to develop meaningful criteria are (1) thick plate manufacture, (2) pressure vessel fabrication under the ASME code, (3) current steels, and (4) Gasifier design. This review has served as the basis for determining specific steel problems and the appropriate design criteria for improved steels.

3.1.1 THICK PLATE MANUFACTURE

Information on thick plate manufacture has been obtained through interaction with Lukens Steel Co. There are several important processes in the steelmaking practice which control properties. First, following steel making, prior to pouring, additional processing can improve the product. Both vacuum degassing and calcium argon blowing can be performed to lower hydrogen content and sulfur content, respectively. The additional procedures, affecting final cost only slightly, are available for thick plate steel. This processing cannot change segregation in the ingot itself. Only electroslag remelting, which also reduces impurity levels, will have a major effect on homogeneity. This procedure is much more prohibitive due to capacity and cost.

Secondly, there are limitations on the size of ingot that can be rolled. This puts an upper limit on plate thickness of approximately 12" and puts a limitation on the amount of cross-rolling which can be performed. Finally, there are constraints on the heat treatments that can be applied to thick plates. ASTM specifications spell out acceptable processes. However, plate properties in thicker gauges are limited by heat flow during quenching from austenitization. These processes also lead to gradients in microstructure from edge to center. Summarizing, it can be stated that although the initial steel composition in the ladle can be controlled, particularly using advanced practices, the thick plates contain gradients in impurities due to initial segregation, variation in deformation due to rolling, and variation in transformation products due to differences in cooling rates.

3.1.2 PRESSURE VESSEL FABRICATION UNDER ASME CODE

Interactions with Babcock and Wilcox Co. as well as ORNL personnel have served as the basis for review of thick walled pressure vessel fabrication. Large complex vessels are built to the ASME code according to section VIII, division 2. The code is restrictive in certain areas as well as lenient in others. The allowable steels and their associated design stresses are specified. The design stress for ferrous materials is essentially 1/3 of the ultimate tensile stress for use up to 650°F. Fabrication procedures are also specified. The following processes, applicable to specific alloys, are addressed by the code:

(1) Welding processes,

(2) Pre- and post-welding procedures,

(3) Overlay cladding methods,

(4) Stress relief procedures.

These procedures are mainly geared toward shop fabrication. Quality control procedures are also specified.

While the code details guidelines for procedures, only minimum requirements for materials are specified. Heat treatment parameters are not clearly defined, e.g., austenitization temperature. Fracture properties are also set at minimum levels. The code must therefore be taken only as a baseline guide in setting acceptable material properties.

3.1.3 CURRENT PRESSURE VESSEL STEELS

The primary candidate steels for thick wall pressure vessel application are A533B, A542, and A543-type steels with the following minimal compositions given in Table II. A general review of each of these steels follows:

3.1.3.1 A533B Steel (Mn-Mo-Ni Steels) These steels have been used extensively in thick section in pressure vessels for nuclear reactors. Gauges up to 12 inches (30 cm) have been used. (A508, class 2 steel is the forging grade equivalent to these steels. It has lower Mn and small amounts of Cr, leading to somewhat lower hardenability.) The steel has been used as a class 1 steel. This specification requires a minimum ultimate tensile stress of 80 ksi (550MPa). In conjunction with nuclear programs, the properties of this steel have been characterized as a function of location in thick slabs. This characterization, performed by the Heavy Section Steel Technology Program sponsored by the Welding Research Council, emphasized fracture properties in thick sections. Both base metal and weldment behavior have been investigated. The steel properties, however, have not been characterized as to behavior in deleterious environments.

3.1.3.2 A542 Steel (Cr-Mo Steels) These steels have also been used extensively in pressure vessels. These steels have been well characterized in terms of high temperature properties and of environmental resistance. However, the steel, when used in thick section, is used in a lower strength condition.

This is due to insufficient hardenability which in turn leads to poor strength and toughness properties in the plate interior. The large amounts of Cr and Mo are associated, however, with good resistance to hydrogen attack. There is a large amount of data gained through use in the petrochemical industry indicating that the steel will not degrade in hydrogen environments.

3.1.3.3 A543 Steel (Ni-Cr-Mo Steels) These steels, high in alloy content, are adapted from HY-series steels that have been used successfully for boat hull application. These steels have high hardenability and are therefore good for thick section application. The steels also have good strength and toughness properties in the as-welded condition, and therefore might be considered useable in a non-stress-relieved application. The steels do show some degradation when aged near 500°C for long-time periods. However, little work has been performed evaluating high temperature properties including resistance to deleterious environments.

3.1.4 GASIFIER DESIGN

The pressure vessels that are forecast for use in coal gasifiers are similar to those built successfully for petrochemical application. However, the anticipated size of the vessel necessary to produce 250 M Btu/day of gas, the quantity seen as economic, is much larger. Two units, 250 ft high, 25 ft in diameter, and having at least 8 in. wall thickness would be required to produce this quantity. These vessels would be three times as massive as any vessel ever shop fabricated. Therefore, a combination of shop and field assembly will be necessary. To construct the vessel within the ASME code, field stress relief would have to be performed. As stated earlier, the code sets down only minimum requirements for steel toughness. However, the petrochemical industry has chosen to require better minimum properties while limiting strength. A minimum operating temperature and a maximum hardness level of

$R_c 23$ would be typical requirements.

Although these added requirements should be used, it should also be realized that the code does not consider embrittlement degradation of materials. Guidelines for preventing hydrogen embrittlement, ageous corrosion, and sulfide scaling in addition to hydrogen attack should be addressed.

Having reviewed the material and vessel fabrication, it is necessary to identify the improvement areas. First, material properties should be improved by using advanced steelmaking practice. As mentioned, additional processing can lower sulfur content, which improves ductile fracture properties. Minor alloy additions to bring about grain refinement should also be incorporated in the practice. This will decrease the brittle-ductile transition temperature and will also improve yield strength. The latter would be of importance only if stress design parameters were changed to depend on yield strength as in European codes. To eliminate segregation and improve through thickness properties, electroslag refining (ESR) could be considered as well. However, the added expense might not be as cost-effective as would be the other processing procedures. The present capability might also limit final plate thickness even more. Only if properties in plate of lower reduction levels were adequate, might ESR be useful.

Finally, present specifications are very loose, particularly with respect to heat treatment parameters. Tightening these procedures could ensure more uniform and reproducible properties. Closer examination of austenitization, cooling, and tempering procedures are those processes which could be tightened.

While processing changes lead to general improvement of mechanical properties, changes that upgrade environmental resistance center around changes to alloy composition. As stated, the ASME Pressure Vessel Code does not address environment. However, petrochemical experience has shown that Cr - Mo steels are environmentally resistant in hydrogen service. Therefore, Cr and Mo carbides are stable to decarburization. Alloy additions promoting carbides other than cementite must be considered to decrease environmental degradation.

Attention must also be paid to other embrittlement processes that can take place during operation and influence room temperature fracture properties, e.g., temper embrittlement. Efforts to keep residual elements, particularly P, at a minimum level should be taken to keep the steels' susceptibility low.

Improvements in the steels' fabricability must be a goal of research. This is required because of the necessity for field assembly and its associated problems. However, improvements must be made in the heat-affected-zone as well as in the weld metal properties. This is difficult to achieve until base metal properties are adequate. Therefore, improvements in toughness levels in plate will be the aim, initially. Alloy additions which promote added toughness must be also considered good for weldability.

From this review, it has been possible to draw several general conclusions as well as specific design criteria for the steels initially being investigated. The general aims are the following:

(1) uniform thick section properties,

(2) resistance to environmental degradation,

(3) good fracture resistance, and

(4) good field weldability.

These general criteria lead to specific criteria which are as follows:

(1) Due to environmental considerations, thick section steels should have an average Charpy impact value of 60 ft-lbs with a single specimen minimum of 48 ft-lbs. This should be established at the minimum operating temperature.

(2) The steels used should be capable of uniform strength properties in section sizes up to 12 in. (30 cm)

(3) The materials should be rich enough in chromium and molybdenum to satisfy operation in the safe Nelson curve regime.

(4) The steels should be resistant to embrittlement in the 600°F to 800°F temperature regime.

(5) The steel should have adequate toughness, in the heat-affected zone, in the as-welded condition as well as following stress relief.

For the specific steels, the research is aimed at producing the following improvements:

A542 (Cr-Mo Steels) - The research will be aimed toward improving through-thickness strength and toughness levels in up to 12-in. (30cm) sections.

A533B (Mn-Mo-Ni Steels) - This alloy will be adjusted in composition to improve environmental resistance with maintenance of strength and moderate improvements in toughness.

A-543 (Cr-Ni-Mo Steels) - This steel will be investigated with lower alloy content in an attempt to reduce cost, susceptibility to embrittlement, and stress relief degradation.

3.2 TASK 2 - THICK PLATE SIMULATION

During the course of the first year, emphasis was placed on developing and evaluating thick plate simulation techniques. Several sub-tasks were undertaken and will be briefly summarized. These tasks were: (1) Furnace Modification, (2) Small Ingot Characterization, (3) Cooling Rate Determination, (4) Commercial Material Evaluation, and (5) Fracture Property Characterization. Results in each area will be discussed briefly.

3.2.1 Furnace Modification

In order to perform heat treatments characteristic of thick plates, it was necessary to modify an existing induction furnace at LBL with a form of feedback control. This was accomplished by modifying a Datatrak programmer and coupling it with a special proportional control unit for the induction power supply. The feedback control is maintained by using a thermocouple attached to the actual material specimen. An additional thermocouple can be used for recording purposes. The furnace is capable of controlling in the range of 1000°C to 200°C. Argon flow retards contamination and can be used with a high flow rate, for accelerated cooling. The control units are shown in Figure 1 while the hot zone is shown in Figure 2. The system is capable of heat-treating fairly massive specimens, such as a typical CTS specimen used in elastic-plastic fracture property characterization. The system has been used repeatedly with success over the first year.

3.2.2 Small Ingot Characterization

In order to simulate cast structures in small ingots that are characteristic of those found in big ingots, investigations were carried out in small ingots (25#) made at LBL. It was found that slower cooling rates led to uniform structures. However, it was felt that deformation levels and interstitial contents were more easily controlled in larger developmental ingots(approximately 150#). Lukens Steel Co. was willing to supply this material in a well-characterized form (chemistry and deformation); therefore smaller ingot characterization was stopped. These ingots (25#) were only used for initial screening tests.

3.2.3 Cooling Rate Determination

In order to simulate cooling rates characteristic of thick slabs, it was necessary to determine the applicable thermal history that plates undergo. This history is a function of cooling process, thickness, and location in the slab. This information was arrived at using the following approach:

(a) Actual cooling rate information for various slab thicknesses (air cooled and immersion quenched), 1/4 thickness location, was obtained from Lukens Steel Co. (The data meets the requirements of paragraph N313.2 of the ASME's winter 1966 Agenda, Nuclear Vessels.)

(b) Polynomialsof the form:
$T = A_o + A_1 t + A_2 t^2 + A_3 t^3 + A_4 t^4$ were fit to the data (where T is the temperature, A_n is a computer determined coefficient, and t is time).

(c) Heat transfer analysis considering both convective and radiative heat loss was performed using stepped values for H, the convective heat loss parameter, and ε, the emissivity. The following equation was used for the analysis:

$$\rho c_p \frac{\delta T}{\delta T} = K \frac{\delta^2 T}{\delta x^2}$$

where ρ is the density, c_p is the heat capacity and k is the thermal conductivity, and x is the location in the slab.

At the boundaries the following conditions were assumed:

$$\text{(Edge)}: \; -k \frac{\delta T}{\delta x} = H(T - T_s) + \varepsilon\sigma \, (T^4 - T_s{}^4)$$

where T_s is surrounding temperature and σ is the Stefan-Boltzmann constant.

$$\text{(Center)}: \quad \frac{\delta T}{\delta x} = 0$$

The heat transfer analysis, which used an implicit numerical method for solution, considered changes in density, heat capacity, and thermal conductivity as well as the latent heat.

The best fit values for the comparison were determined for each thickness and process. The best fit parameters varied from slab to slab. This would be expected because the rates used for comparison were conservative estimates of commercial practice capability by Lukens. After evaluating three different thicknesses for each process, intermediate values of H and ε were determined to be characteristic. For immersion quenching H = 0.006 cal-gm/sec-cm^2 - °c and ε = 0.2 were used. For air cooling the values of H = 0.0008 cal-gm/sec-cm^2 - °C and ε = 0.5 were chosen to give the best fit. Figures 3 through 6 give the cooling curves for 8" and 12" thicknesses for each process. These cooling rates will be used for thermal history simulation in the alloy development program.

3.2.4 Commercial Material Evaluation

In order to evaluate simulation techniques, efforts were taken to evaluate commercial material at the appropriate location in thick slabs. The materials that were investigated are listed in Table III. The properties of the steels checked are discussed in the next section. For comparison with the steel properties, it was necessary to evaluate re-heat treated steels, using the proper reheat treatment in the induction furnace. As stated in

Table III, the supplied material condition was not that desired (the steel was either normalized or annealed). Therefore reheat treated properties necessarily stand as the base properties. As a final check on small ingot properties, small ingots (25#) of commercial composition were also heat treated and characterized as a check on variation between commercial heats and developmental heats.

3.2.5 Fracture Property Characterization

In addition to simulation of thermal history, it is also necessary to characterize the thick-section fracture properties in small laboratory-size specimens. The development of procedures for quantitative property assessment began during the first year. For the special case of pressure vessel steels, steels that exhibit large amounts of crack tip plasticity in thin section, it has not been established whether a one-parameter fracture criterion can be determined. Two single criterion parameters that have received the most attention are (1) the critical value of crack opening displacement (COD), and (2) the critical value of quasi-strain energy release rate (J_{Ic}). Both are derived assuming non-linear elastic behavior. The normal method of COD measurement relies on using a clip gauge to monitor displacement at the specimen's "mouth" which is converted to a COD. In this method, the point of initiation is not determined. It is not understood what effect (1) geometry and (2) loading condition have on the critical COD.

The experimental techniques for J_{Ic} evaluation are based on an energy interpretation. The methods used to measure it may require many specimens to determine the crack initiation event. Again, the effect of specimen geometry on the J_{Ic} value is not well established. A test matrix to determine the effect of geometry on the J_{Ic} value was planned. However, it has not been completed because of equipment difficulties.

It is planned that J_{Ic} calculations will be undertaken during the second year. Guideline procedures, developed by task group E24.01 of ASTM, will be used in A508 and A533B as references. Single specimen tests will also be performed with good instrumentation to evaluate the effectiveness of J_{Ic} methods for developmental alloying screening.

3.3 TASK 3 - EVALUATION OF CURRENT MATERIALS

The studies undertaken in the commercial steels have been performed to (1) assess commercially supplied material behavior and properties, (2) assess reheat treatment properties, (3) asssess small laboratory ingot properties and (4) assess, to a limited extent, the variation in properties due to composition variation allowed by the specification. These results are discussed for the three commercial steels investigated.

3.3.1 A583B (Mn - Mo - Ni Steel)

Both A533B plate steel and A508, class 2 forging steel have been evaluated. The compositions are given in Table III. The continuous cooling transformation (CCT) behavior is shown in Figures 7 and 8. The A508 steel of lower alloy content contained free ferrite at slower cooling rates (thicker sections) while the A533B steel was fully bainitic. The commercial tensile properties are listed in Table IV. Compared in this table are vendor heat treated and reheat treated commercial material. The tempering treatments were different explaining differences in tensile properties. The reheat treatment procedures do lead to reproducible properties.

Charpy impact properties for commercial material were measured as well. Figures 9 and 10 show the transistion temperature behavior for the A533B and A508 steels, respectively. (The reheated material is presently being examined in a thicker 9" plate). The important features are the following: (1) The transition temperature for the A533B, class 1 material is near 0°C, (2) the upper shelf energy is less than 100 ft-lbs, (3) the transition temperature for the A508, class 2 forging grade is below 0°C consistent with the steel's low strength, and (4) the upper shelf for A508 is 140 ft-lbs reflecting the steel's chemistry and strength.

The influence of chemistry changes on transformation behavior was investigated in the Mn - Mo - Ni steels in a limited fashion. Examination of the CCT behavior for A533B with maximum alloy content revealed an increased martensite range, but little change in banite transformation characteristics. The CCT behavior of A508 steel represented the influence of lean alloy content. Free ferrite was associated with slower cooling rates, leading to decreased strength. The changes in behavior, however, were too small to warrant extensive property examination.

3.3.2 A542 (Cr - Mo Steel)

No commercial steel was obtained in thick section over 6" or in the immersion quenched conditon. Therefore annealled material was examined in the reheat treated condition. The CCT behavior is shown in Figure 11. For cooling rates that corresponded to thick sections significant amounts of polygonal ferrite were observed. The steel's microstructure changed appreciably as the plate thickness increased.

The tensile properties for the 8", 1/4T plate material are given in Table IV. The properties seemed to be a strong function of tempering temperature because of the steel's secondary hardening characteristics. Developmental ingot properties are also listed in Table IV. The properties were very similar, with the ultimate tensile strength high due to the higher carbon level in the ingot. The ductility was strongly controlled by the tempering process even though hardness (strength) was less sensitive. The poor ductility emphasized the need to require higher tempering temperatures in the specification. These properties are certainly linked to the carbide type and morphology promoted by the tempering process.

The impact properties for the reheat treated commercial material are displayed in Figure 12. Properties for both 8" and 12", 1/4T locations are shown. The behavior for the two thicknesses, both of which contain significant amounts of polygonal ferrite, are consistent with the tensile data. The important features of the curves are the following: (1) the transition temperature is around 0°C (If a minimum energy of 60ft-lb is used as the criteria for minimum temperature of use, this temperature is above room temperature.) (2) The upper shelf energy is around 90ft-lbs; this energy is low for the recorded uniaxial strength properties.

Evaluation of the CCT behavior and properties of the Cr-Mo steels with small compositional changes were undertaken and are discussed in Task 4. The bainitic hardenability was low enough that significant alloy additions were necessary to change the transformation characteristics.

3.3.3 A543 (Ni - Cr - Mo Steel)

Commercial steel in 10" thickness was obtained for examination. The CCT diagram is displayed in Figure 13. The steel has excellent hardenability with structures cooled at 0.5°C/sec being fully martensitic. The tensile properties for the steel at both 1/4T and 1/2T locations are listed in Table IV. As expected, following tempering at 625°C, the yield and tensiles strengths are high and the variation between 1/4T and 1/2T locations is negligible. The steel also has excellent ductility, over 20% elongation.

The impact properties are very good but characteristic of high strength martensitic steels. The impact properties at the 1/4T location are displayed in Figure 14. The transition temperature is below -20°C and the upper shelf energy is approximately 90 ft-lb.

Evaluation of the effects of alloy changes within the specification were made. Both maximum and minimum allowable alloy contents were investigated. The changes in composition did affect transformation characteristics with temperatures for transformation start appreciably higher for the steel with alloy content at specification minimum. The nominal alloy content level was the optimum alloy level with the higher alloy content steel showing little added hardenability.

3.4 TASK 4 - MODIFICATION OF CURRENT ALLOYS

The largest effort during the first year has been aimed at characterizing modified commercial alloys. The new alloys, based around the A533B and A542 type steels, have been investigated in small laboratory ingots (5 to 25 lb). This work has served as the basis for alloy selection for full characterization in larger developmental ingots (150#) during the second year.

3.4.1 Modification of Mn - Mo - Ni Steels

As stated in Task 1, the major design goals for this steel were (1) improved environmental resistance, (2) improved toughness, and (3) maintainence or improvement in strength. The major alloy modifications were selected on the basis of these criteria. These major additions considered were Cr and Si for improved environmental resistance and Mn for added hardenability and associated strength and toughness improvements. The compositions that were studied are listed in Table V. The results will be reviewed for each type of addition.

(a) Chromium addition

Only one level of chromium was considered, 1% to the base composition. The modified steel, had a lower Ms (∿20°C lower), an increased martensite range, and a displaced bainite start temperature following continuous cooling as shown in Figure 15. No free ferrite was observed for even the slowest cooling rates. The bainite microstructure is displayed in Figure 16. The mechanical properties were more markedly affected. Table VI lists the tensile properties, showing a 15% increase in UTS over the base composition.

The Charpy impact properties were influenced in an equally good fashion. Figure 17 shows impact properties as a function of temperature for the modified steel. The steel exhibited 100 ft-lb energy at -20°C even with the increased strength, in the simulated 8" slab, 1/4T location. The additional Cr will also influence carbide stability for environmental resistance.

(b) Si Addition

Silicon additions have been shown to influence low alloy steel properties drastically. It has two major effects: (1) it increases strength through solid solution hardening, and (2) it drastically influences the kinetics of tempering reactions. The silicon was considered primarily for the latter influence. Hydrogen attack degradation depends on the interaction of hydrogen with existing carbides. In steels with high susceptibility, the interaction leads to the formation of methane concurrent with carbide dissolution. Silicon could influence the kinetics of this reaction drastically and possibly prevent any degradation.

Ingots with 1% and 2% silicon addition were investigated. Transformation studies showed that only silicon at the 2% level affected CCT characteristics, promoting free ferrite. The tensile properties are given in Table VII. Two tempering temperatures were used for mechanical property investigations, 625°C and 675°C. The lower tempering temperature led to much higher tensile strengths in the steels, particularly for the 1% silicon addition which in thick section contained no free ferrite. The associated impact properties were very poor, with the transition temperature above 100°C. Tempering at 675°C produced much lower strengths (influenced in the 1% material from a new ingot by low Mn). The associated Charpy impact properties were much better than those of the other Si material as shown in Figure 18. The properties, displayed with the commercial properties, however, are still poor. The 2% silicon addition leads to a transition temperature above 100°C, even with the lower strength effected through a higher tempering temperature.

It is clear that silicon alone as an additive is not beneficial. It does, however, influence the tempering response of the steel, retarding carbide coarsening. In combination with other alloy additions, silicon could lead to desirable properties in steels for application in deleterious environments.

(c) Mn addition

Two levels of Mn above specification were investigated. These combinations are listed in Table V. The CCT behavior for these steels is different from base behavior. Figure 19 shows that the CCT behavior for the 2% Mn steels has (1) an extended martensite range and (2) a lower start temperature for bainite reactions. These changes lead to increased as-cooled hardness levels. The microstructure for the as-cooled 8" 1/4T location (2% Mn) is bainitic as shown in Figure 20. No free ferrite is present. The changes in tensile properties are listed in Table VI. (tempered at 675°C). There is little change over the base steel properties. This is expected because of the small influence Mn has on tempering response, the response that controls the final strength. The impact properties are changed, however. The properties, displayed in Figure 17, show increased values at every temperature. The temperature for change in fracture appearance, to be determined, is expected to be shifted to a lower temperature.

(d) Combined additions

Three ingots, with combinations of Cr, Si and Mn additions were also investigated. Their compositions are listed in Table V. The CCT behavior was significantly changed for all three alloys. Figures 21, 22 and 23 show this behavior for these ingots. The M_s temperature was affected as would be expected using emperical formulations. The martensite range was also increased. The bainite transformation, however, was most radically altered.

In all cases the transformation start temperature was decreased. In the alloy with the ternary addition this temperature was decreased to near 400°C. Therefore this steel would exhibit uniform microstructures in thick section even if a normalizing treatment were used instead of immersion quenching. (Rate 6 corresponds to 8", 1/4T accelerated cooling.)

The microstructures corresponding to the 8", 1/4T location are shown in Figure 16, and 24-1. The structures are bainitic with no evidence of free ferrite. The hardness is high, and the structures are acicular in appearance, characteristic of lower bainite.

The mechanical properties of these three alloys, in the tempered state, are much improved. The tensile properties are listed in Table VIII. The yield strength levels are 90 ksi or higher with the ultimate strength 110 ksi or higher. The alloys containing silicon display the highest UTS even after tempering at 675°C for 4 hours. These strength levels are consistent with class 2 properties.

Along with the increased strength levels the steels exhibit improvements in charpy impact properties. These impact properties as a function of test temperatures are shown in Figure 24-2. The Cr - Si - Mn alloy and the Cr - Mn alloy exhibited lower transition temperature and an improved shelf energy at the high strength level. The Cr - Si alloy displayed impact behavior equivalent to the base steel properties (although the upper shelf energy is higher.) These properties are recorded for a steel with a UTS $\sim$ 30 ksi higher.

(e) Alloys for Full Scale Investigation

Relying on the data from the small developmental alloys, compositions of large developmental ingots were determined. These compositions are listed in Table IX. The data has shown that in these four alloy systems, improvements in strength and toughness are concurrently possible. The ingot with a Mn addition will serve as the base line data for comparison. Grain refinement was specified for the four ingots.

3.4.2 Modification of the Cr - Mo Steels

The Cr - Mo steel was modified to meet the design criteria determined in Task 1. The steel composition was changed to (1) improve hardenability leading to more uniform thick section microstructures containing no polygonal ferrite, and (2) improve toughness. The major additions chosen for this purpose were Ni and Mn additions which affect hardenability and in turn improve toughness. The benefits of additional Cr, Mo and Si were also explored. Cr and Mo were considered to improve hardenability and to lend added environmental resistance while silicon, explored in one ingot, could improve strength and retard tempering kinetics. The effects of these additions are discussed.

(a) Single Element Addition

The influence of Cr, Mo, Ni and Mn were investigated to understand the influence of each individual addition on the base composition (up to an additional 0.5%). The compositions are given in Table X. The Cr and Mo additions had little influence on the CCT behavior of the base material. For cooling rates corresponding to those experienced by thick sections, the microstructures developed contained significant amounts of polygonal ferrite, as did the base material. The tensile properties of these modified steels are listed in Table XII, for the 8", 1/4T cooling rate followed by tempering at 650°C. The properties were unaffected by the composition changes. This is indicative of the little change in CCT behavior and the overriding importance of the tempering treatment. Properties are most dependent on (1) the tempering temperature which in turn dictates the stable carbide present as well as (2) the carbon content which dictates the amount of carbide.

The Charpy properties are shown in Figure 25 for the Cr and Mo modified steel. Neither addition improved the properties. The Mo addition, in fact, was detrimental. Because both are strong carbide formers, they promoted the formation of alloy carbides reducing toughness.

The single additions of Ni and Mn were also investigated. The CCT behavior was changed for these new compositions. Polygonal ferrite was only found for the cooling rate corresponding to 8", 1/4T immersion quenched material. This improvement was obviously not adequate to insure uniform microstructures in thickness up to 12". The mechanical properties were also changed. The tensile properties, given in Table XII, showed a moderate increase in YS and UTS, $\sim$95 ksi and $\sim$ 112 ksi respectively for both new alloys. The Charpy properties, however, were much improved. Both alloys, at the increased strength exhibited transition temperatures below room temperature, clearly better than the base material as shown in Figure 25. These two alloy additions showed the most potential for achieving the design goals and were the focus of the second group of modified alloys.

(b) Ni/Mn Alloy Investigations

Having determined that Ni and Mn were the most effective alloy additions, several other compositions with increased Ni/Mn were investigated. Table XI lists those compositions. Grain refinement using Nb and Al was promoted in several of the ingots. The compositions investigated used the following modifications to the base alloy system: (1) 1% Ni, (2) 1% Mn, (3) 0.5% Ni and 0.5% Mn, and (4) 1% Ni and 0.5% Mn. CCT behavior was characterized for these alloy modifications and is displayed in Figures 26 through 30.

The Ni and Mn additions, at the 1% level, lead to similar effects on the M_s temperature, ($M_s \sim 400°C$) and to the B_s temperature(shown in Figures 26 and 27) at the slow cooling rates ($B_s \sim 470°C$). Manganese is somewhat more effective as would be expected. The highly alloyed steels with high Ni and Mn with/without Cr have low M_s temperatures, but more importantly, low B_s temperatures ($\sim 450°C$) (shown in Figures 29 and 30). Rate 6 leads to bainitic structures that are therefore formed at lower temperatures giving higher as-cooled hardness. In all cases the alloy additions are sufficient to retard free ferrite sufficiently, so that it was not present in 12", 1/4T section as represented by rate 6. The compositions lead to uniform microstructures in as-cooled thick section and thereby satisfy the first design goal for this steel. Figures 31 and 32 show the as-cooled structure corresponding to the 8", 1/4T cooling material for the Ni and the Ni-Mn alloys. The strucutures are homogeneously bainitic microstructures. The microstructure of the 0.5Ni, 0.5Mn alloy is better observed using carbon replicas. Figure 33 shows the fine uniform distribution of carbides formed after tempering. These features are very different than those obtained in the commercial steels. The developmental steels do have higher carbon content ($\sim$ .18%) which influences hardenability. This content, characteristic of the developmental ingot of nominal composition, does not account for the majority of the increase in hardenability, however. The additional 1% alloy content is necessary to achieve uniform properties for the thick sections of interest.

The tensile properties are listed in Table XIII. All properties were measured for material austenitized at 1000°C, immersion quenched to represent 8", 1/4T location and tempered at 650°C for 4 hours.

The tensile properties were improved over those exhibited by the steel of nominal composition. The improvement over the first set of alloys is not very large indicating the strong role of the tempering process on strength. Ni and Mn are not carbide formers and should have little influence on the amount of carbide produced during the tempering process. (The role of Ni and Mn on the tempering process is to be investigated.) The alloys did have yield strengths around 100 ksi and ultimate tensile strengths around 115 ksi. All the steels exhibited very good tensile ductility with elongations over 22% and reduction in areas over 70%.

The best criteria for evaluating the modified alloys are the fracture properties. Charpy impact properties for the Ni and Mn modified alloys were measured.

These properties are displayed as a function of test temperature in Figure 34 and 35. The base line data is also shown. The developmental ingots showed (1) enhanced upper shelf energies and (2) decreased transition temperature. These improved properties are definitely attributable to the uniform microstructures which were free of polygonal ferrite. The best alloy was the base steel modified with 1% Ni, 0.5% Mn and was also grain refined. It had an ultimate tensile strength of 118 ksi, an upper shelf energy of 120 ft-lb, and a transition temperature below -40°C.

The alloy that contained additional Si as well as Ni and Mn exhibited atypical structure and fracture properties. The silicon addition led to large amounts of ferrite as shown in Figure 36. This did not adversely influence strength, but did reduce the elongation. The Charpy impact properties were severely degraded when compared to the other developmental alloys. The transition temperature was above room temperature as shown in Figure 37. Long term tempering did little to improve properties as shown.

(c) Alloys for Full Scale Investigation

Using the data developed through the first year's small ingot characterization as the basis, compositions of large developmental ingots (150 lb.) were selected. Those compositions are listed in Table XIV. Six ingots have been manufactured. The first ingot is the base composition. However, the carbon level is specified near the composition maximum. Normally, Cr-Mo steel used for thick section application has a lower carbon level because the quenched and tempered property specifications cannot be met and use is restricted to the low strength condition. The other ingots were chosen using the small ingot results. Only one ingot was grain refined in an attempt to evaluate this effect on tensile and fracture properties, and hydrogen attack resistance.

3.4.3 Modification of Ni - Cr - Mo (A543 type) Steels

During the first year, only a small amount of work was performed on modified alloys. This is due in a large part to the steel's excellent properties. It was decided that emphasis would be placed on investigating the steel's sensitivity to embrittlement. Steels with adequate hardenability for thick section application are potentially susceptible to temper embrittlement if used at elevated temperature. An investigation was undertaken to (1) ascertain whether A543 was susceptible as anticipated, and (2) modify composition to eliminate the phenomenon. The composition modifications were based on adding B and N which will segregate to the grain boundary, the site for decohesion after high temperature exposure. The justification for these additions is based on the premise that the tramp elements, which are large, increase the average equilibrium separation between the grain boundary interface atoms. The resultant decohesion encourages intergranular fracture.

However, if the sites are occupied by small atoms, prior to the embrittling treatment, the large tramp elements are excluded from the interface region preventing this increased separation. The test ingots with the heat treatment schedules are listed in Table XV. Ingots have been made and embrittlement treatments are being performed.

3.5 TASK 5 - DESIGN ALLOYS

During the first year, work on the new eutectoid alloys was initiated as part of another program. The aim of this study was to characterize and then control the microstructures of interphase precipitation alloys to make them useful for thick wall pressure vessel application. Interphase precipitation has been observed in low carbon steels which contain alloy carbide formers. A very fine dispersion of alloy carbides in a ferrite matrix is developed by direct decomposition of austenite held isothermally or cooled continuously. It has been reported that when vanadium or molybdenum is added to a 0.2% carbon steel, the steel develops a favorable microstructure for mechanical properties. This work was performed on two systems, iron-carbon-vanadium, and iron-carbon-molybdenum steels. The design criteria for alloy development which were established was that the new steels should:

1. Develop uniform mechanical properties throughout a thick section using the simplest heat treatment (preferably a continuous cooling process),
2. be weldable requiring no post-weld heat treatment,
3. have a composition close enough to the eutectoid composition to develop uniform microstructures.

Discussions of the two systems follow.

3.5.1 Fe-0.2C-1V-3Ni Alloy

Work by Honeycombe and his coworkers showed that an Fe-0.2C-1V alloy formed the most favorable structure when it was transformed at relatively high temperatures (600°C - 800°C). The addition of 3%Ni was made to lower this transformation temperature regime, promoting a finer precipitation and wider applicability to pressure vessel use. The TTT diagram for this alloy system is shown in Figure 38. All specimens were austenitized at 1200°C for 15 minutes to allow vanadium carbide dissolution. The diagram clearly shows that the addition of 3% Ni depresses the C-curve expected to be associated with the desirable interphase precipitation. Room temperature Charpy impact properties were measured along with Rockwell hardness (C scale) for the following heat treatments:

Treatments	C_v (ft-lb)	Hardness
a) Isothermally held 30 minutes, 600°C	2	40
b) Isothermally held 15 minutes, 650°C	30	40
c) Isothermally held 30 minutes, 700°C	20	30

However, microstructural observation by TEM showed that there was no interphase precipitation as reported in the Fe-0.2C-1V system. The microstructure corresponding to the alloy transformed at 650°C for 15 minutes, which exhibited the best combination of hardness and Charpy impact value, is shown in Figure 39. The structure is not typical of interphase precipitation, displaying some carbide-dispersed islands and martensitic and/or bainitic laths in Figure 39a. Evidence from the TTT diagrams supports this finding. The austenite decomposition has not progressed to completion, leading to additional low temperature transformation upon quenching. The lath size, 0.5 μm, however, is inconsistent with optical observations. Carbide analysis in this structure was difficult. Figure 39b shows an area of extensive precipitation. Dark field analysis tentatively identified the carbide as VC. However, the morphology is more characteristic of cemenite.

Efforts to extend the work to continuous cooling conditions have been made for increased thick section relevance. Figure 40 shows the CCT diagram for the V-Ni alloy. As expected, the CCT diagram is displaced down and to the right from the TTT diagram. Microstructures characteristic of material cooled at 1.3°C/sec and 0.16°C/sec are shown in Figure 41. The faster cooling rates led to a uniform bainitic structure. This structure formed at below 600°C, implying poor properties. The slower cooling rates led to a duplex structure dominated by a grain boundary nucleated plate, probably related to the eutectoid decomposition reaction. The reaction was incomplete, implying slower rates would be necessary to develop a uniform structure. Complete evaluation of microstructure-mechanical property relationships will be made for this alloy for various transformation processes. This will be necessary to develop an alloy meeting the design criteria.

3.5.2 Fe-0.2C-2Mo-2Si Alloys

Because Fe-C-Mo steels also show a favorable eutectoid microstructure, investigations have been initiated in these steel systems. Silicon additions to the base alloy have been made to reduce the eutectoid carbon content and to influence the kinetics of carbide formation. Ni and Mn additions have been made to lower the eutectoid temperature. Initial compositions have been chosen (listed in Table XVI) and transformation characteristics will be determined. More emphasis will be placed on achieving good properties in material receiving thick-section processing.

WORK FORECAST

4.1 TASK 1 - ALLOY DESIGN CRITERIA

Efforts will be made to stay abreast of current work on thick section pressure vessel steels for coal gasification. This will include maintaining contact with commercial firms as well as interacting with other researchers conducting programs for NASA, EPRI, AND ERDA. Emphasis will be placed on incorporating new understanding on environmental effects into development programs.

4.2 TASK 2 - THICK PLATE SIMULATION

Work will continue on developing methods to quantitatively characterize the fracture properties of the pressure vessel steels. The evaluation program planned last year will be completed. Efforts will be made to establish methods to simulate heat affected zone properties. This will be undertaken to develop test techniques to evaluate weldability. Finally, determination of the appropriate test specimen and test environment will be made for evaluating hydrogen attack resistance in conjunction with NASA-Ames.

4.3 TASK 3 - EVALUATION OF CURRENT MATERIALS

This task will be completed with the evaluation of A533B in 9" section and of A543 at the 1/2T location. Reheat-treated material from these plates will also be carried out.

4.4 TASK 4 - MODIFICATION OF CURRENT ALLOYS

After the large developmental ingots are received from Lukens Steel Co., full scale evaluation will begin. The study will concentrate on the characterization of material receiving a 12", 1/4T location, immersion quenching heat treatment. However, 8" immersion quenching and 8" air cooling treatments will also be performed. The studies will involve evaluation of tensile, charpy,

J_{IC} properties, hydrogen attack resistance, and weldability.

4.5 TASK 5 - DESIGN ALLOYS

Work on the V-Ni eutectoid steels will be completed, with mechanical properties and microstructures being characterized for several treatments. However, the emphasis will be shifted to the study of continuous cooling behavior in alloy systems based on molybdenum. The program will use transformation behavior to determine desirable heat treatments. Property characterization will also start.

5. CONCLUSIONS

The conclusions of the Design Criteria Study have already been given in Section 3 - Task 1. The conclusions for the other tasks follow. As a result of Task 2, Simulation of Thick Section Steel, the conclusions are:

1. Methods to simulate final thick plate heat treatments have been developed. These methods allow simulation of different processes, different thicknesses, and different locations within the slab.

2. Cooling paths characteristic of 8" and 12" plates, 1/4 T location have been determined for immersion quenching and normalizing.

3. Initial evaluation data verifies that the simulated cooling methods lead to good reproduction of commercial materials' microstructures and properties.

The conclusions for Task 3, Evaluation of Commercial Material, are as follows:

1. Investigations in Mn-Mo-Ni steels (A533B type) show that the nominal composition has enough hardenability, so that the formation of proeutectoid ferrite is avoided.

2. Reduced alloy content in A533B steel could lead to the appearance of free ferrite in thick section.

3. Commercial processing to insure adequate toughness, leads to reduced strength in A533B steels.

4. The fracture properties of the base composition of Cr-Mo steel (A542 type) are poor. The ductile to brittle transition temperature is above room temperature.

5. Additions of Ni and Mn to Cr-Mo steels decrease the polygonal ferrite level in thick section which is desirable in achieving a uniform microstructure.

6. Strength levels in A542 steels are controlled by the tempering process with substitutional additions having little effect.

7. The transformation characteristics of Ni-Cr-Mo steels (A543 type) are excellent and affected little by minor alloy variation.

8. The mean composition of A543 steel does possess the optimum hardenability, leading to uniform properties in thick section.

9. Both the strength and fracture properties in A543 steel are very good with little variation through the slab thickness.

10. Sulfur level in commercial steels has a significant influence on upper shelf energy with reduced levels being beneficial.

The conclusions drawn from Task 4, Evaluation of Modified Alloys, are the following:

1. Alloy modification, based on Cr additions to A533B steel for added environmental resistance, can lead to improved strength as well as improved fracture properties.

2. Alloy modifications based on additions of Mn to Mn-Mo-Ni steel, are beneficial in promoting better impact properties.

3. The influence of silicon on A533B type steels is two-fold. It alone degrades fracture properties. However, it also increases strength significantly, and in combination with other additions, can lead to good combinations of properties.

4. A Cr-Mn-Si modification of A533B leads to a tensile strength of 120 ksi, an elongation of 23 per cent, an upper shelf energy of 120 ft-lb, and a transition temperature of less than -25 °C in the steel.

5. Manganese and/or Nickel additions to A542 type steels, at 1% or greater, give the steel adequate hardenability for use in thick section.

6. Added Mn/Ni enhanced toughness properties significantly in Cr-Mo steels.

7. Silicon has a very detrimental influence on fracture properties in A542 type steels.

8. A Cr-Mo steel modified with 1%Ni and 0.5%Mn had a tensile strength of 118 ksi, an elongation of 22 pct, and upper shelf energy of 120 ft-lb, and a transition temperature of less than -40°C.

9. Modified alloys of commercially available steels are capable of achieving the design properties needed for coal gasification pressure vessel application.

Finally, in Task 5, Design Alloys, it has been concluded that

1. A V-Ni steel, is capable of good properties after isothermal treatment.

2. This steel does not exhibit interphase precipitation as initially anticipated. Therefore other eutectoid steels need to be investigated.

Table I. Schedule - FY1977

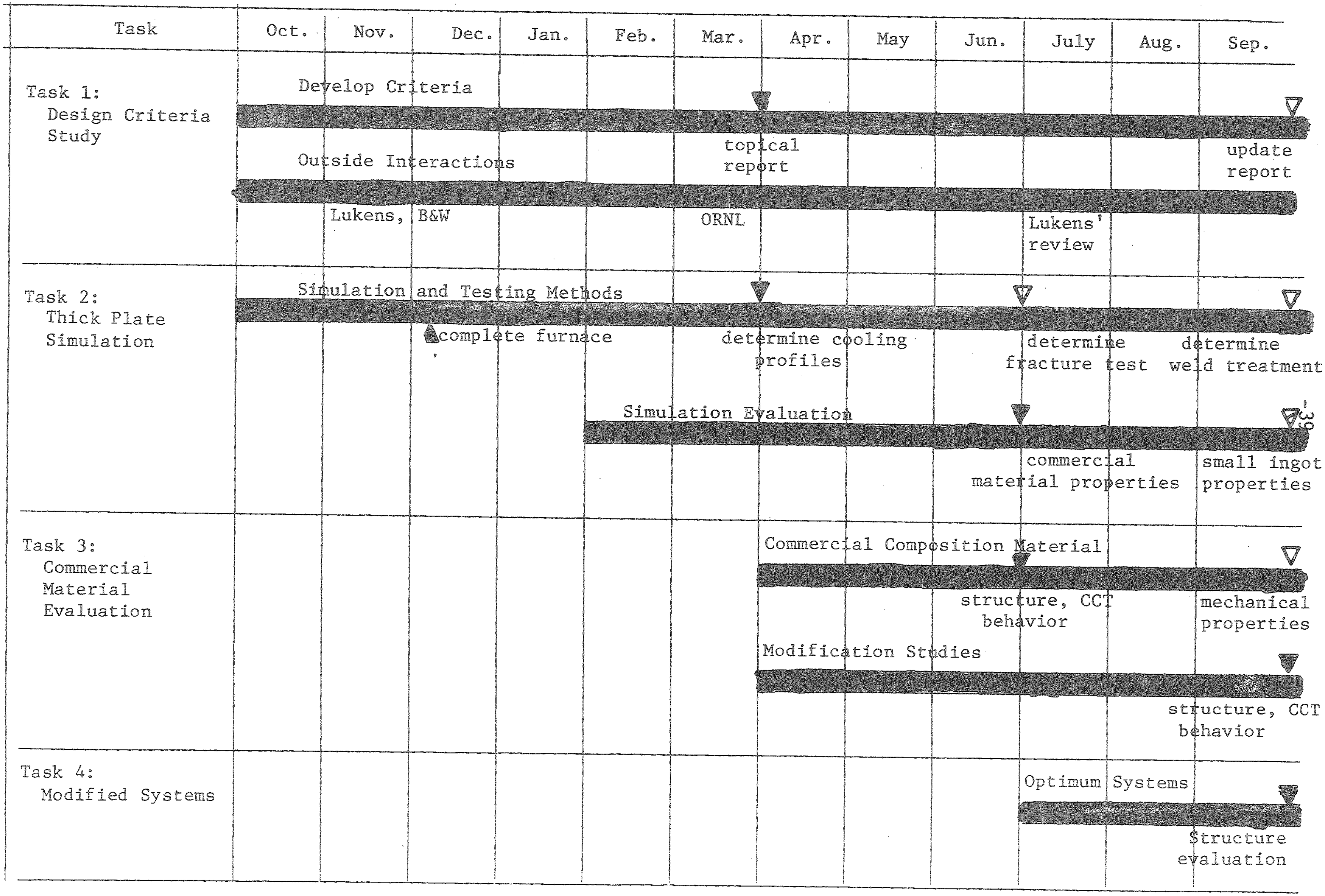


Table II.

Alloy Systems Presently Considered for Coal Gasification Pressure Vessels

Steel Identification[a]	SA533[d]	SA-542	A 543
Grade and Class	B	2	B, 1
Max Content and Range, wt %			
Carbon[b]	0.25	0.17	0.23
Manganese	1.15-1.50	0.27-0.63	0.40
Phosphorus	0.035	0.035	0.020
Sulfur	0.040	0.035	0.020
Silicon	0.15-0.30	0.50	0.20-0.35
Molybdenum	0.45-0.60	0.85-1.15	0.45-0.60
Nickel	0.40-0.70		3.00-4.00
Chromium		1.88-2.62	1.50-2.00
Max Available Plate Thickness m (in.)	c	c	c
Strength, MPa (ksi)			
Ultimate tensile	550-690	517-689	724-862
	(80-100)	(75-100)	(105-125)
Max Yield Point	345(50)	310(45)	586(85)
Max Elongation (in 2 in.), %	18	22	14
Max Reduction of Area, %		40	

[a]SA denotes ASME Section II Part A. A denotes ASTM specification.

[b]Maximum carbon content based on requirements for thickest plates.

[c]Maximum thickness is limited only by the capacity of the chemical composition to meet specified minimum mechanical properties.

[d]Forging grade SA508, class 2 is similar except for an additional 0.25-0.45% Cr and 0.05% V (max.).

Table III. Commercial Steel Chemistry
Alloy Addition (w/o)

Steel and Process History	C	Mn	Mo	Ni	Cr	Si	S	P	V	Al	Cu
A533B (B&W) - 6-in. quenched & tempered	0.20	1.30	0.54	0.61	-	0.17	0.015	0.010	-	-	-
A508, class 2 (B&W) - 14-in. quenched, tempered and stree-relieved	0.21	0.67	0.63	0.74	0.33	0.29	0.005	0.005	-	-	-
A533B (Lukens) - 10-in. normalized	0.22	1.32	0.57	0.65	-	0.20	0.007	0.009	-	0.036	0.07
A387 (Lukens) - 6-in. furnace cooled	0.10	0.41	1.06	-	2.28	0.21	0.019	0.008	-	0.003	-
A543 (Lukens via ORNL) - 10-in. quenched and tempered	0.17	0.33	0.57	3.40	1.65	0.25	0.014	0.019	0.02	0.019	0.16

Table IV. Commericial Tensile Property Evaluation

Steel & Heat Treatment	0.2% Y. S. (ksi)	UTS (ksi)	% Elong.(1")	% R.A.
A533B (B&W)				
Aust. @ 925 °C	66.0	89.3	25.7	68.6
Tempered @ 680 °C	66.4	89.5	25.3	69.7
A533B - Reheat Treated				
Aust. @ 900 °C	69.4	93.3	24.5	65.4
Tempered @ 625 °C	77.6	100.0	24.3	63.4
A508 (B&W)				
Aust. @ 895 °C	59.3	83.3	26.8	70.3
Tempered @ 670 °C	58.7	82.7	28.4	73.3
Stress Relieved @ 625 °C				
A508 - Reheat Treated				
Aust. @ 900 °C	71.4	93.2	22.6	61.9
Tempered @ 625 °C	73.3	94.4	22.9	58.9
A387 - Reheat Treated-8", 1/4T	81.4	95.4	23.7	78.4
Aust. @ 1000 °C				
Tempered @ 650 °C				
A387 - Developmental-8", 1/4T*	81.4	114.6	18.5	54.9
Aust. @ 900 °C	77.8	110.4	20.3	55.1
Tempered @ 625 °C				
A543 -10", 1/4T	--	115.0	22.1	67.8
Aust. @ 900 °C	102.9	117.1	24.4	65.9
Tempered @ 625 °C				
A543 - 10", 1/2T				
Aust. @ 900 °C	99.2	112.7	22.7	70.6
Tempered @ 625 °C	101.9	115.9	21.6	69.8

* Developmental Ingot - C = .17; Mn = .41, Mo = .92, Cr = 2.1; A387 and A542 have same composition specifications.

Table V. Modified Alloys Based on Mn - Mo - Ni Steel (A533B)

Alloy Additions (w/o)

Type	C	Mn	Mo	Ni	Cr	Si	S (max)	P (max)
Si	.24	1.44	0.6	0.6	-	0.97	0.01	0.01
high Si	.19	1.38	0.6	0.68	-	1.94	0.01	0.01
Si*	.22	0.64	0.51	0.6	-	0.92	0.01	0.01
high Si*	.22	1.40	0.6	0.6	-	1.91	0.01	0.01
Mn*	.17	1.73	0.6	0.6	-	.25	0.01	0.01
high Mn*	.20	2.02	0.6	0.6	-	.25	0.01	0.01
Cr*	.22	1.42	0.6	0.6	1.01	.25	0.01	0.01
Cr-Si*	.23	1.33	0.6	0.6	1.04	0.97	0.01	0.01
Cr-Mn*	.22	1.92	0.6	0.6	1.01	0.26	0.01	0.01
Cr-Si-Mn*	.22	1.87	0.6	0.6	0.99	1.05	0.01	0.01

* Grain Refined with 0.02 w/o Al and 0.03 w/oV.

Table VI. Tensile Properties for Cr or Mn Additions - A533B Steel

Type	0.2% Y.S. (ksi)	UTS (ksi)	%Elong.(1")	% R. A.
Base with	86.6	104.0	21.6	69.5
1% Cr	85.1	103.7	25.3	74.2
Base with	75.2	94.4	23.0	60.9
0.5% Mn	72.9	86.9	24.5	65.0
Base with	72.7	98.7	25.4	61.4
1.0% Mn	67.0	93.8	23.9	60.9

Grain refined,

Aust @ 925°C, 1/2 hour

Immersion quenched, 8", 1/4T location

Tempered @ 675°C, 4 hours.

Table VII - Tensile Properties for Si Additions - A533B Steel

Type	0.2% Y.S. (ksi)	UTS (ksi)	Elong (%1")	%R. A.
Base with *	98.4	126.5	18.2	55.4
1% Si	98.0	131.1	19.3	50.7
Base with *	87.5	118.3	20.5	51.9
2% Si	86.8	116.8	23.8	58.3
Base with **	70.2	92.2	26.7	61.9
1% Si	73.3	94.4	23.8	61.6
Base with **	79.8	104.6	24.5	61.4
2% Si	86.6	108.4	24.1	60.7

* Aust @ 900°C, 1/2 hour
Immersion quenched, 8", 1/4T location
Tempered @ 625°C, 1 hour

** Grain refined; Aust @ 925°C, 1/2 hour
Immersion quenched, 8", 1/4 T location
Tempered at 675°C, 4 hours

Table VIII. - Tensile Properties for Combined Alloy Additions - A533B Steel

Type	0.2% Y.S.(ksi)	UTS (ksi)	Elong.(%1")	%R. A.
Base with	89.6	109.4	24.6	71.5
1 Cr-0.75 Mn	91.0	109.8	23.7	70.5
Base with	94.5	118.0	21.6	67.8
1 Cr-0.75 Si	93.8	117.4	22.6	68.1
Base with	97.6	119.4	21.6	68.9
1 Cr-0.75 Si-0.75 Mn	98.1	119.9	24.7	68.1

Grain refined
Aust. @ 925°C, 1/2 hour
Immersion quenched, 8", 1/4T location
Tempered @ 675°C, 4 hours

Table IX - Composition for Full Scale Evaluation
Mn - Mo - Ni (A533B Type) Steels*

Type	C	Mn	Mo	Ni	Cr	Si	S	P	V	Al
	Alloy Content (%)									
high Mn	0.22	2.0	0.55	0.60	-	0.25	0.01	0.01	0.03	0.02
high Cr	0.22	1.3	0.55	0.60	1.0	0.25	0.01	0.01	0.03	0.02
high Mn-Cr	0.22	2.0	0.55	0.60	1.0	0.25	0.01	0.01	0.03	0.02
high Mn-Cr-Si	0.22	2.0	0.55	0.60	1.0	1.0	0.01	0.01	0.03	0.02

* all ingots are grain refined

Table X - Modified Alloys Based on Single Element Changes
in Cr - Mo (A542 type) Steel

	Alloy Content (%)							
Type	C	Mn	Mo	Ni	Cr	Si	S (maximum)	P (maximum)
Mo	0.19	0.44	1.13	-	2.44	0.48	0.01	0.01
Cr	0.17	0.44	0.92	-	3.15	0.41	0.01	0.01
Ni	0.16		0.84	0.49	2.35	0.44	0.01	0.01
Mn	0.20	0.92	0.90	-	2.52	0.44	0.01	0.01

Table XI - Modified Alloys Based on High Ni/Mn Additions - Cr - Mo (A542 type) Steel

	Alloy Content (%)							
Type	C	Mn	Mo	Ni	Cr	Si	S (maximum)	P (maximum)
high Ni	0.20	0.37	1.0	1.04	2.10	0.50	0.01	0.01
high Ni*	0.18	0.43	0.94	0.95	2.07	0.45	0.01	0.01
high Mn*	0.19	1.41	0.94	-	2.15	0.48	0.01	0.01
Ni + Mn	0.18	0.82	0.92	0.49	2.16	0.45	0.01	0.01
high Ni+Mn*	0.18	0.90	0.94	0.99	2.16	0.48	0.01	0.01
high Ni, Mn, Cr*	0.18	0.93	0.92	0.98	3.09	0.45	0.01	0.01
high Mn-high Ni Si	0.18	1.35	0.94	1.0	2.13	1.42	0.01	0.01

* Grain refined with Al, Nb

Table XII - Tensile Properties for Single Element Addition to Cr - Mo (A542 type) Steel

Modification* and Heat Treatment	0.2% Y.S. (ksi)	UTS (ksi)	Elong. (%)	R.A. (%)
0.5% Ni Addition				
8Q	94.0	111.5	21.4	75.0
12Q	94.0	112.3	21.9	67.9
8AC	94.4	112.5	22.5	73.0
0.5% Mn Addition				
8Q	95.0	112.2	19.4	70.6
12Q	92.8	110.5	22.5	74.6
8AC	95.5	112.7	19.1	62.2
0.5 w/o Cr Addition				
8Q	94.2	111.8	23.1	74.0
12Q	93.6	110.3	18.1	73.0
8AC	90.7	108.7	19.7	63.4
0.5 w/o Mo Addition				
8Q	101.8	118.3	20.2	70.1
12Q	95.6	119.5	17.0	53.2
8AC	93.8	114.3	21.0	71.2

* All material austenitized at 1000°C, and tempered at 650°C for 4 hours. Cooling process is indicated by identity with number representing thickness and Q, immersion quenching; AC air cool.

Table XIII - Tensile Properties for Mi/Mn Additions to Cr - Mo (A542 type) Steels

Type	0.2% Y.S. (ksi)	UTS (ksi)	Elong.(%)	R. A. (%)
high Ni	103.1 98.9	120.7 116.8	22.1 22.3	75.6 72.3
high Ni*	99.3 100.4	115.2 116.1	22.2 21.6	76.8 78.6
high Mn*	98.2 99.3	113.8 115.8	22.4 23.7	74.6 74.8
Ni + Mn	88.9 88.2	108.3 107.8	23.6 23.1	76.0 73.5
high Ni + Mn*	102.2	118.4	21.6	71.4
high Ni, Mn, Cr*	90.2 90.4	111.4 110.6	24.5 23.0	74.4 77.7
high Ni, high Mn, Si	98.6 101.8	122.5 125.4	18.4 20.5	65.0 64.0

Aust. @ 1000°C, 1 hour
Immersion quenched, to represent 8", 1/4T location
Tempered @ 650°C, 4 hours.

* Grain refined

Table XIV - Composition of Modified Alloys for Thorough Study - Cr - Mo (A542 type) Steels

	Alloy Content (w%)							
Type	C	Mn	Mo	Ni	Cr	Si	S (maximum)	P (maximum)
Base	0.15	.45	1.0	-	2.25	0.3	0.01	0.01
Mn	0.15	1.45	1.0	-	2.25	0.3	0.01	0.01
Ni, Mn	0.15	0.95	1.0	0.5	2.25	0.3	0.01	0.01
Ni, Mn*	0.15	0.95	1.0	0.5	2.25	0.3	0.01	0.01
high Ni, Mn*	0.15	0.95	1.0	1.0	2.25	0.3	0.01	0.01
high Ni, Mn Cr*	0.15	0.95	1.0	1.0	3.0	0.3	0.01	0.01

* Grain refined with 0.03% Al and 0.02% V.

Table XV - Alloys - Temper Embrittlement Study
(A543 Type Steels)

Type	C	Mn	Ni	Mo	Cr	S	P	B	N	Al
Commercial	0.17	0.33	3.4	0.57	1.65	0.014	0.019	-	-	0.019
Commercial* (Remelt)	0.17	0.33	3.4	0.57	1.65	0.014	0.019	-	-	0.019
Remelt* with Boron	0.17	0.33	3.4	0.57	1.65	0.014	0.019	0.005	-	0.019
Remelt* with nitrogen	0.17	0.33	3.4	0.57	1.65	0.014	0.019	-	0.015	0.019

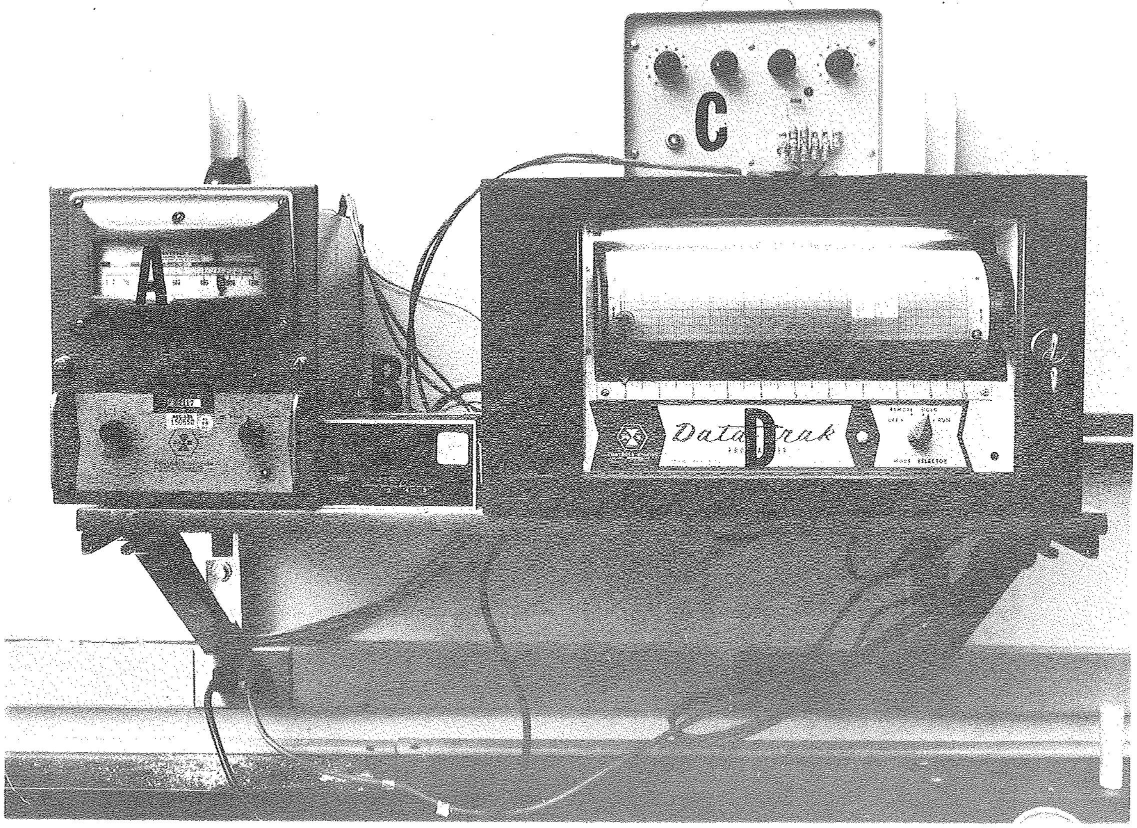
*Anticipated

Heat Treatment:

Aust. @ 900°C, 2 hours
Oil quenched
Tempered @ 625°C, 3-1/2 hours
Oil quenched
Aged @ 490°C (900°F) for various times

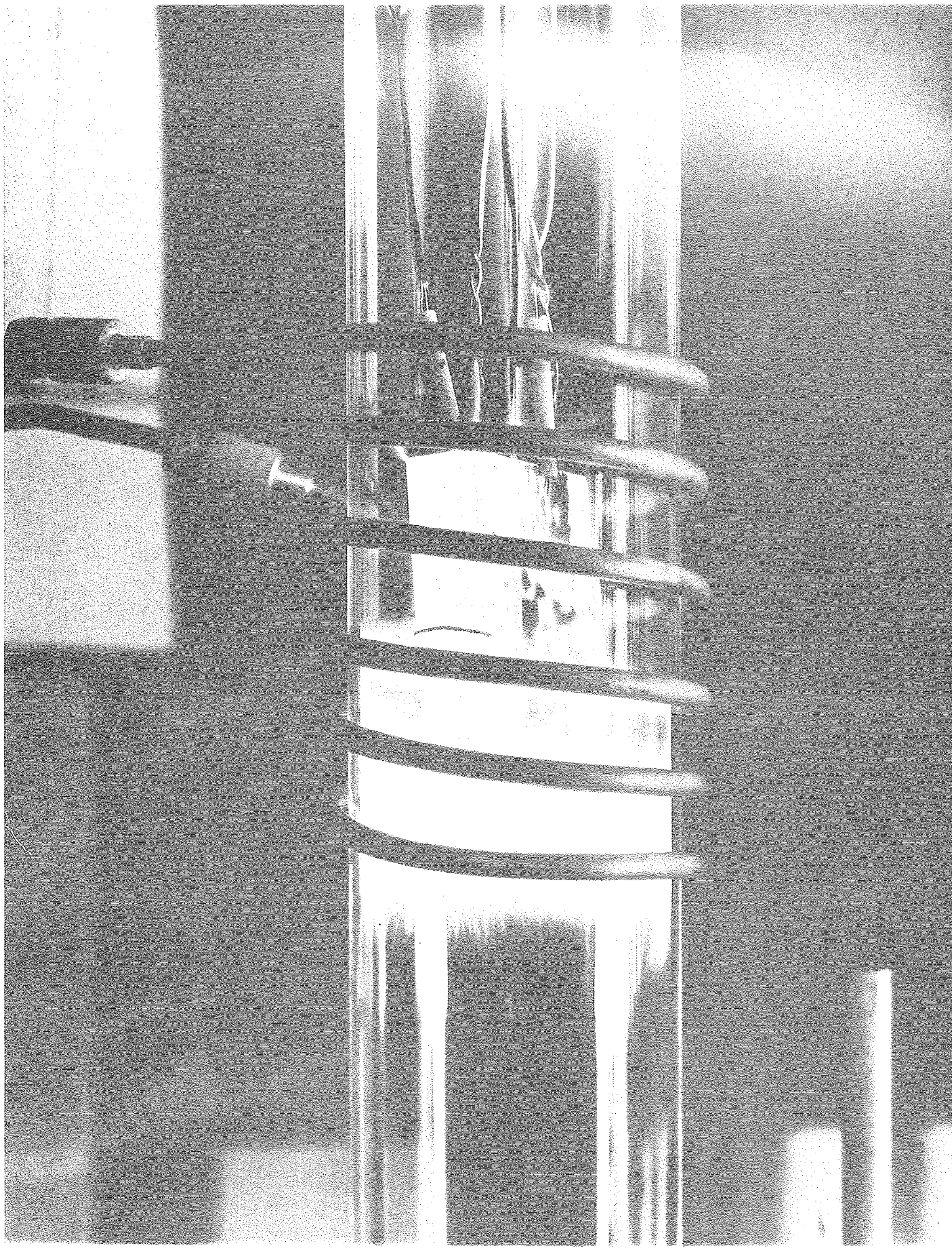
Table XVI. Compositions for Eutectoid Steels

	Alloy Additions(w/o)				
Type	C	Mo	Si	Mn	Ni
Mo-Si	0.21	0.96	1.01	0.95	-
High Mo-Si	0.22	1.92	0.95	0.45	-
High Si-Mo	0.18	0.99	1.86	0.47	-
Mo-Si-Ni	0.21	0.96	0.97	0.48	1.98



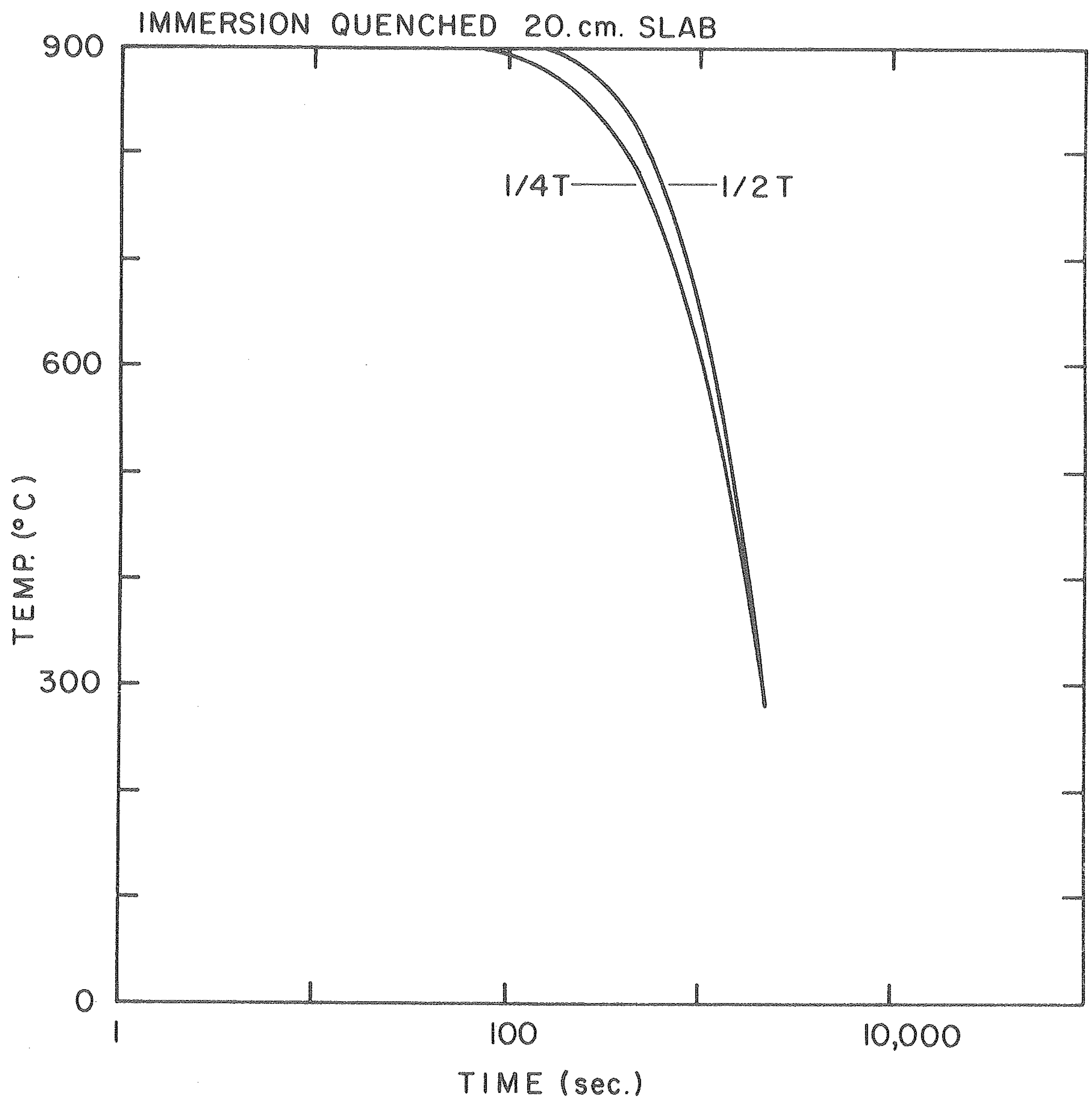
XBB 771-141

Figure 1. Added control features used to obtain programmed temperature control of the furnace. Shown are controller (A), temperature readout (B), added proportional control unit (C), and Datatrak programmer (D).



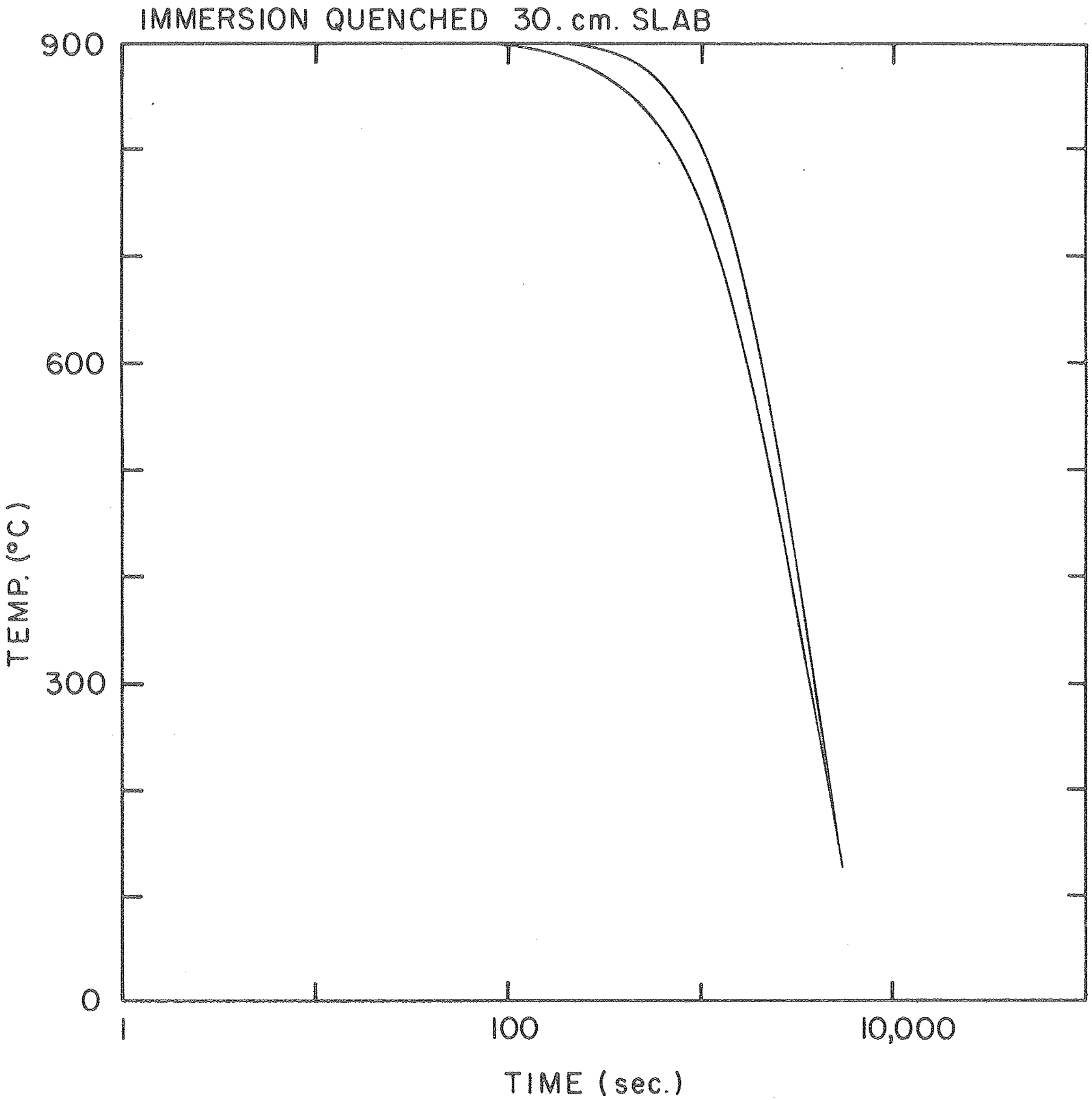
XBB 771-139

Figure 2. Close-up of heated specimen in induction field. Feedback thermo-couples are shown.



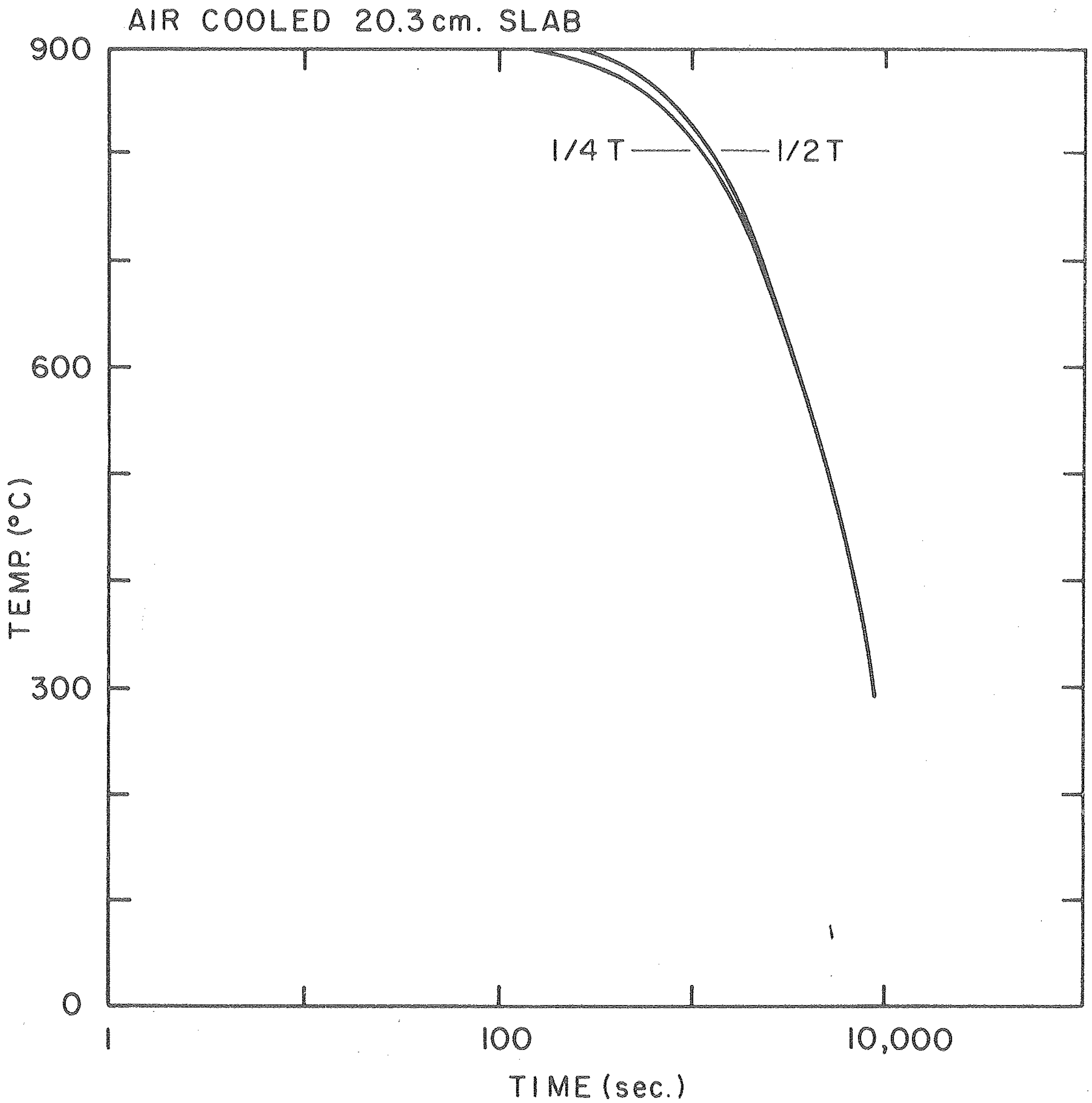
XBL 781-6851

Figure 3. Computer determined rates for 1/4T and 1/2T locations in 8-in. (20 cm) slab immersion quenched. H=0.006 cal-gm/sec-cm^2-°C and ε=0.2.



XBL 781-6859

Figure 4. Computer determined rates for 1/4T and 1/2 locations in 12-in. (30 cm) slab immersion quenched.



XBL 781-6850

Figure 5. Computer determined rates for 1/4T and 1/2T locations in 8-in. (20 cm) air cooled slab. H=0.0008 cal-gm/sec-cm^2-°C and ε=0.5.

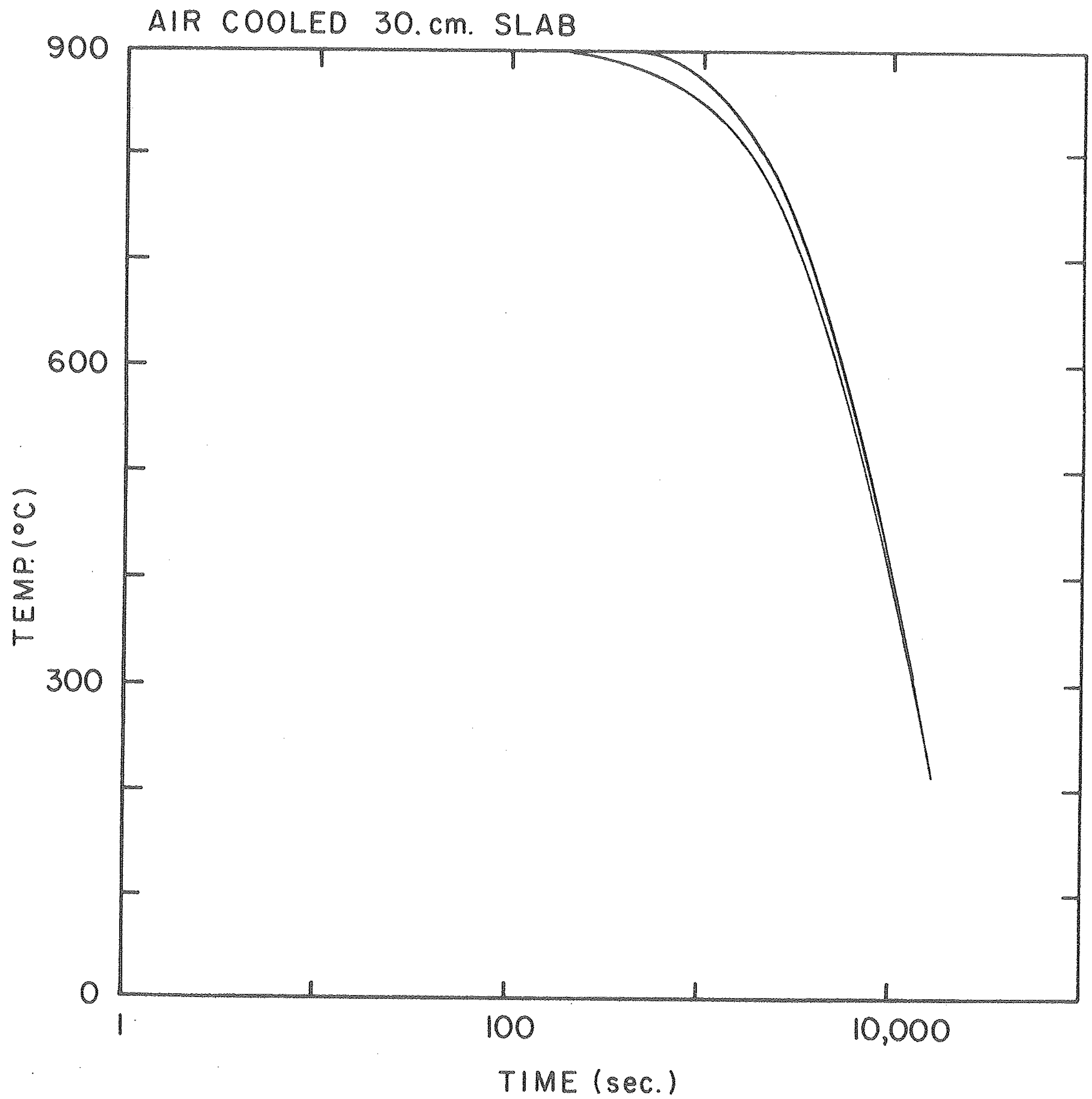
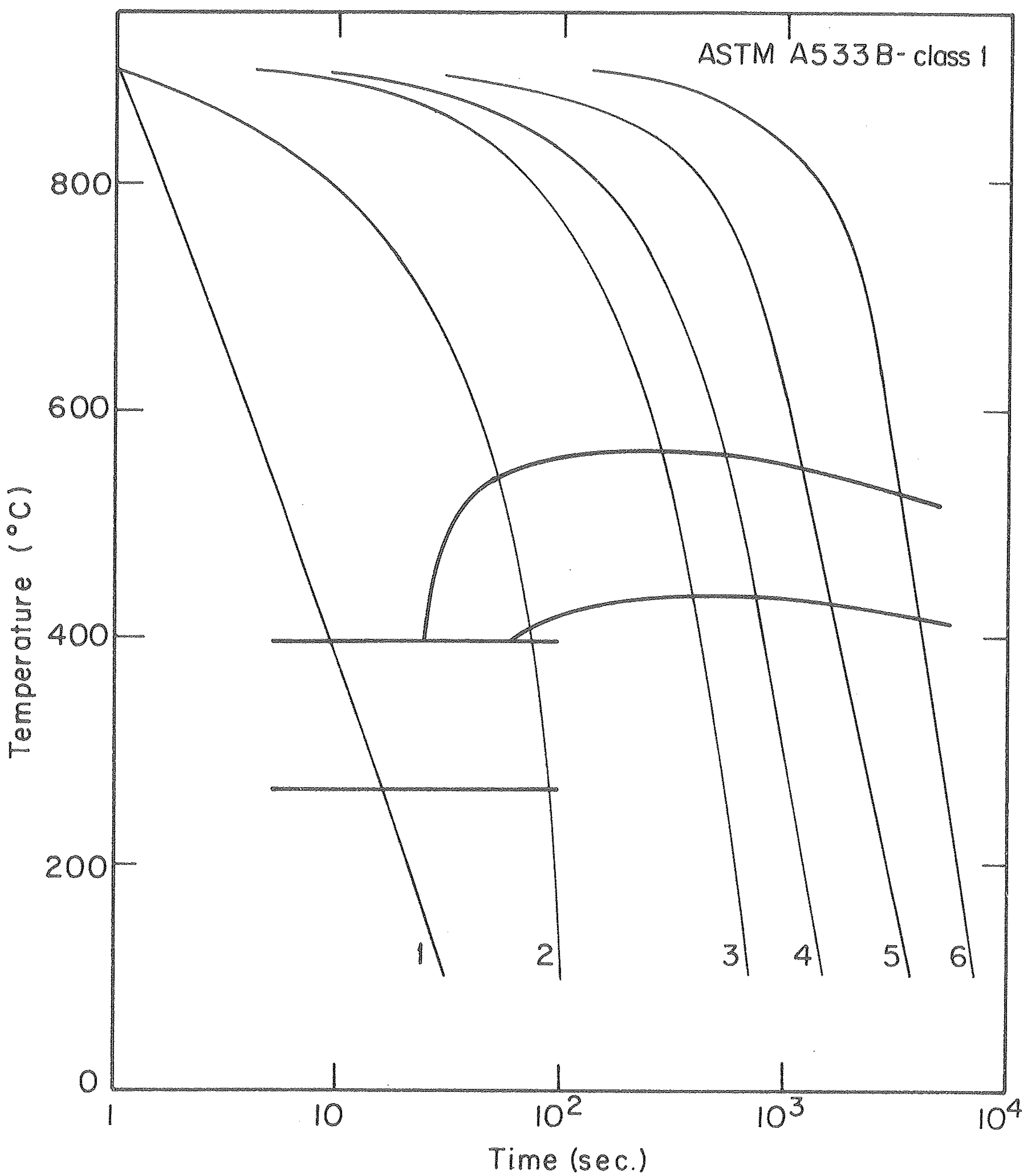


Figure 6. Computer determined rates for 1/4T and 1/2TXBL 781-6860 locations in 12-in (30 cm) air cooled slab.



XBL 7710-6329

Figure 7. Continuous cooling transformation diagram for Nominal A533B steel (Mn-Mo-Ni base).

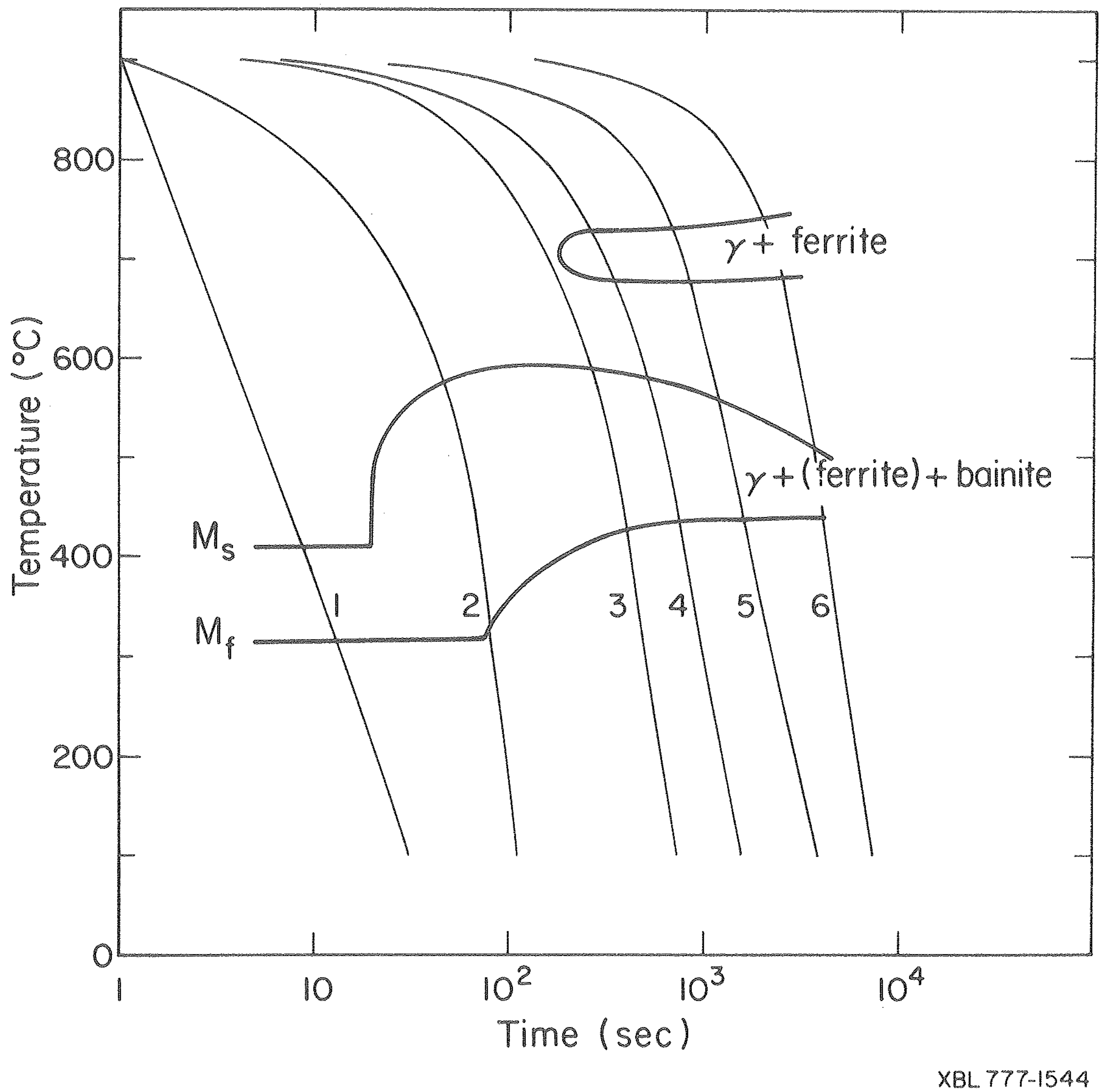


Figure 8. Continuous cooling transformation diagram for Nominal A508, class 2 steel (Mn-Mo-Ni-Cr base).

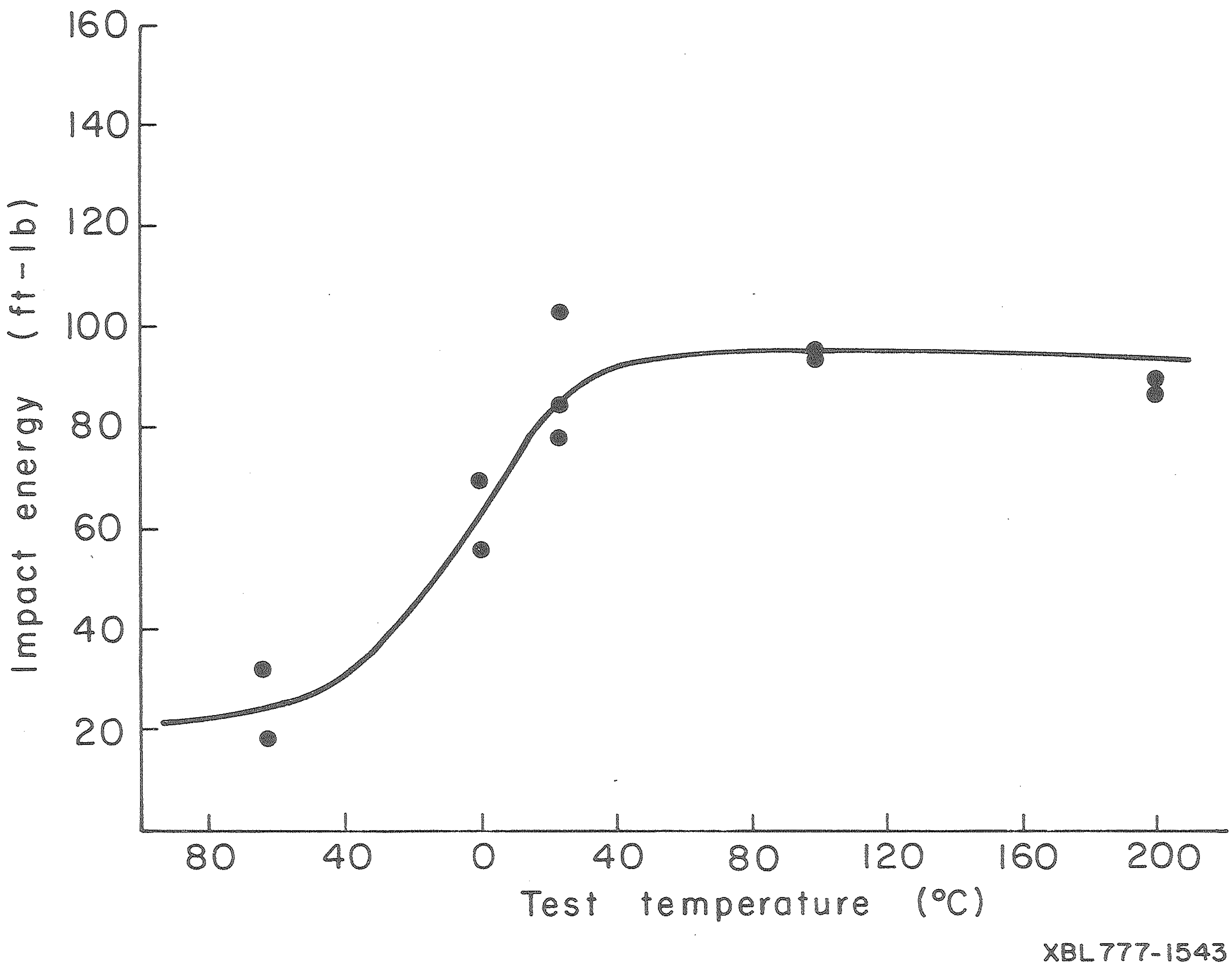


Figure 9. Charpy impact energy as a function of test temperature for nominal A533B steel.

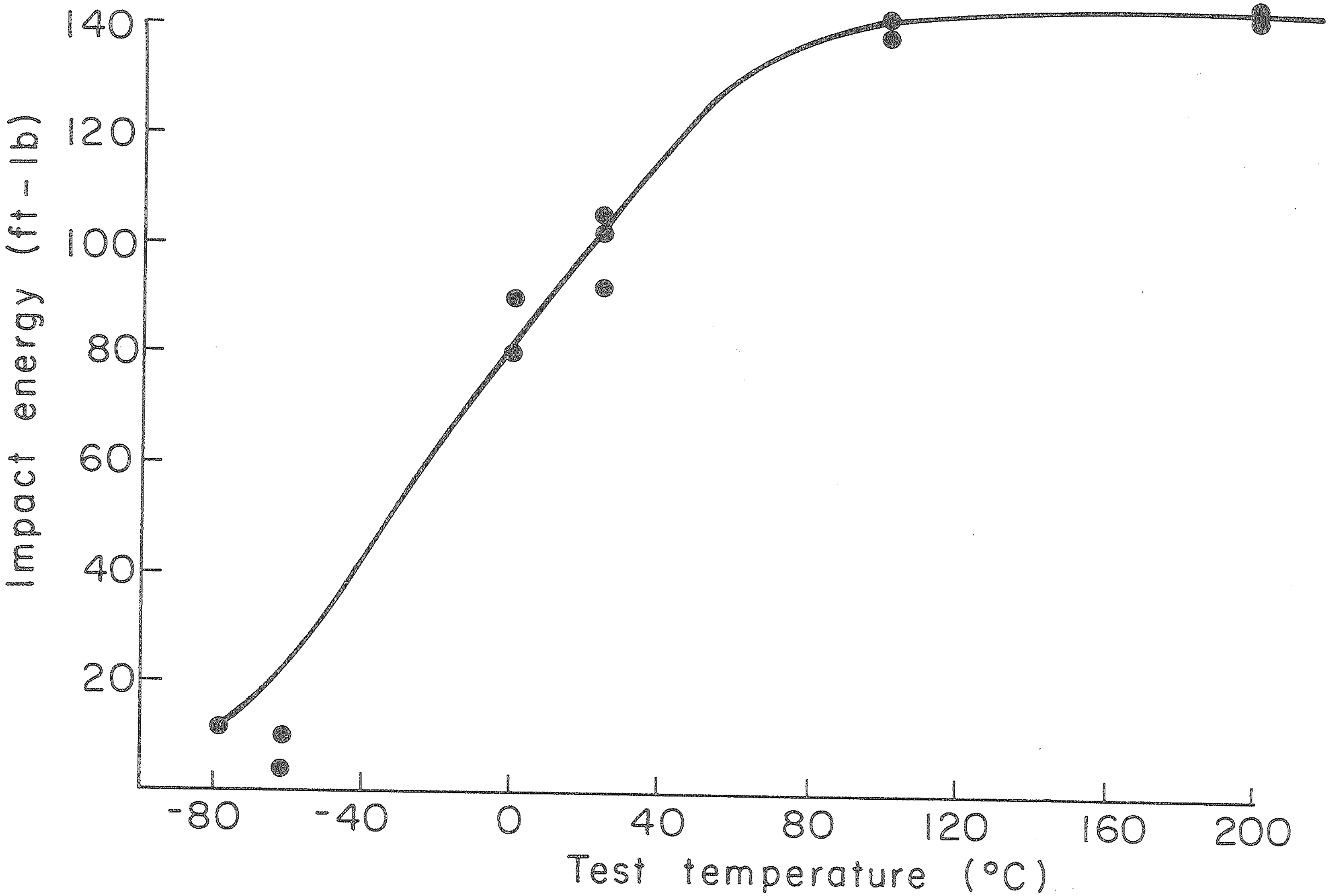
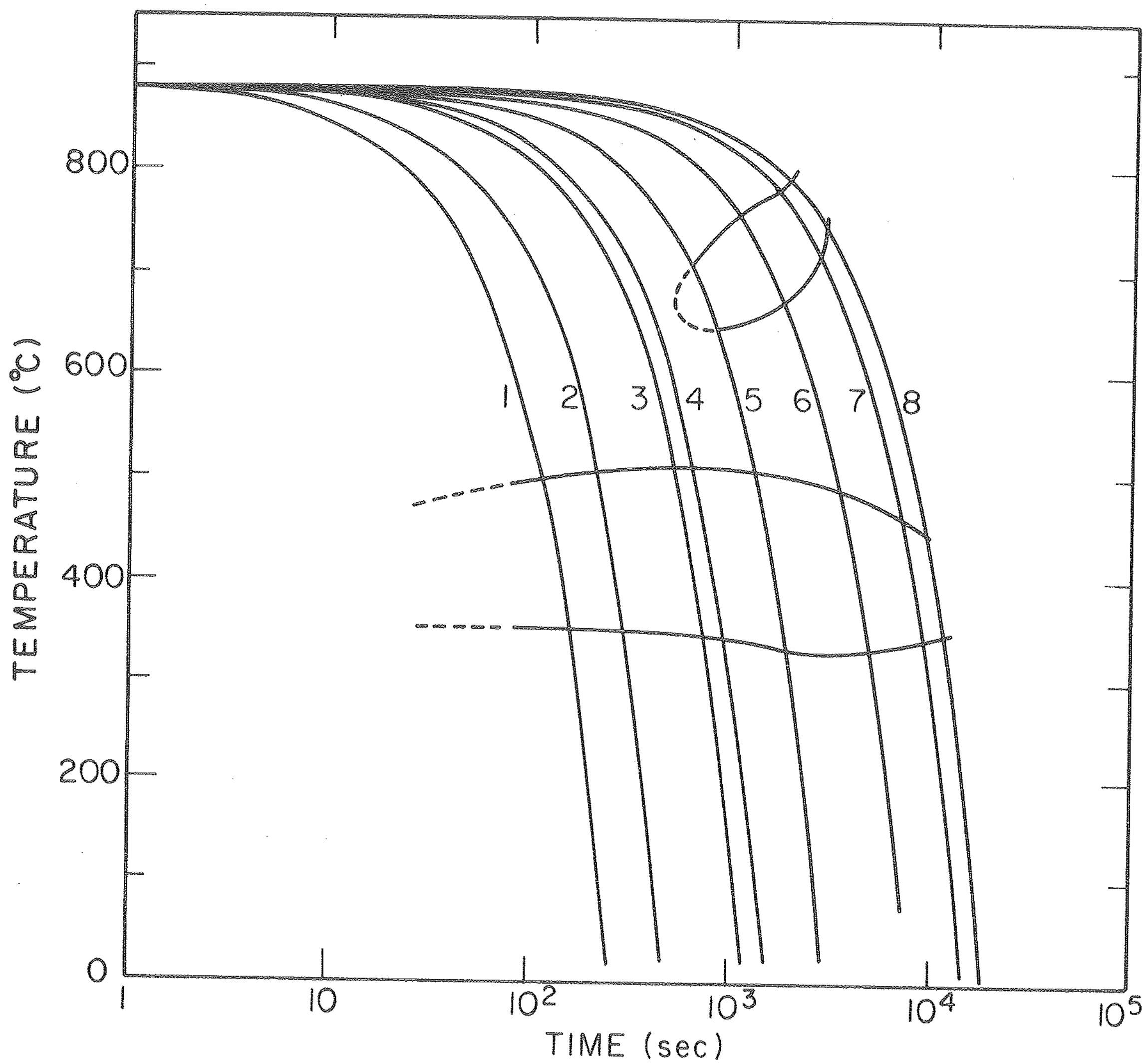
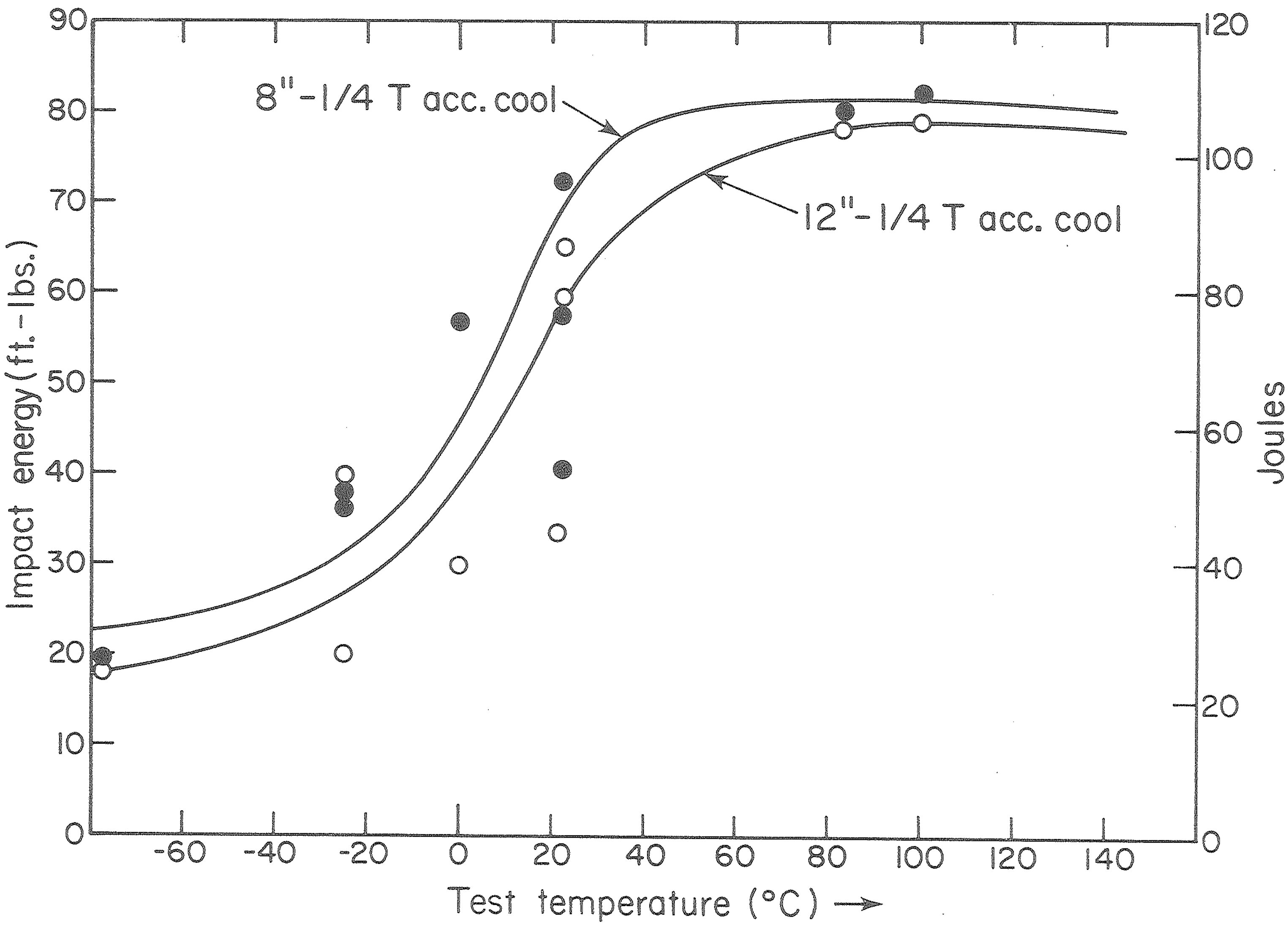


Figure 10. Charpy impact energy as a function of test temperature for nominal A508, class 2 steel.



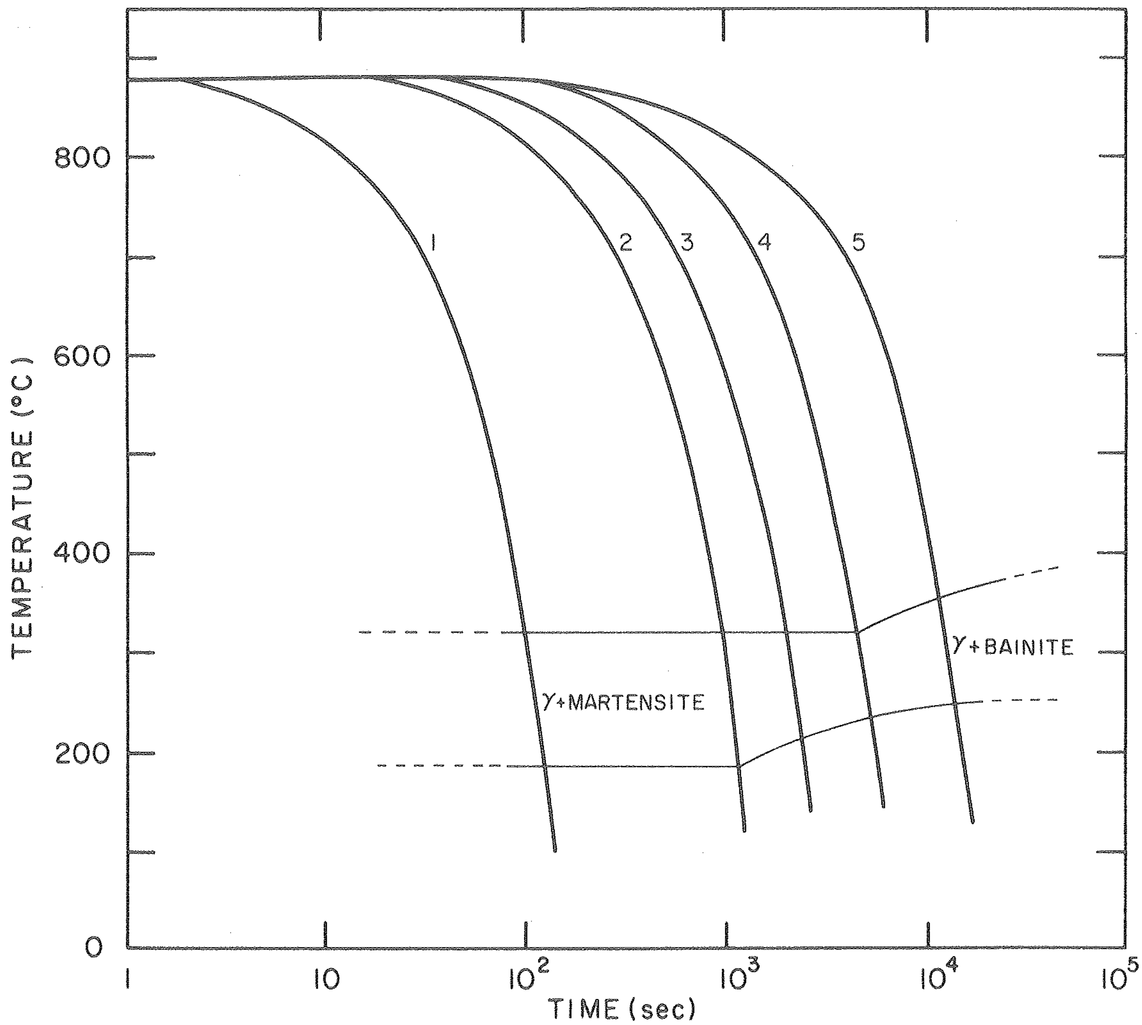
XBL 771-4983

Figure 11. Continuous cooling transformation diagram for nominal A542 steel (Cr-Mo base).



XBL777-1538

Figure 12. Charpy V-notch impact energy vs. test temperature for commercial A542 reheat treated to represent 8" and 12" accelerated cool sections.



XBL 781-6848

Figure 13. Continuous cooling transformation diagram for nominal A543.

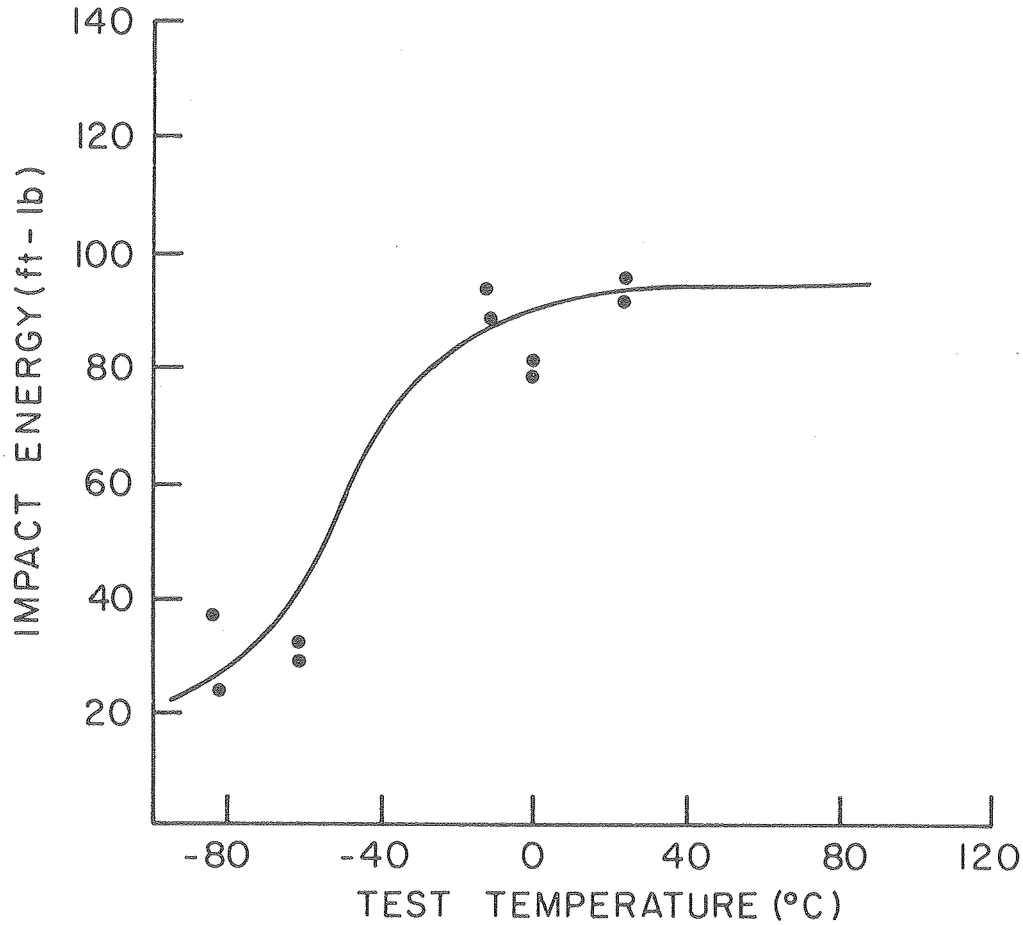


Figure 14. Charpy V-notch impact energy vs. test temperature for commercial A543 steel.

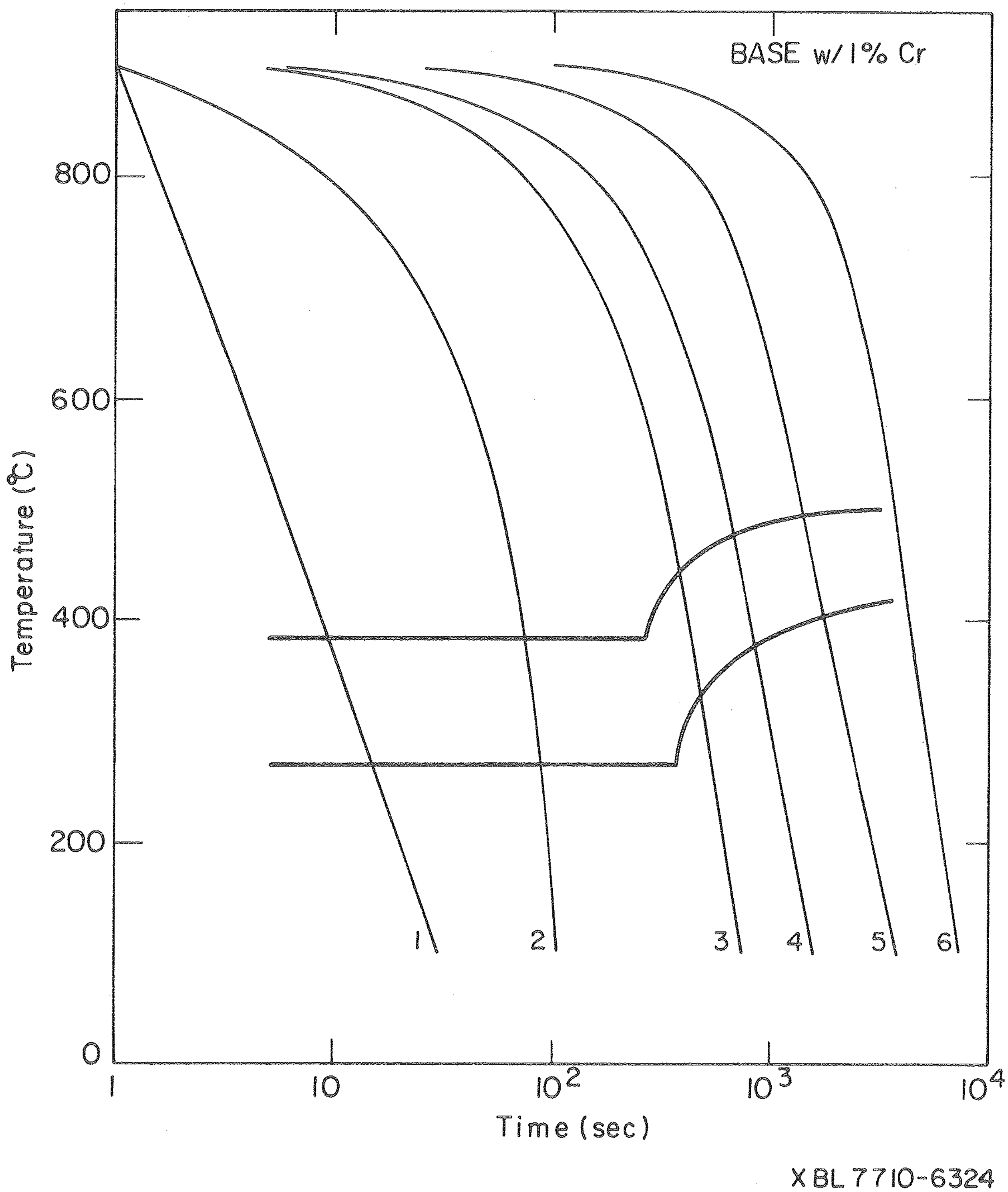
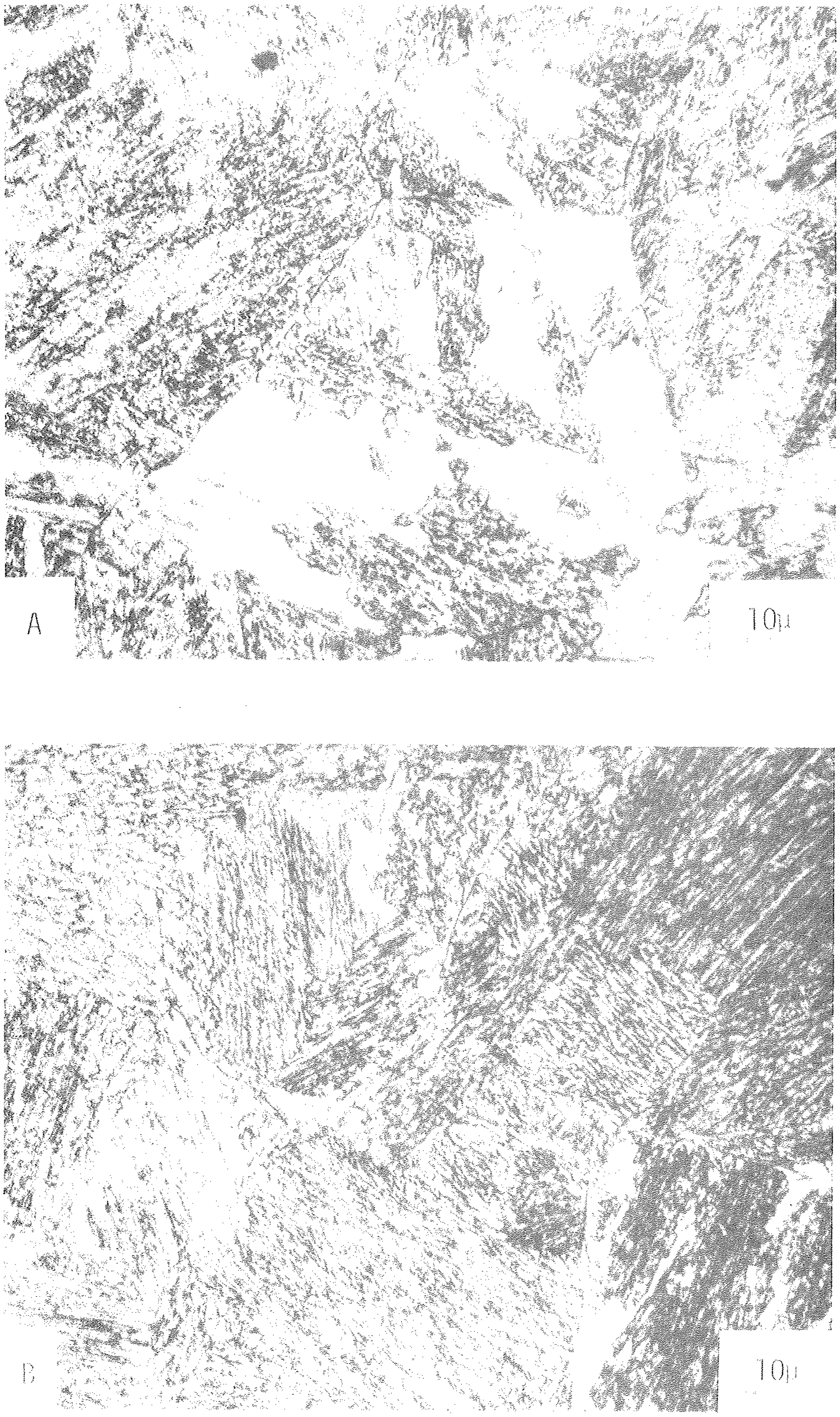
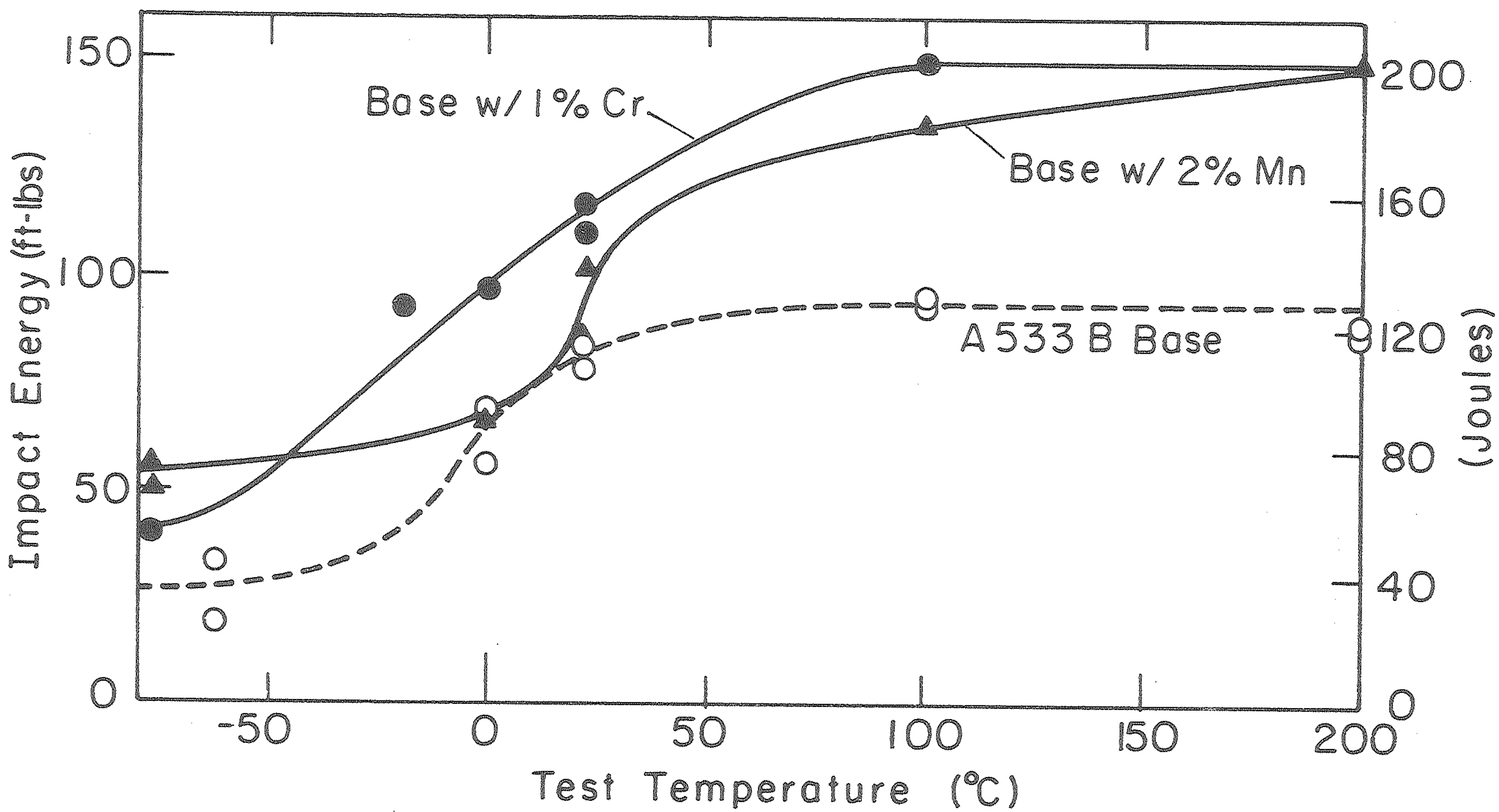


Figure 15. Continuous cooling transformation diagram for Mn-Mo-Ni steel (A533B) modified with 1% Cr and grain refined.



XBB 770-10709

Figure 16. Micrographs of Mn-Mo-Ni alloys (a) modified with 1% Cr and (b) modified with 1% Cr, 1% Si. Both structures cooled to represent 8", 1/4T accelerated cooling path. Both structures are bainitic.



XBL 7710-6323

Figure 17. Charpy impact energy versus test temperature for A533B Base steels modified with (1) Cr and (2) Mn. (Base line data shown).

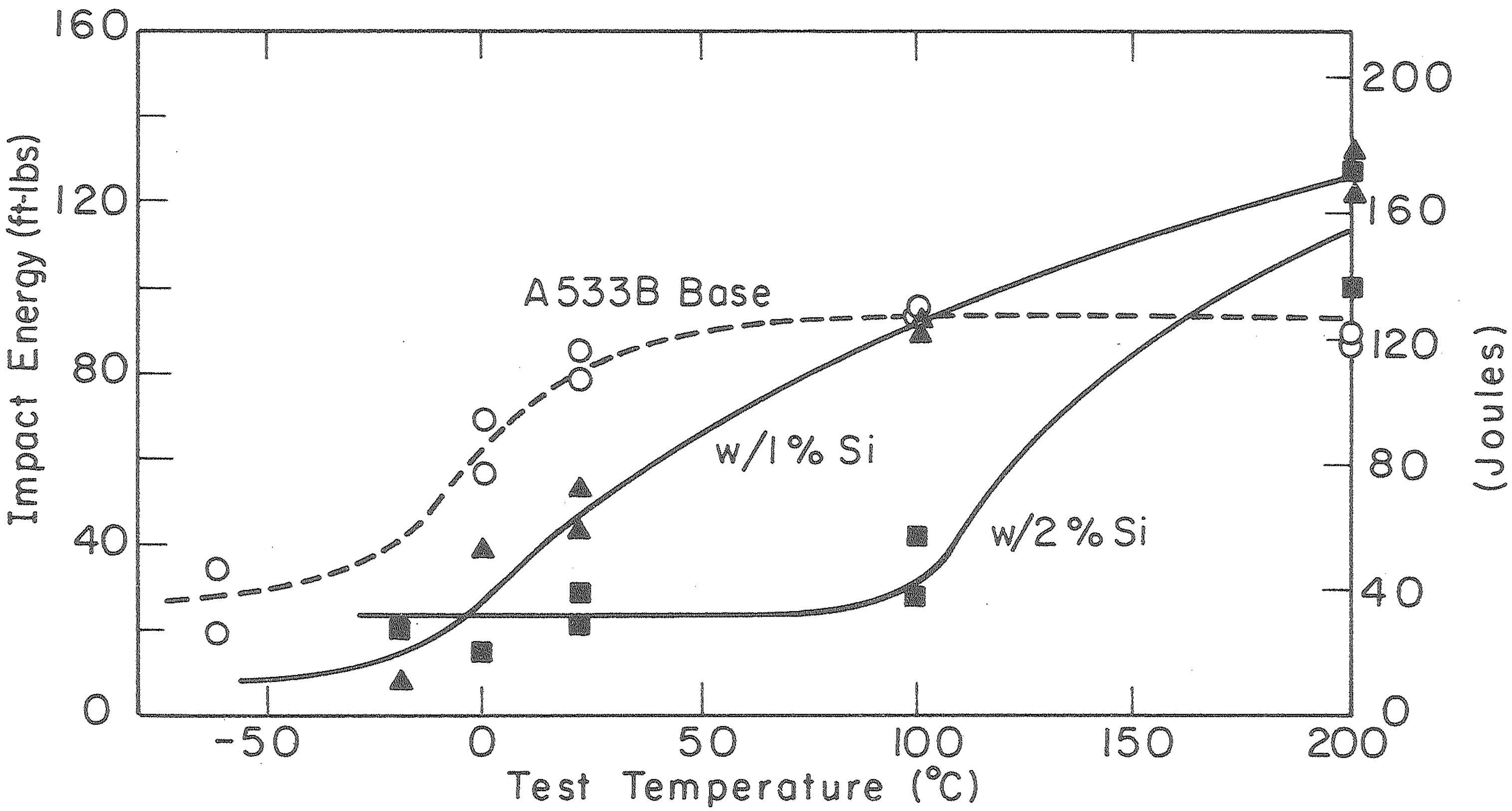
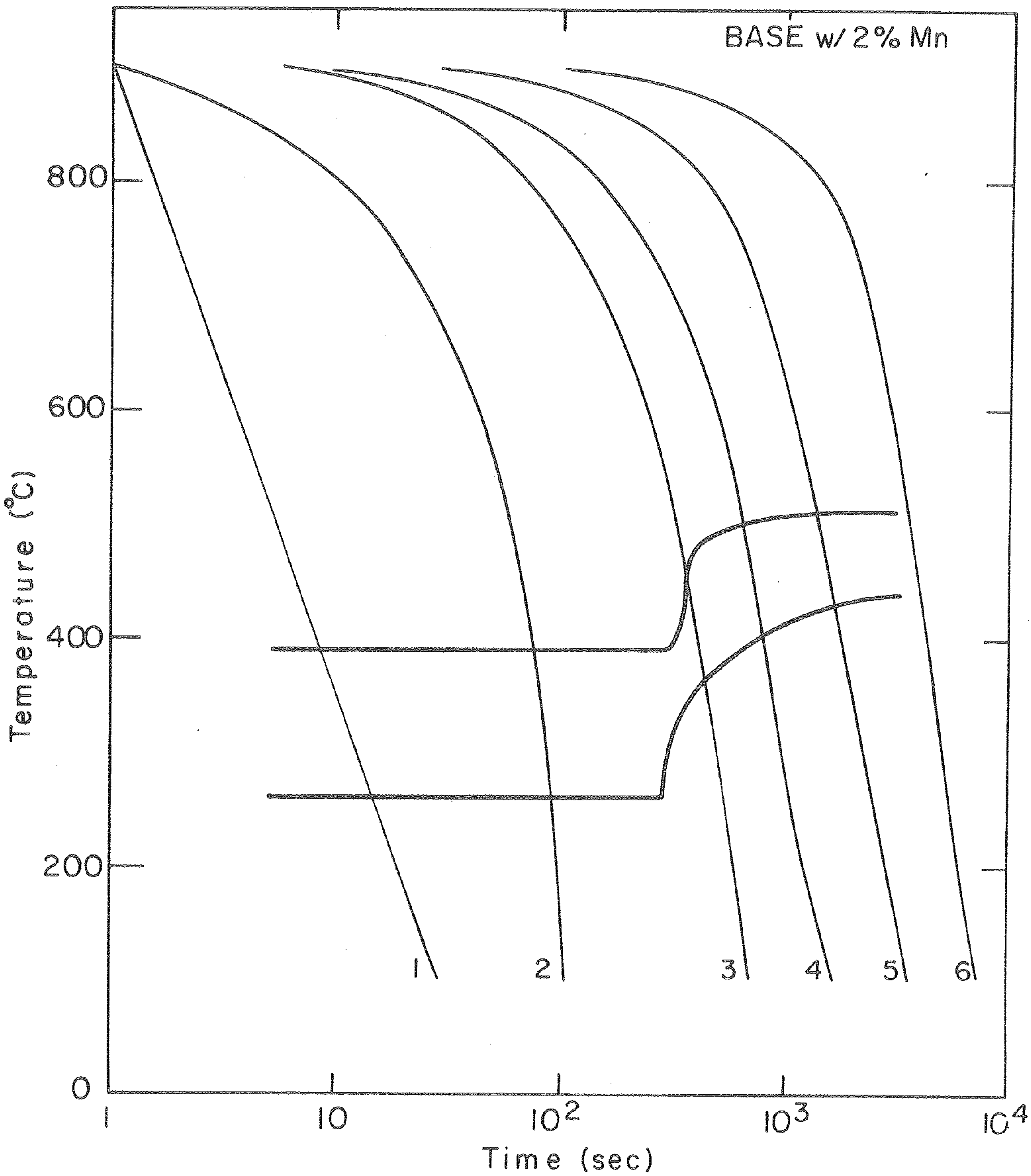


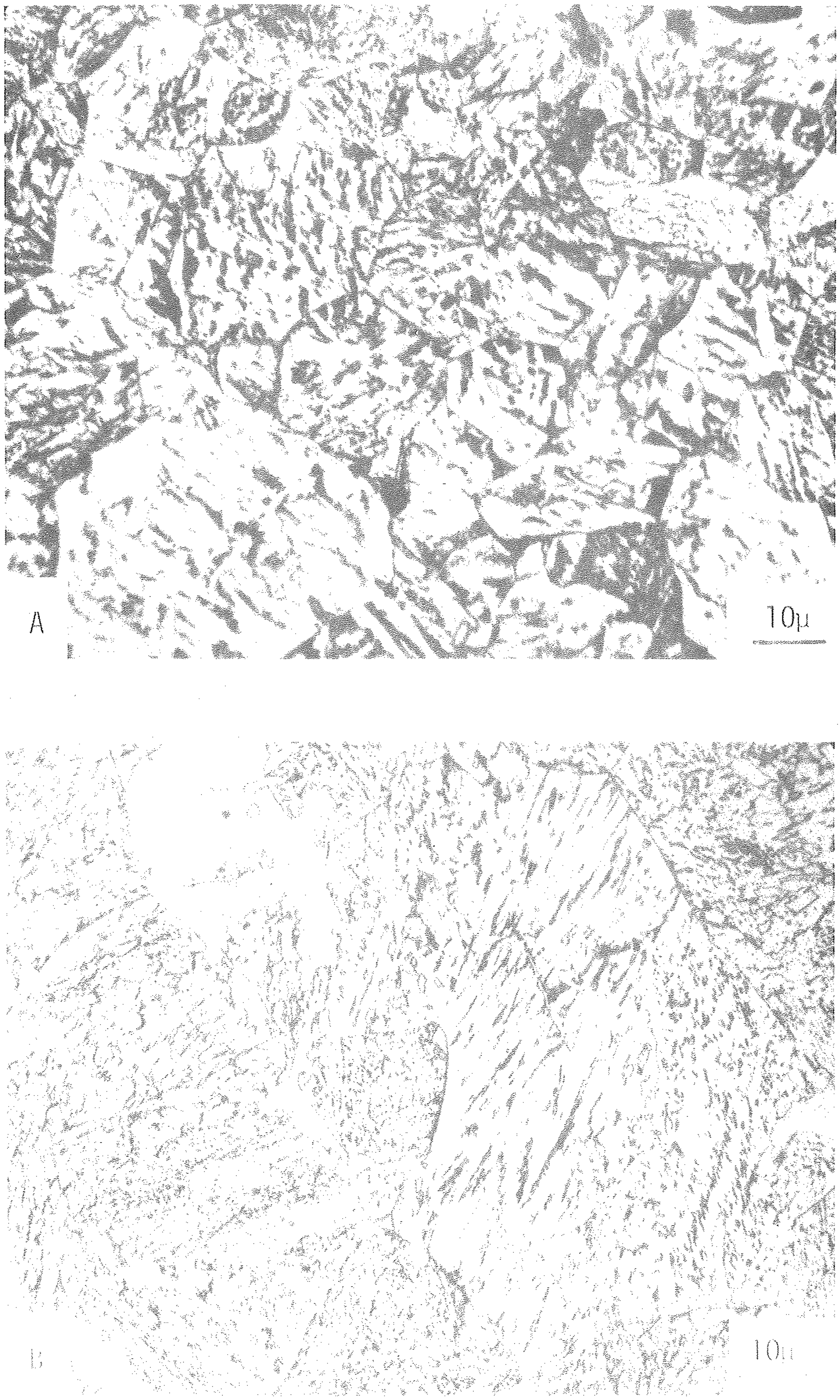
Figure 18. Charpy impact energy versus test temperature for A533B steel modified with Si.

XBL 7710-6328



XBL 7710-6326

Figure 19. Continuous cooling transformation diagram for Mn-Mo-Ni steel modified with 2% Mn grain refined.



XBB 770-10708

Figure 20. Micrographs of 8", 1/4T accelerated cooled structures in A533B steel. Structures are bainitic (a) base steel, (b) base steel modified with 0.75% Mn.

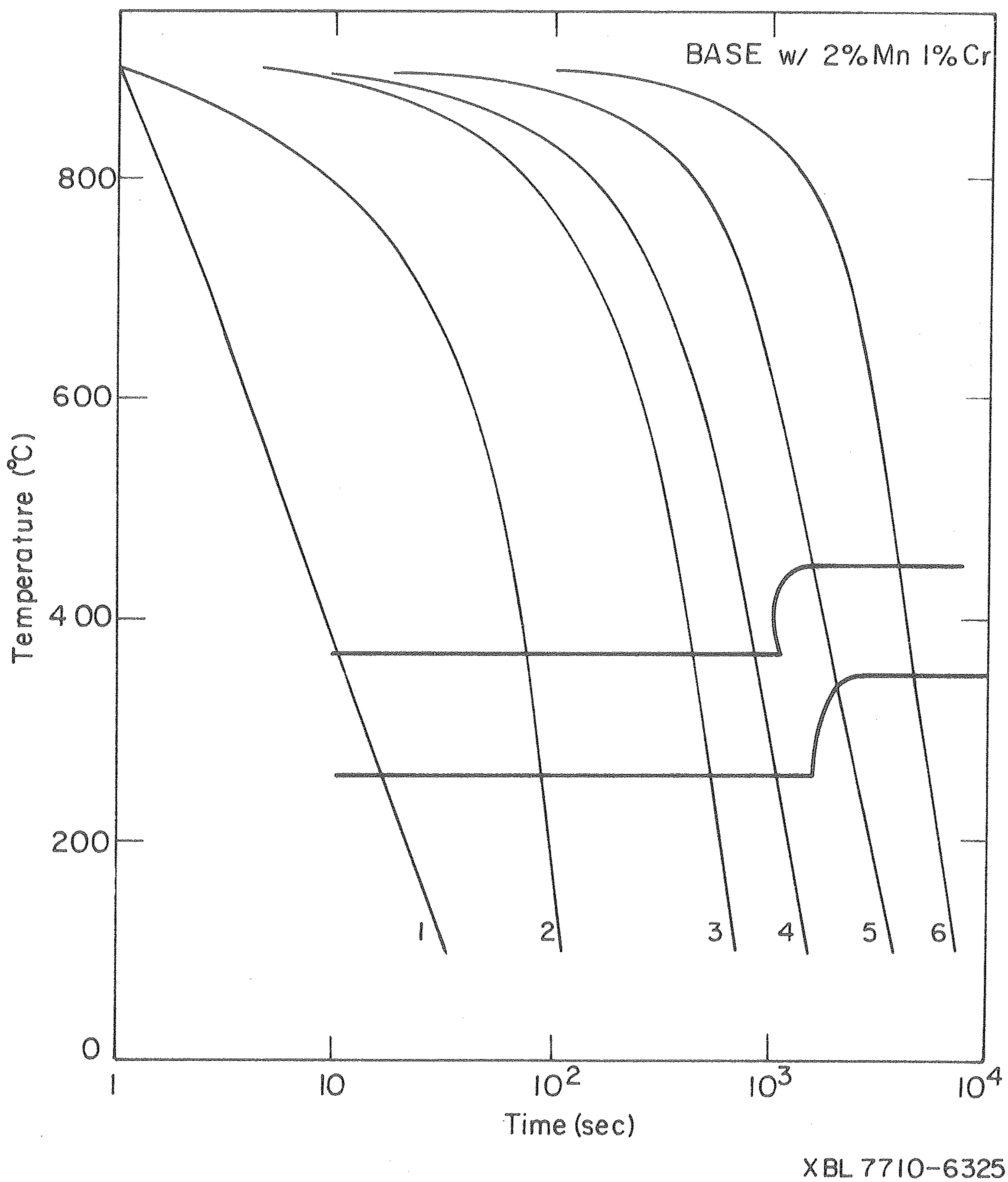


Figure 21. Continuous cooling transformation diagram for Mn-Mo-Ni steel modified with 2% Mn, 1% Cr and grain refined.

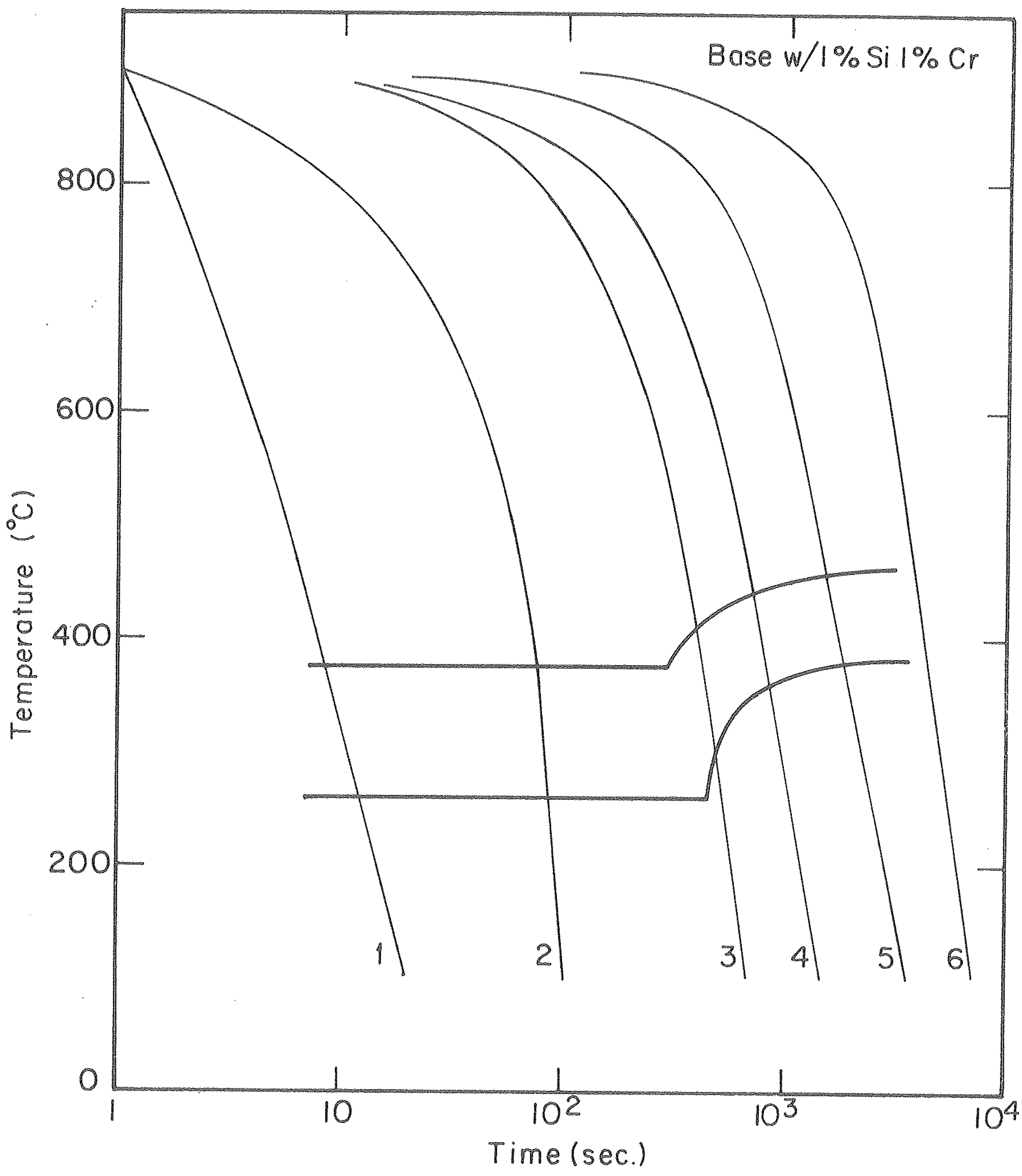
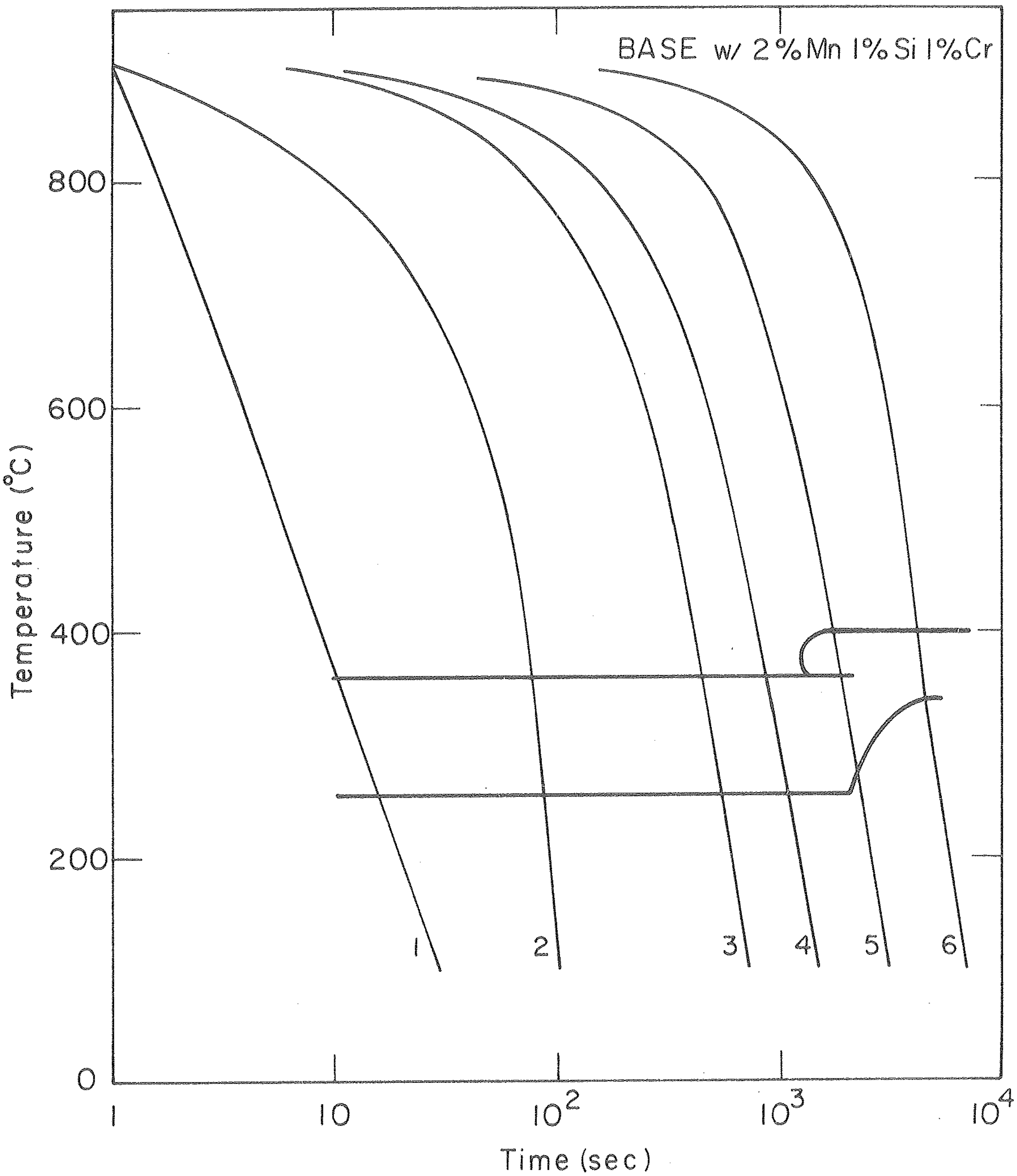
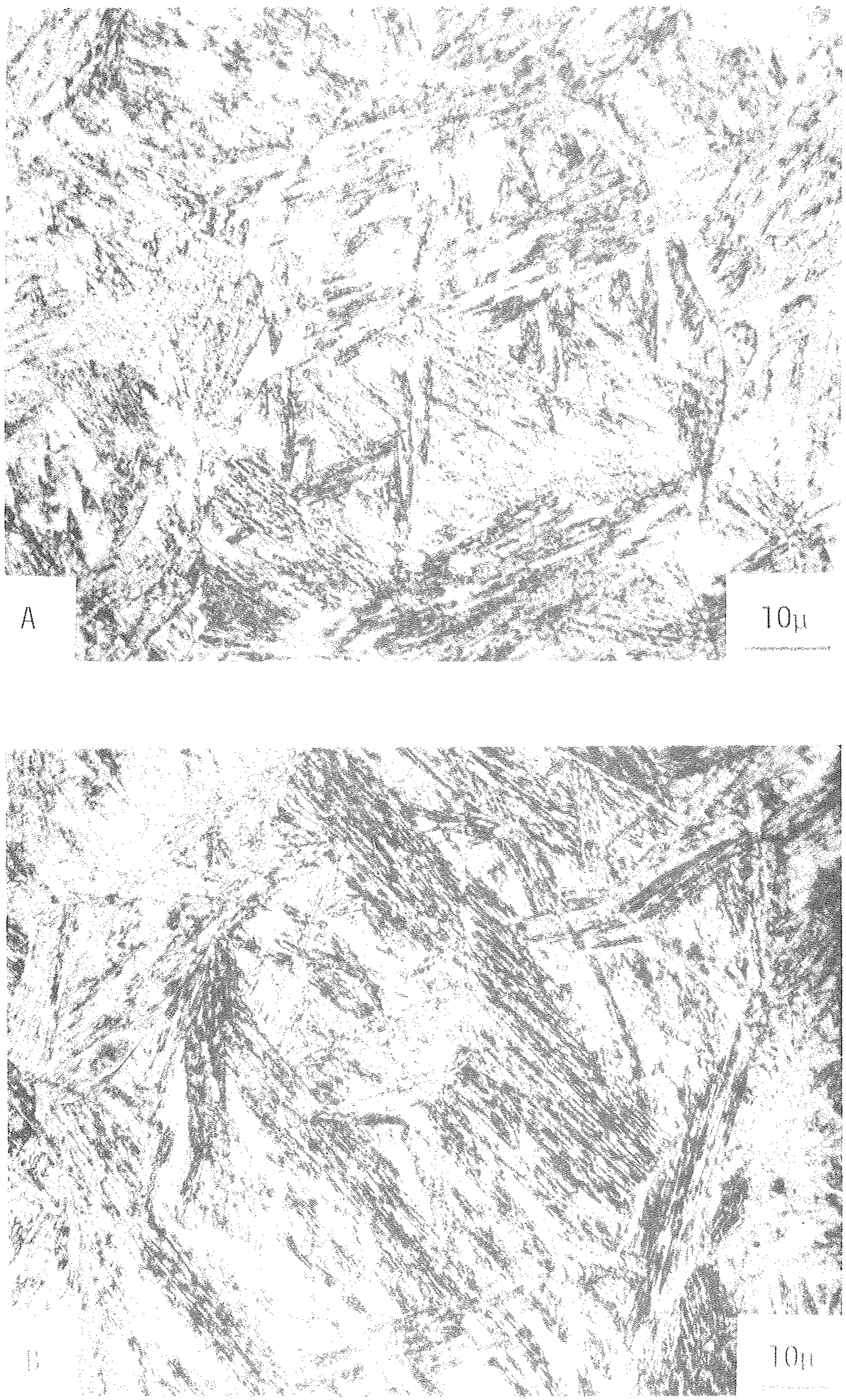


Figure 22. Continuous cooling transformation diagram for Mn-Mo-Ni steel modified with 1% Si, 1% Cr and grain refined.



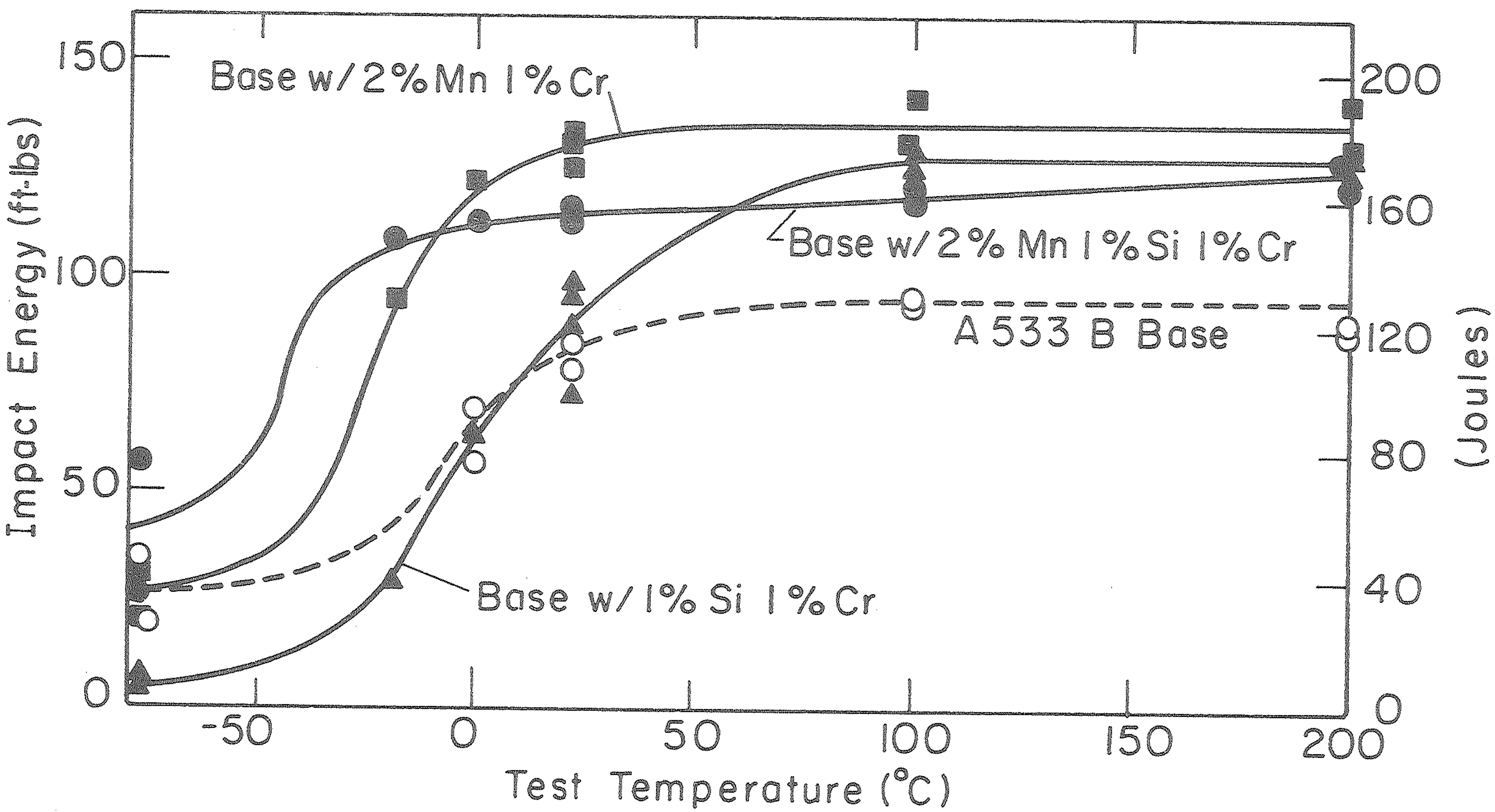
XBL 7710-6 327

Figure 23. Continuous cooling transformation diagram for Mn-Mo-Ni steel modified with 2% Mn, 1% Si, 1% Cr and grain refined.



XBB 779-9395

Figure 24-1. Micrographs showing bainitic in (a) A533B with additional Mn and Cr, (b) A533B with additional Mn, Si, Cr. (8", 1/4T immersion quenched).



XBL 7710-6322

Figure 24-2. Charpy impact properties versus test temperature for Mn-Ni-Mo modified alloys with combined additions.

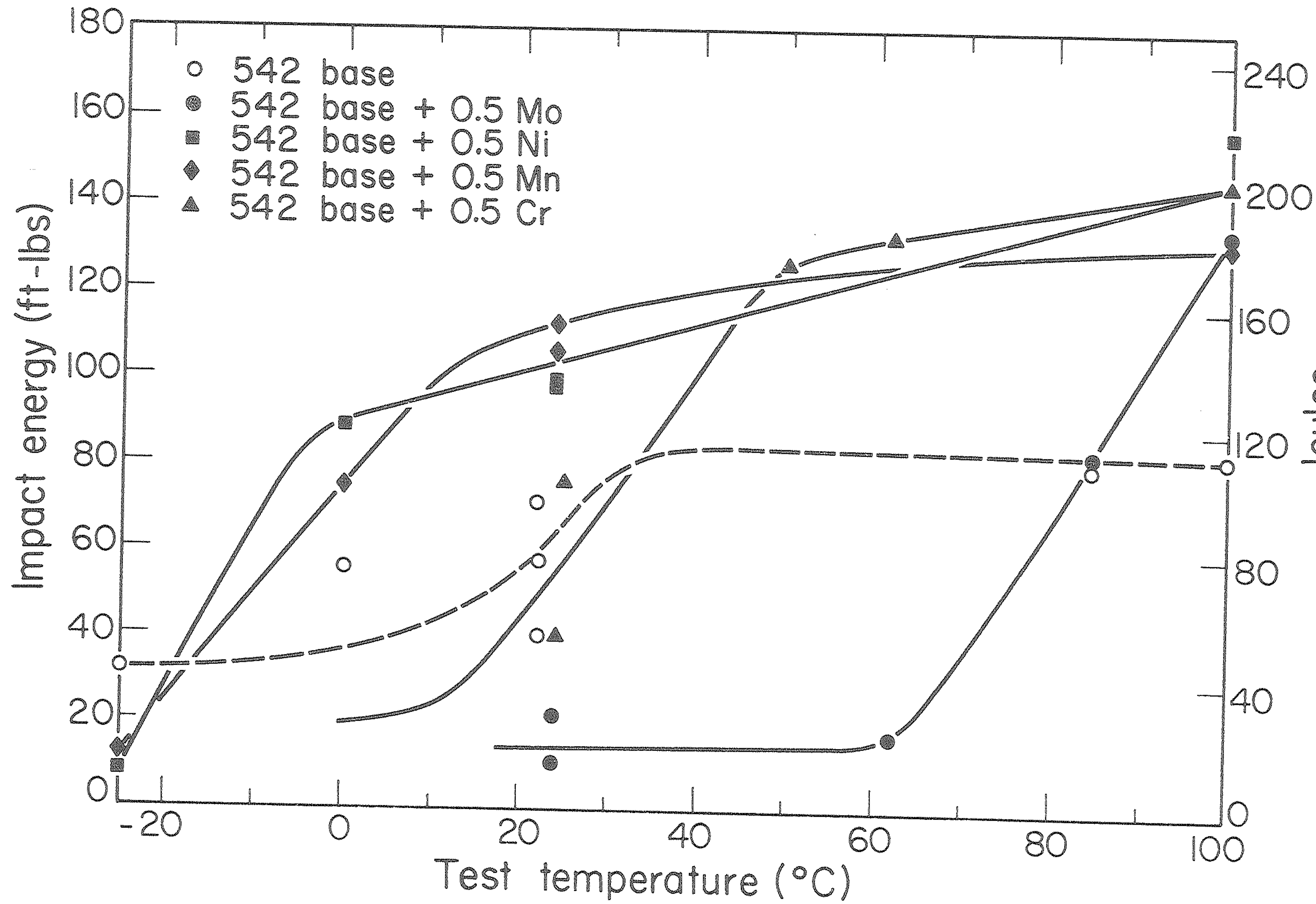


Figure 25. Charpy V-notch impact energy vs. test temperature for modified alloys of A542 steel in 8" thick section, accelerated cooled. Dashed line represents base line properties. XBL 777-1552

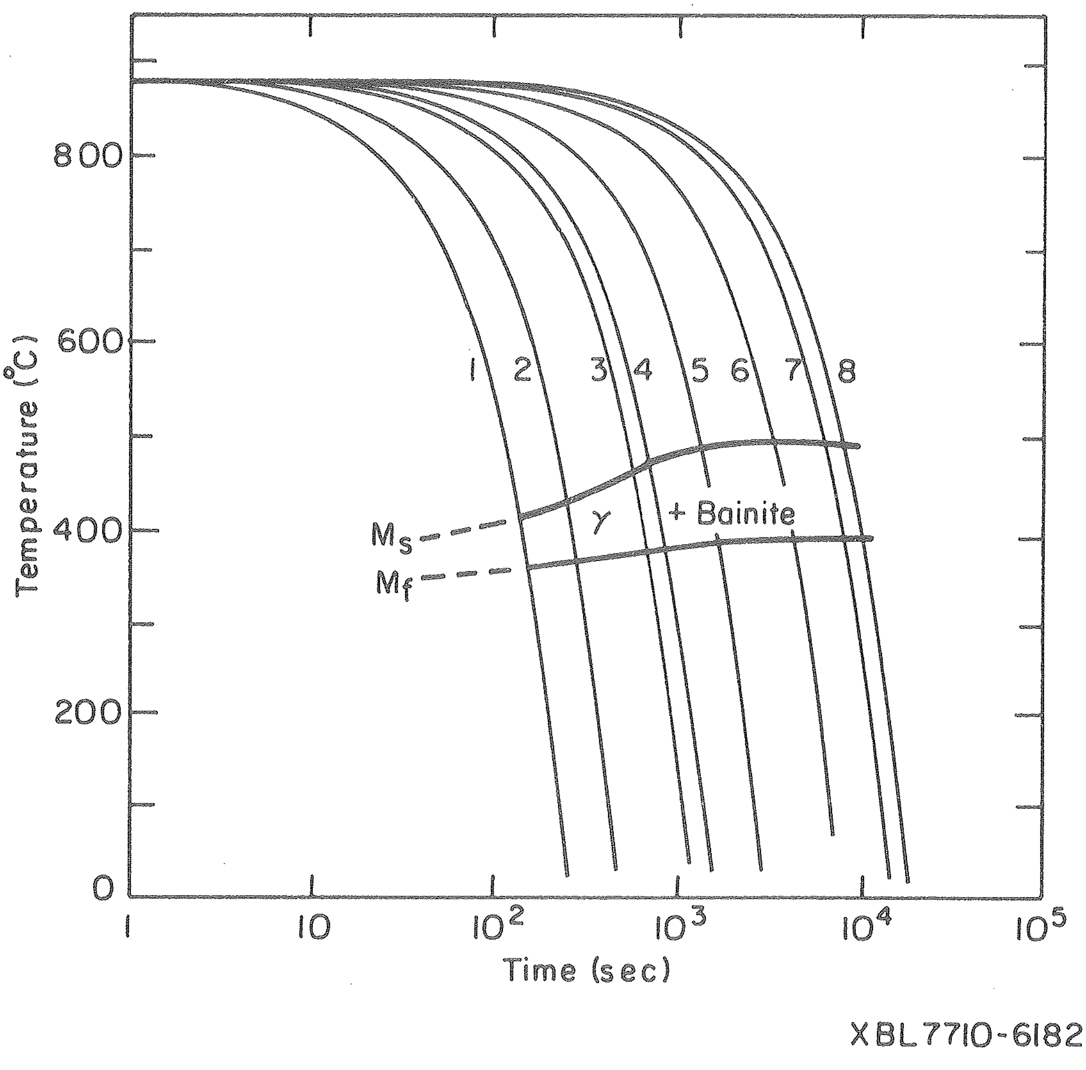


Figure 26. Continuous cooling transformation diagram for Cr-Mo steel (A542) modified with 1% Ni and grain refined.

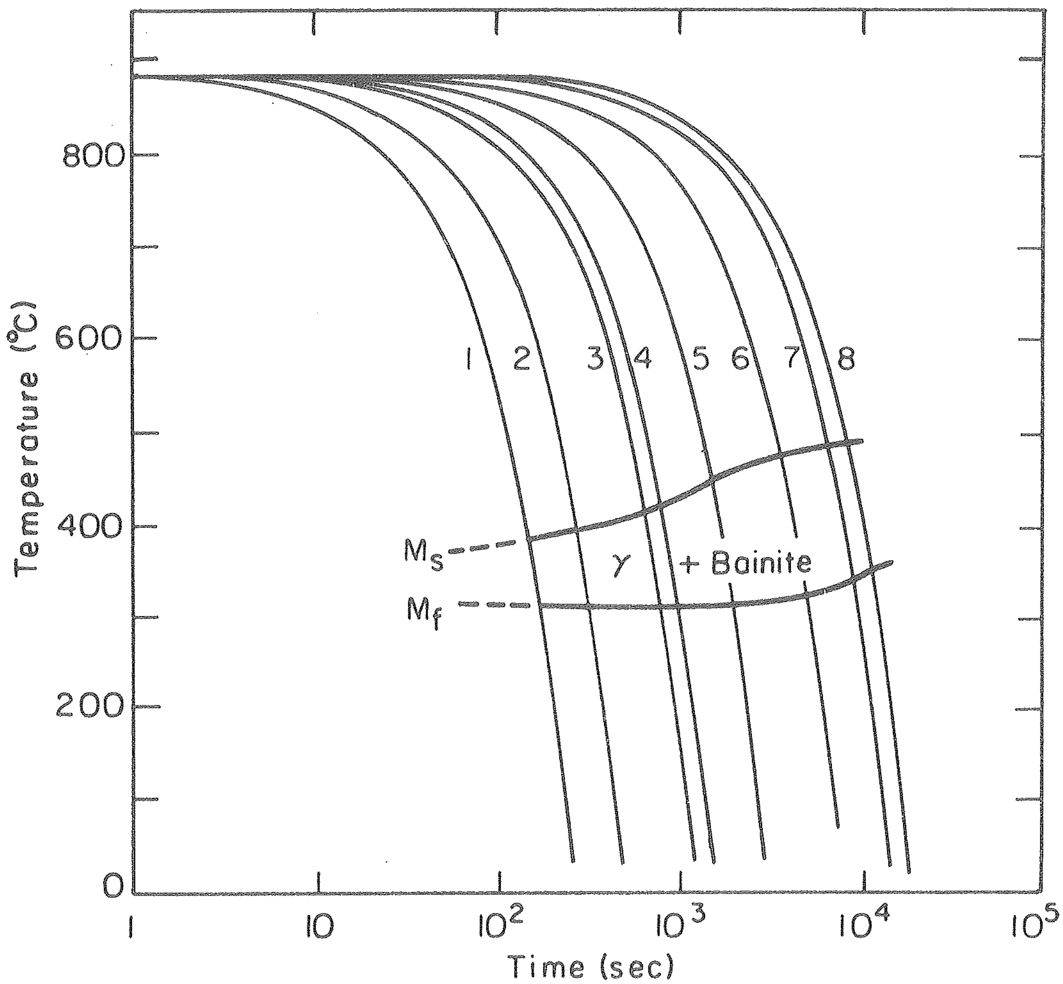


Figure 27. Continuous cooling transformation diagram for Cr-Mo steel modified with 1% Mn and grain refined.

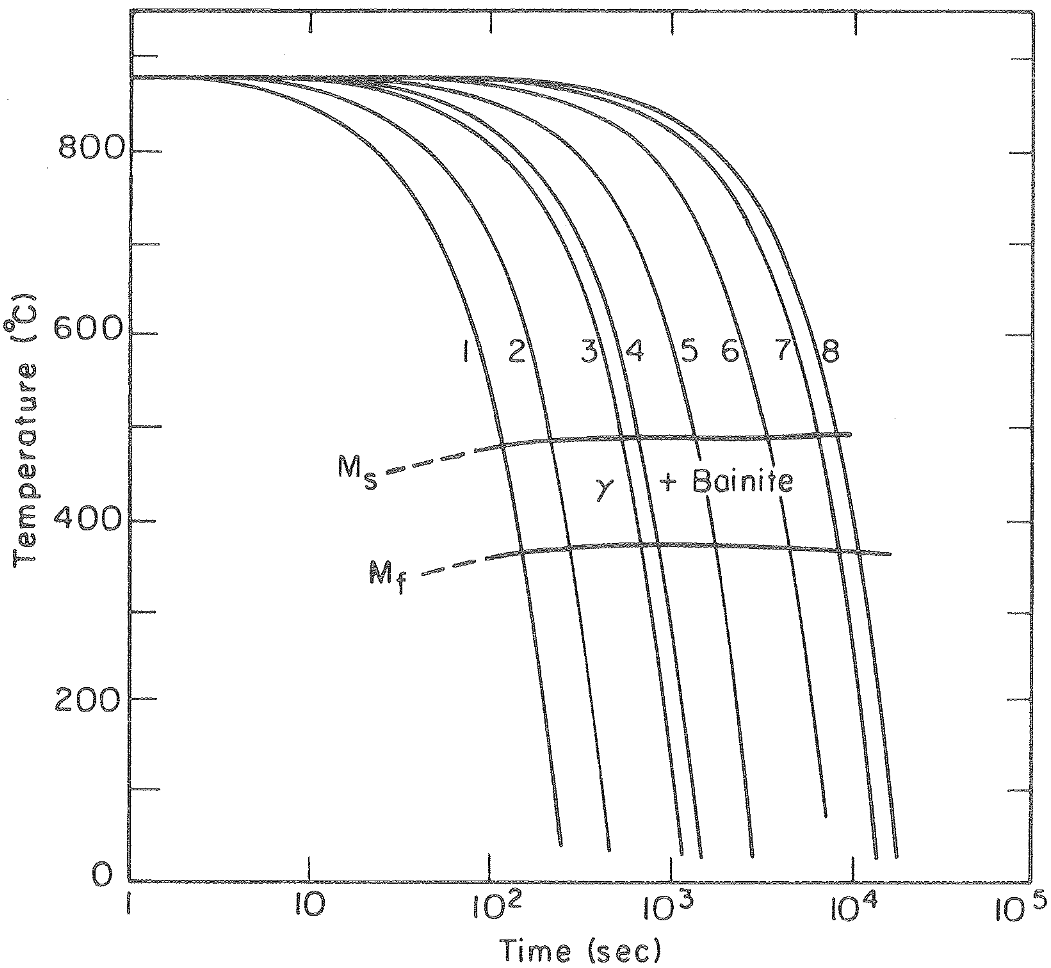
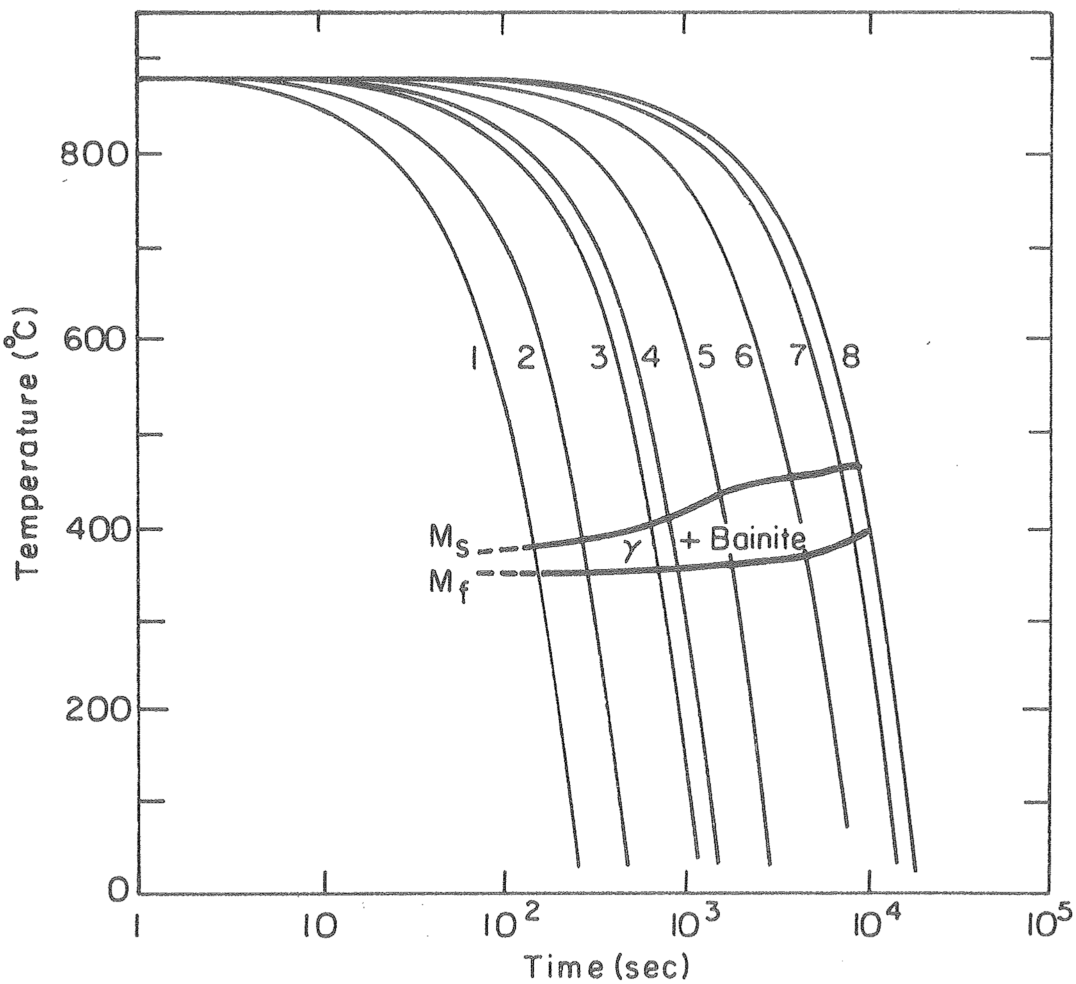
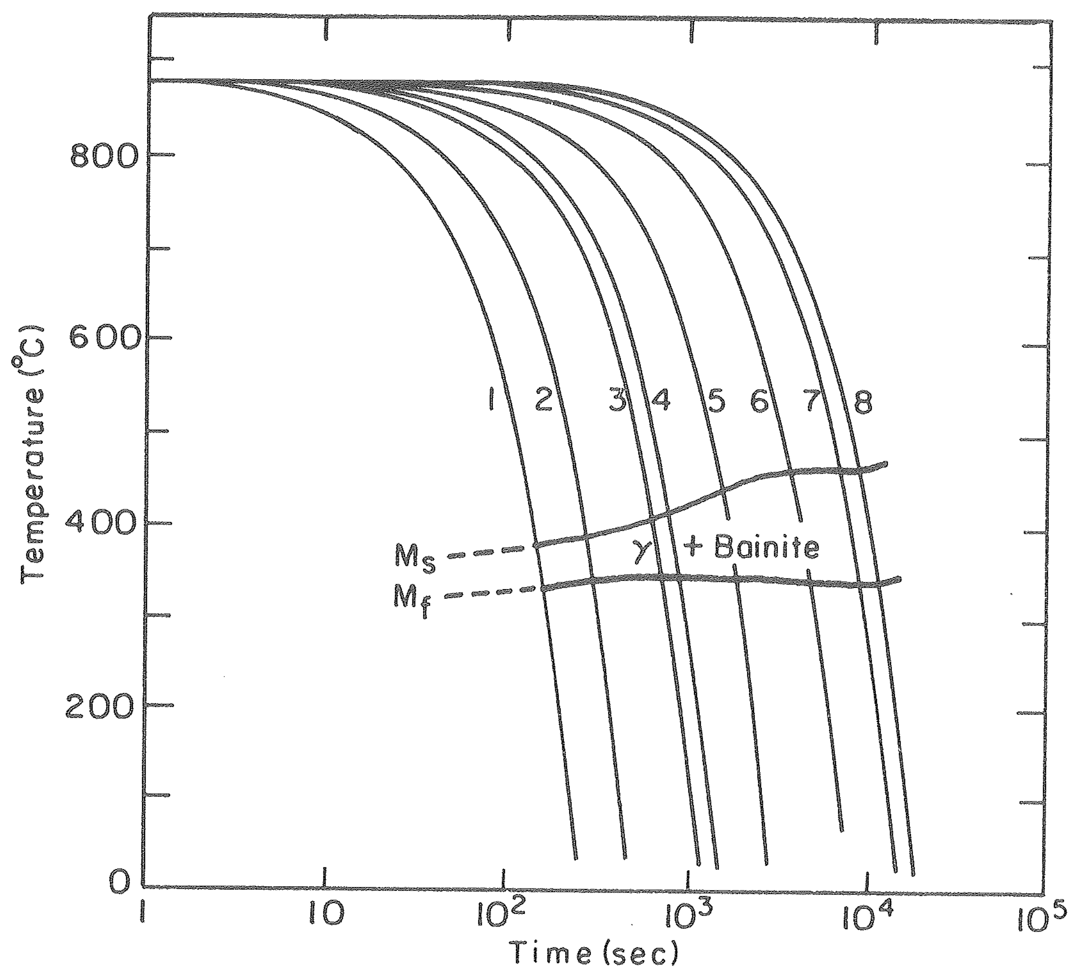


Figure 28. Continuous cooling transformation diagram for Cr-Mo steel modified with 0.5% Ni, 0.5% Mn.



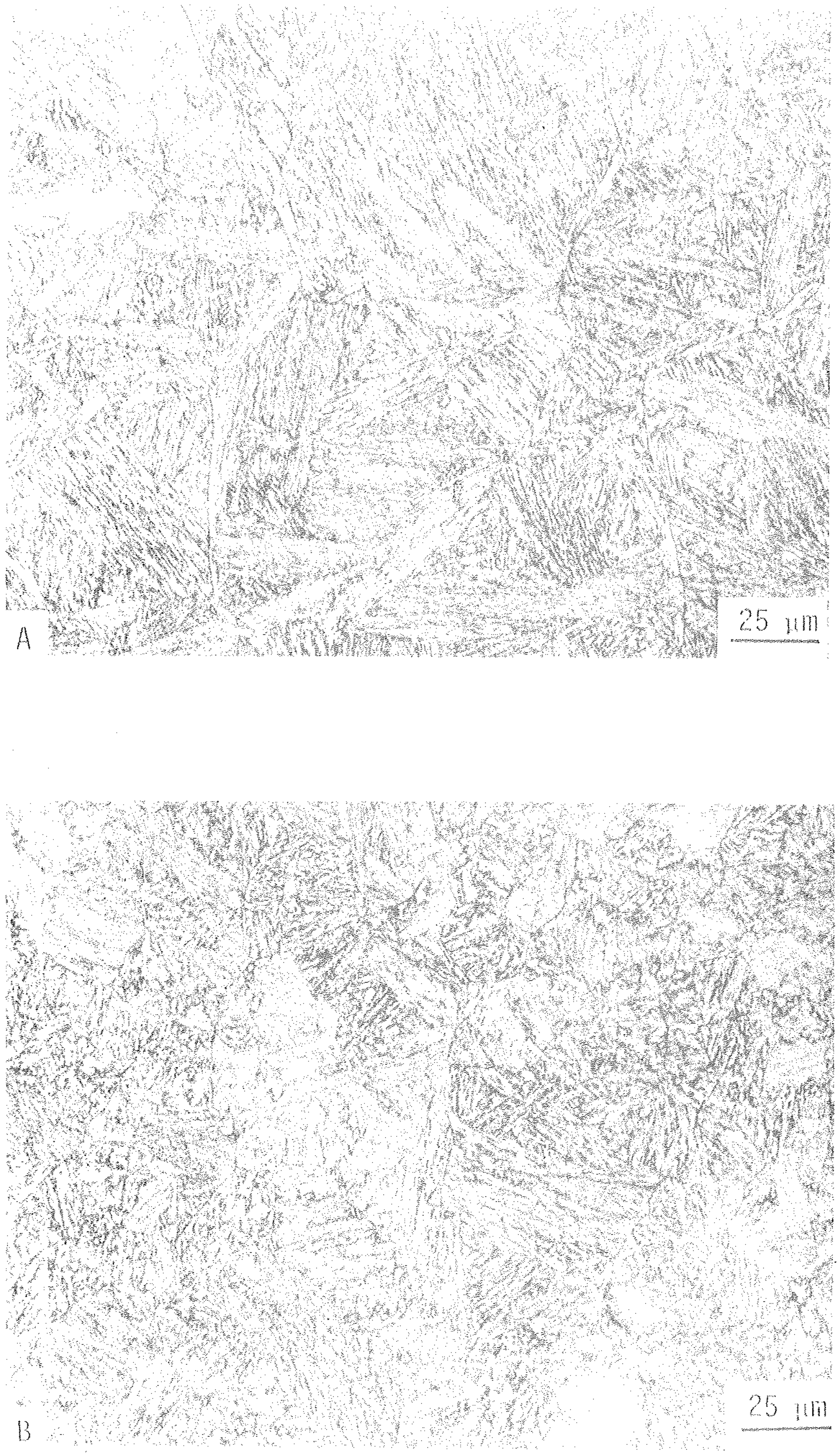
XBL 7710-6184

Figure 29. Continuous cooling transformation diagram for Cr-Mo steel modified with 1% Ni, 0.5% Mn and grain refined.



XBL 7710-6183

Figure 30. Continuous cooling transformation diagram for Cr-Mo steel modified with 1% Ni, 0.5% Mn and 1% Cr.

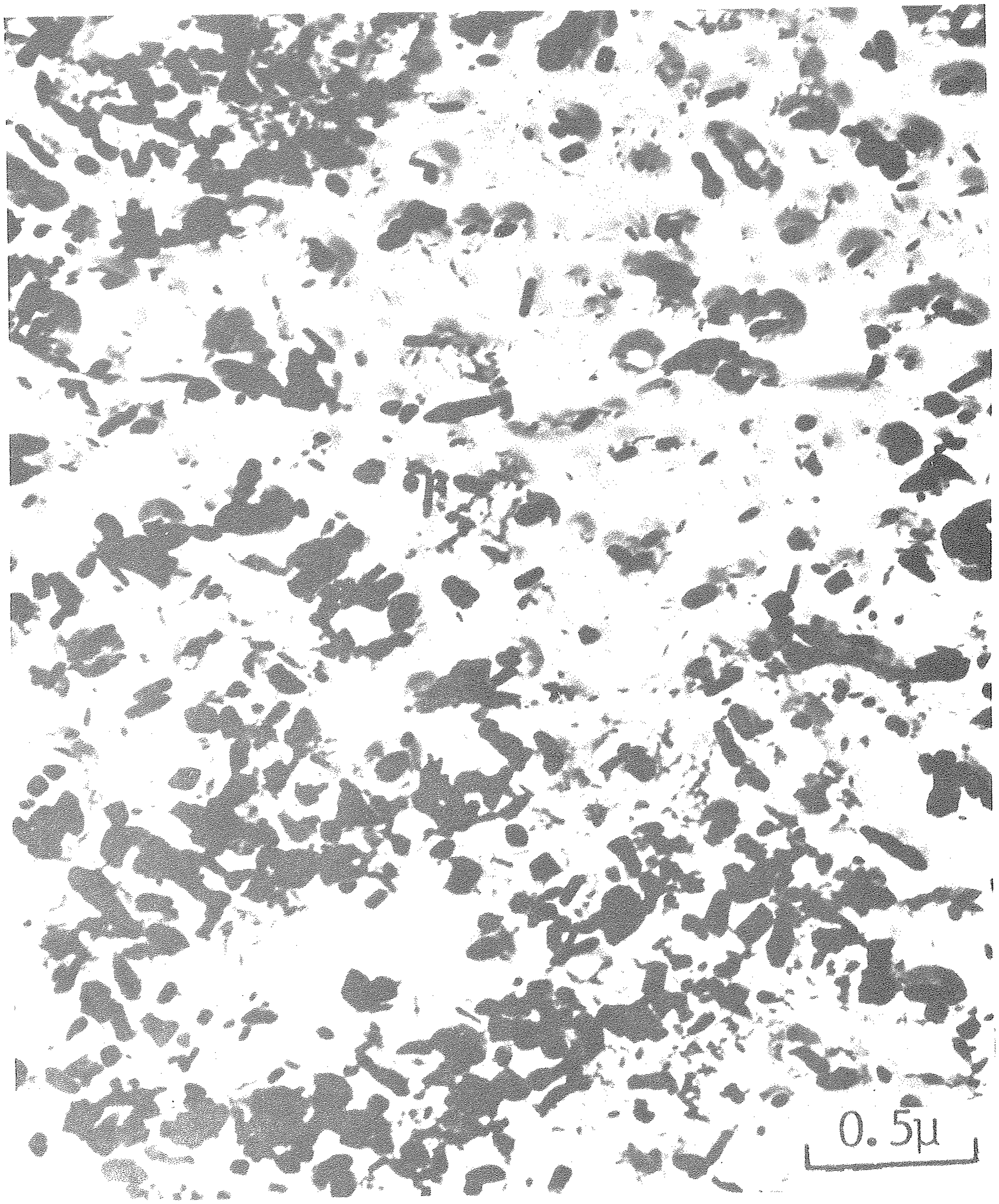


XBB 781-69

Figure 31. Optical photomicrograph of Cr-Mo steel showing bainitic structure. (a) Modified with 1% Ni, (b) modified with 1% Ni and grain refined.

XBB 781-67

Figure 32. Micrograph showing bainitic microstructure in Cr-Mo steel modified with 0.5% Ni and an additional 0.5% Mn.



XBB 770-9706

Figure 33. Carbon replica showing fine dispersion of Mo carbides in Cr-Mo steel with 0.5% Ni, 0.5% Mn.

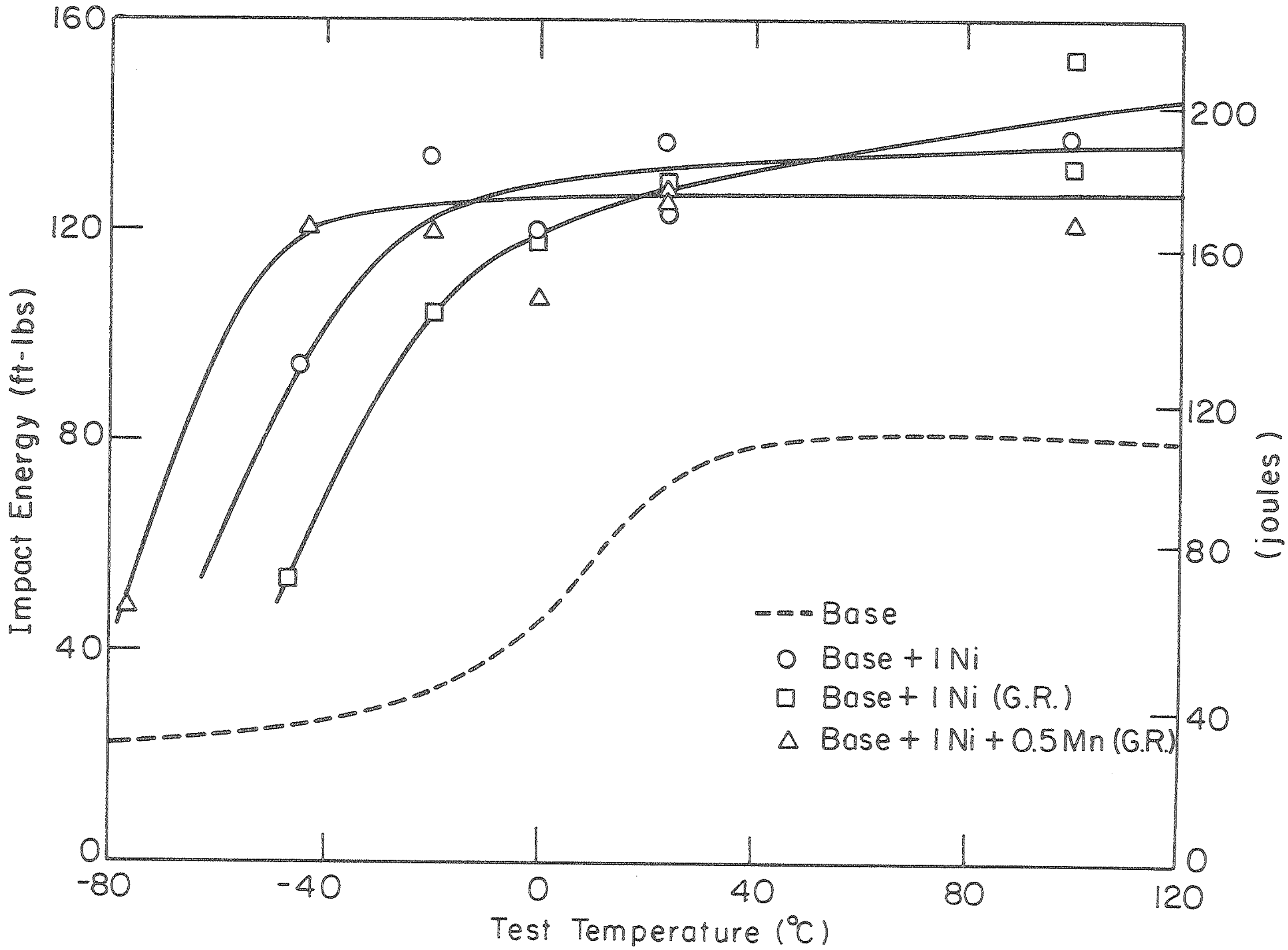
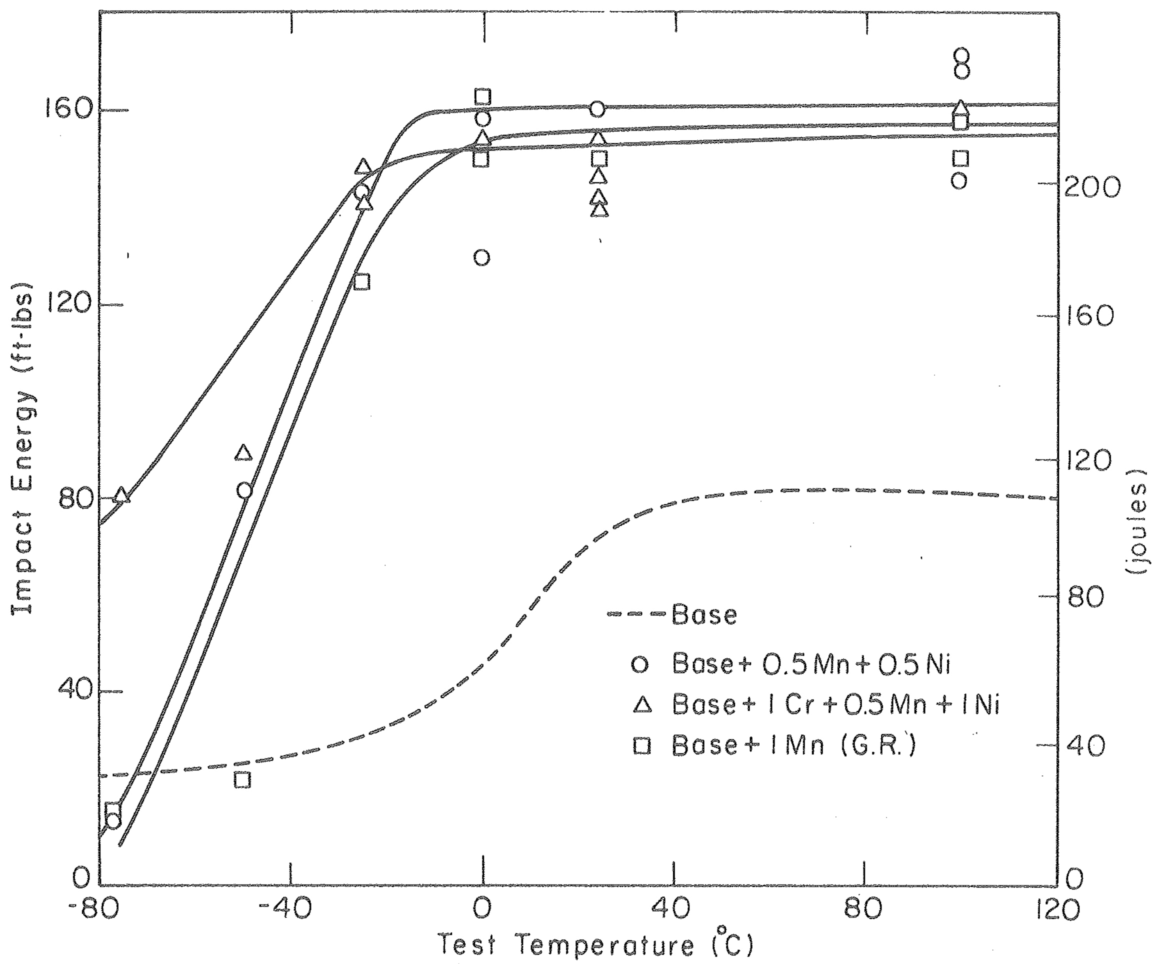


Figure 34. Charpy impact energy versus test temperature for Cr-Mo modified steels containing only Ni additions.

XBL7710-6187

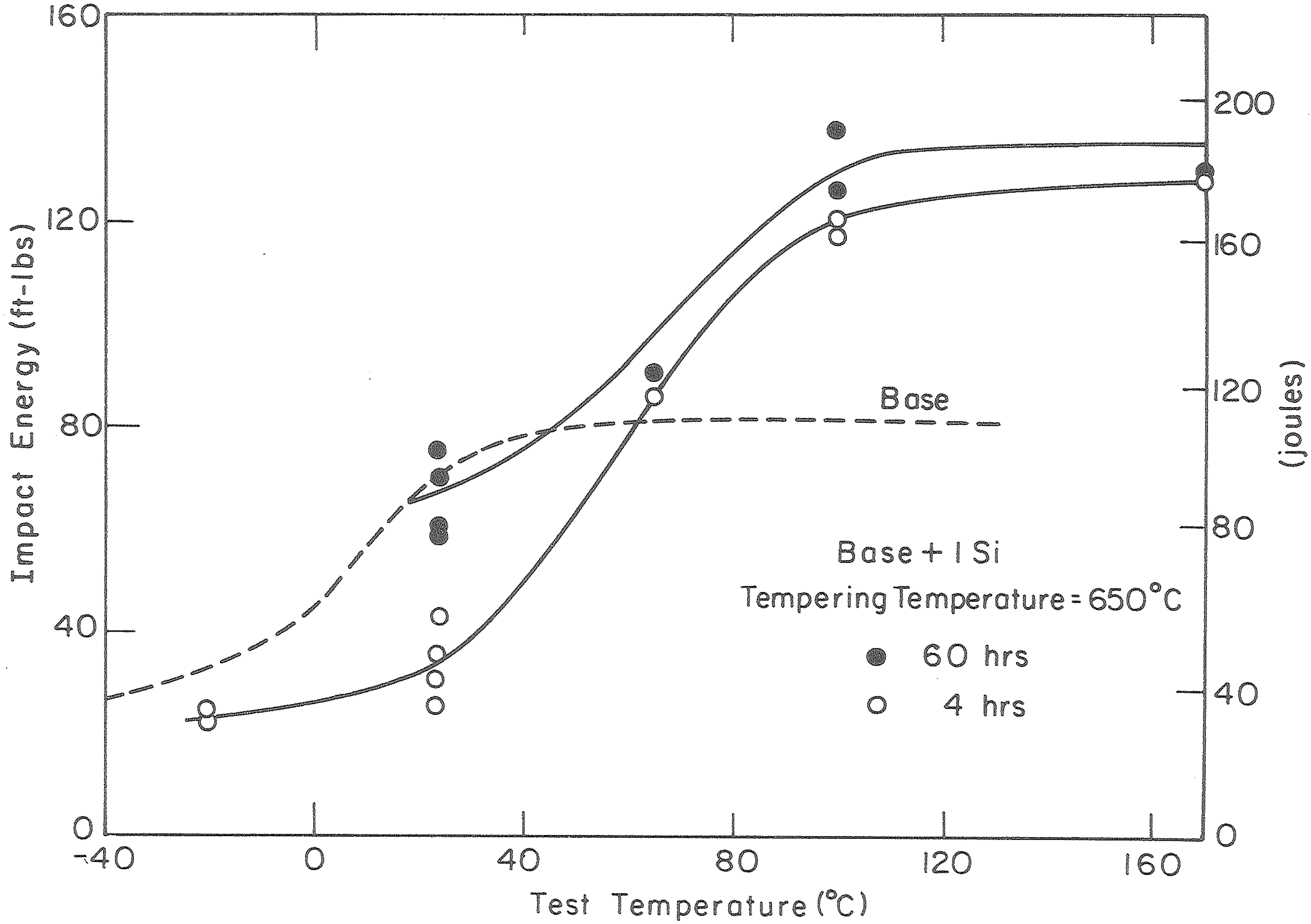


XBL 7710-6186

Figure 35. Charpy impact energy as a function of test temperature for Cr-Mo alloys with additional Mn.

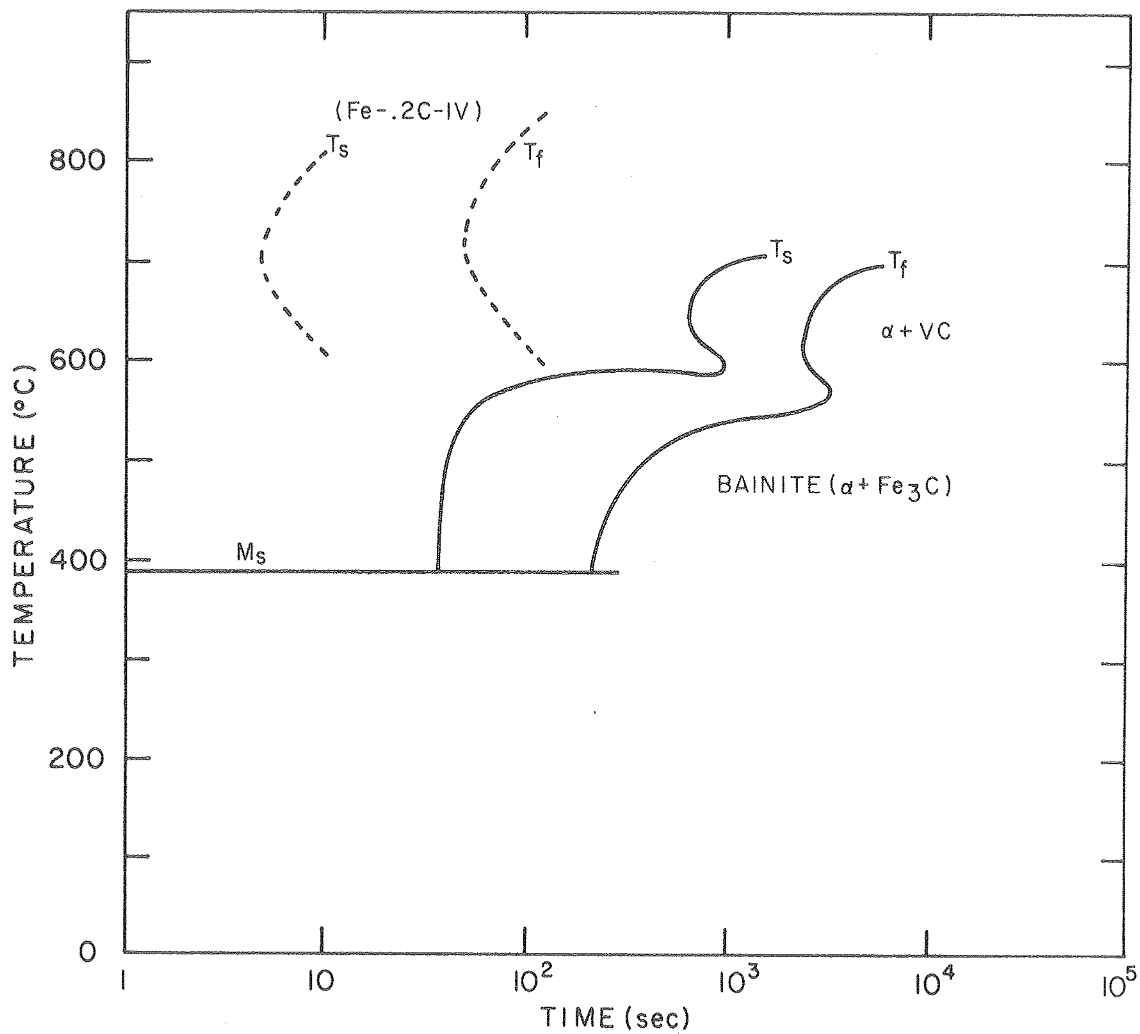
XBB 781-68

Figure 36. Optical microscope of Cr-Mo steel with additional Ni, Mn and Si. Fine areas of ferrite are present.



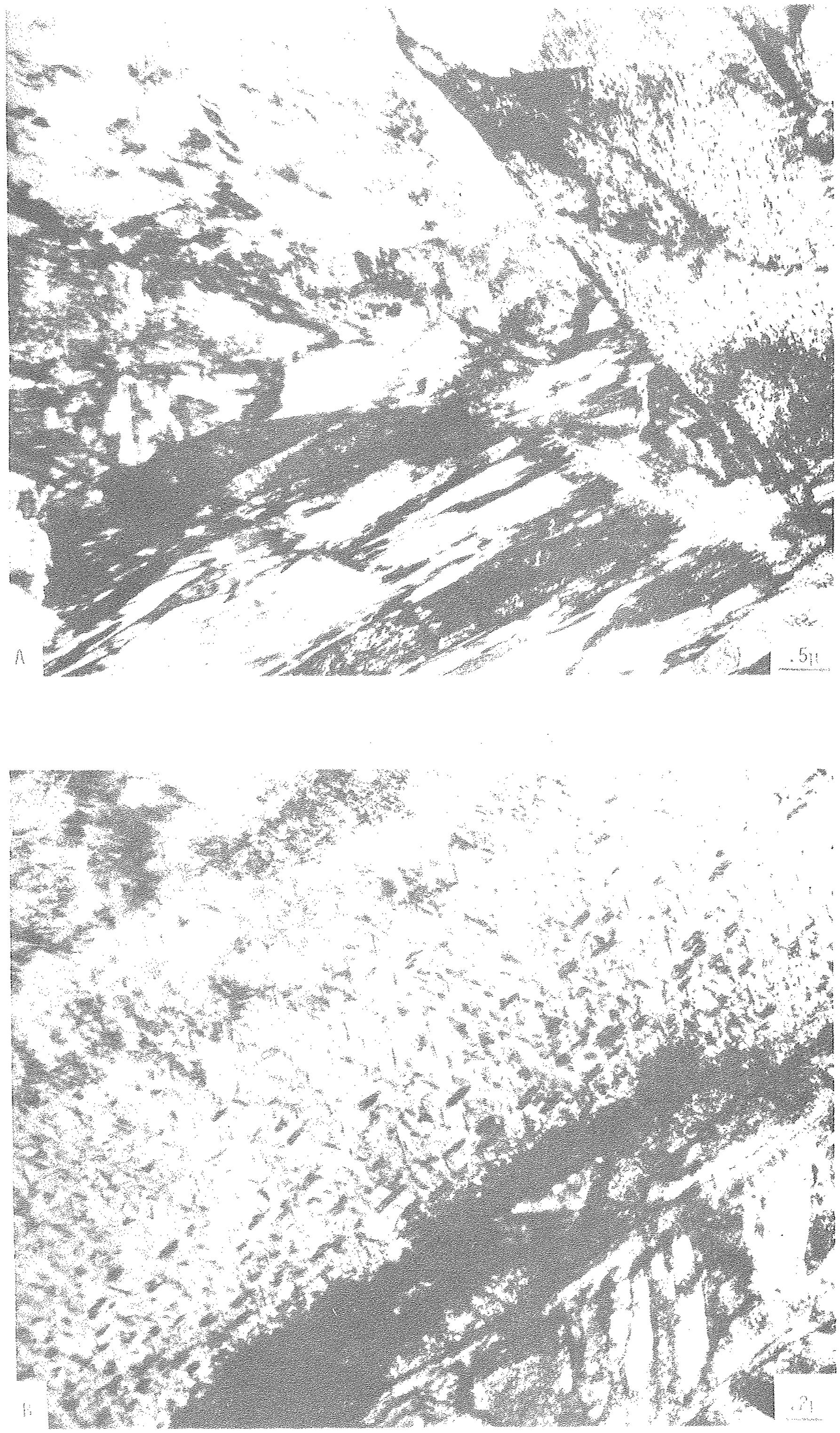
XBL 7710-6188

Figure 37. Charpy impact energy versus test temperature for Cr-Mo steel with/without 1% Si additions. (Two tempering times used.)



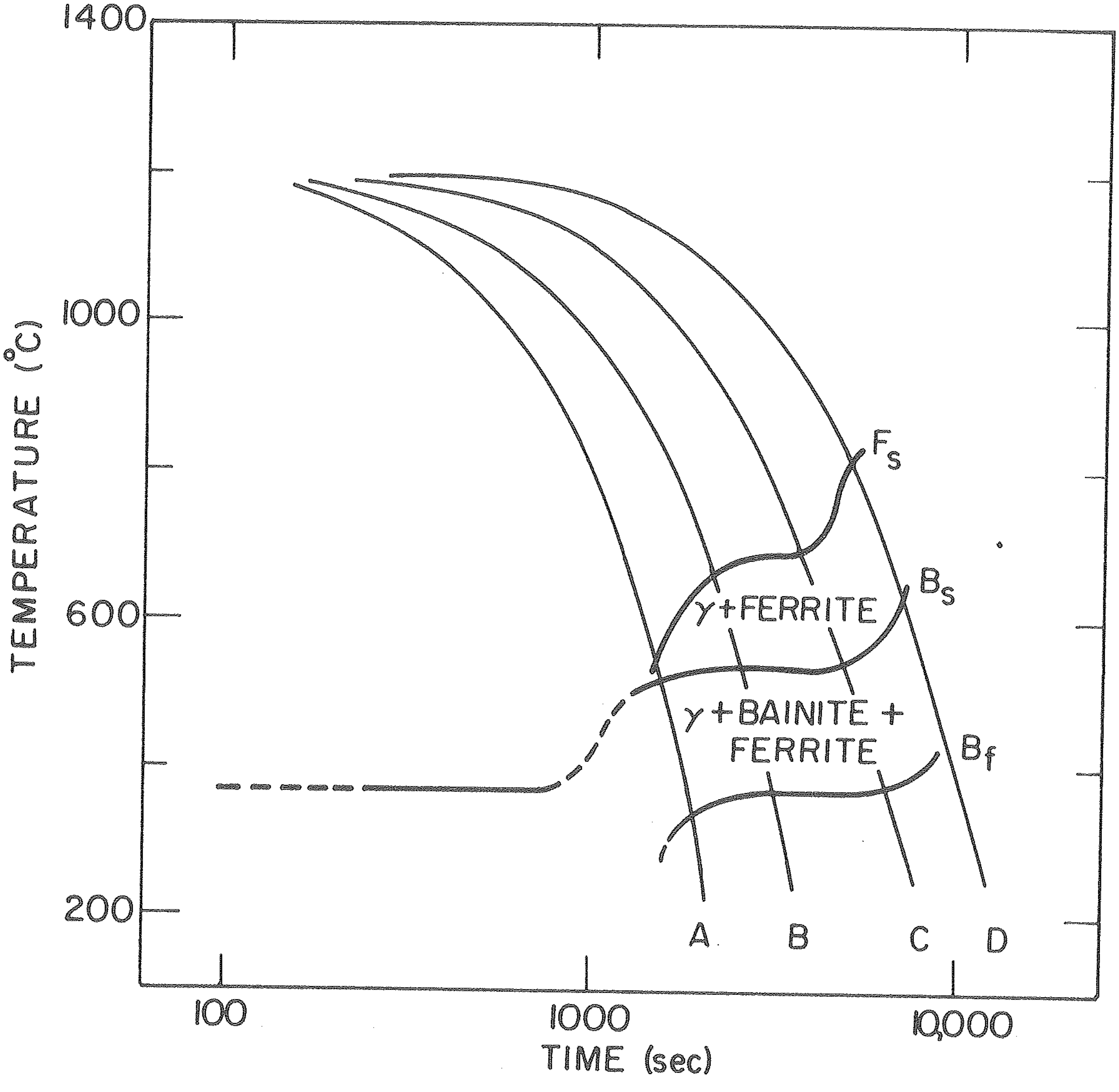
XBL 781-6847

Figure 38. TTT diagram for Fe-0.2C-1V-3Ni alloy.



XBB 777-7148

Figure 39. Transmission electron microscopy of V-Ni eutectoid steel showing (a) general mixed morphology including carbide precipitation and (b) area of internal carbide precipitation.



XBL778-5893

Figure 40. Continuous cooling diagram with TTT for V-Ni steel.

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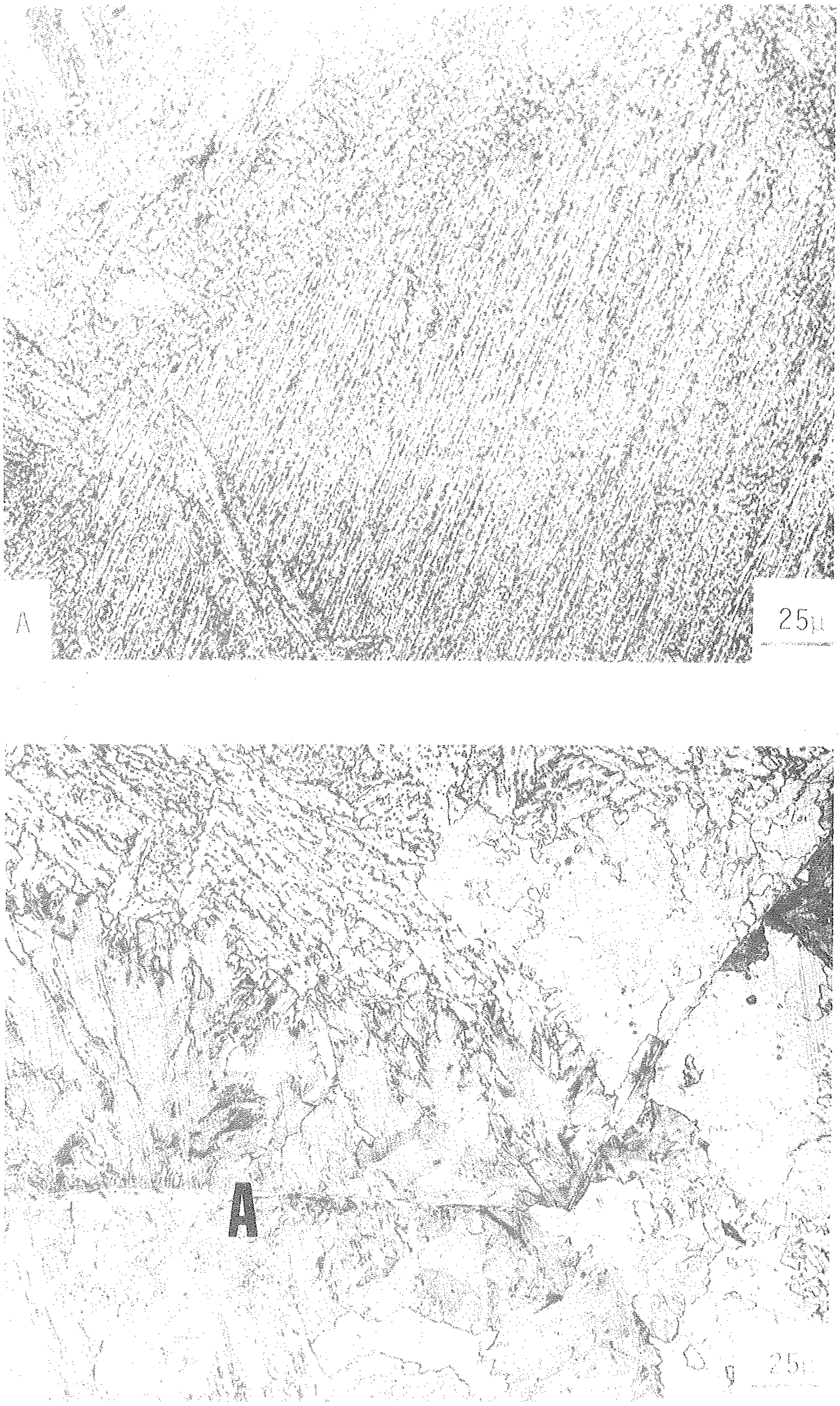

XBB 777-7149

Figure 41. Optical micrograph showing continuously cooled microstructure, (a) 1/3°C/sec and (b) 0.16°C/sec with two-phase structure, shown at A.