HIGH-TEMPERATURE EFFECTS OF BORON IN IRON AND
IRON ALLOYS

DISSERTATION

Presented in Partial Fulfillment of the Requirements
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By

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1935

Approved by:

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Adviser
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Dedicated

To my wife
ACKNOWLEDGEMENTS

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HIGH-TEMPERATURE EFFECTS OF BORON IN IRON AND IRON ALLOYS

1. INTRODUCTION

This research work has been undertaken in connection with establishing the mechanism by which boron enhances the hardenability of heat treatable steels. The working hypothesis for the boron mechanism by Spretnak and Speiser \(^{1,2}\) indicated the importance of studying high-temperature effects in boron steels. These effects may be listed as follows:

a. The occurrence of solute adsorption to grain boundaries, i.e., the possibility that boron is surface active with respect to gamma iron.

b. The phenomenon of temporary loss of hardenability.

c. A reported permanent loss of boron hardenability effect after homogenization heat treatment.

d. The effect of boron on grain growth in the gamma phase.

The most important of these is the possibility of adsorption effects involving boron. Such an effect might significantly
influence the kinetics of austenite decomposition as well as be intimately involved with the remainder of the high-temperature effects outlined.

Primarily, then, the purpose of this research is

a. to establish whether or not boron is adsorbed in gamma solid solution,

b. to determine the nature of any such adsorption effects, i.e., whether it is positive or negative as well as its temperature coefficient, and

c. to estimate the magnitude of any such effect.

In addition, this research purports to investigate the other high-temperature effects and their interrelation, if any, with adsorption phenomena.
A. Thermodynamics of Adsorption

It has been well established that adsorption phenomena in metals is thermodynamically feasible. A number of authors have referred to the applicability of Gibbs' treatment of liquid-liquid interfaces to solid systems. Recently Spretnak and Speiser have presented a detailed theoretical treatment of this subject. They start with the equation

\[ d\sigma = -\frac{\sigma}{T}dT + \tau dP - \sum_{i} \phi_i d\mu_i \]  

where

- \( \sigma \) = surface tension
- \( S^\sigma \) = entropy per unit area in the surface phase
- \( \tau \) = thickness of the surface phase
- \( \phi_i \) = the excess of solute of species i in the surface over that in the homogenous phase
- \( \mu_i \) = chemical potential of species i in the surface

Equation 1 is due to Guggenheim who improved on the Gibbs theory of surface adsorption by ascribing a definite volume to the surface phase. This equation represents the change in surface tension with a change in pressure, temperature, and composition in the system.
The Gibbs-Duhem relation is then applied to the equation for change in surface tension of a two-component system at constant temperature and pressure and leads to

\[
N_2 \left( \frac{\Gamma_2^\sigma}{N_2} - \frac{\Gamma_1^\sigma}{N_1} \right) = - \frac{\partial \sigma}{RT \ln(f_2 N_2)}
\]

where
- \( N \) = mole fraction
- \( \Gamma \) = surface excess
- \( f \) = activity coefficient, and subscript 1 refers to solvent and 2 to the solute.

The positive adsorption of solute occurs when

\[
\frac{\Gamma_2^\sigma}{N_2} > \frac{\Gamma_1^\sigma}{N_1}
\]

and negative adsorption occurs when

\[
\frac{\Gamma_2^\sigma}{N_2} < \frac{\Gamma_1^\sigma}{N_1}
\]

When \( \left[ \frac{\partial \sigma}{\partial \ln(f_2 N_2)} \right]_T \) is negative, the adsorption will be positive and when \( \left[ \frac{\partial \sigma}{\partial \ln(f_2 N_2)} \right]_T \) is positive the adsorption will be negative. Since the activity coefficient must be positive \( \partial \ln(f_2 N_2) \) will increase with concentration increases so that the sign of \( \left[ \frac{\partial \sigma}{\partial \ln(f_2 N_2)} \right]_T \) depends upon the direction of change of the surface tension. Stated explicitly, if the surface tension decreases as the mole fraction of solute in the homogenous phase...
increases, an excess of solute will be present in the surface phase, whereas if the surface tension increases, there will be a deficiency of solute in the interface.

A further extensive thermodynamic treatment of adsorption by Speiser and Spretnak shows which of two components of a binary alloy is positively adsorbed at the grain boundary. The explicit conditions for this occurrence are inferred from a relation derived by Guggenheim for ideal solutions:

\[
e^{-\gamma/RT} = N_1 e^{-\gamma_1/RT} + N_2 e^{-\gamma_2/RT}
\]

(5)

where

- \(\gamma\) = surface tension of the solution
- \(\alpha\) = surface area per atom on the surface
- \(\gamma_i\) = surface tension of pure component \(i\)
- \(N_i\) = mol fraction of component \(i\)

Differentiation of equation 5 with respect to \(N_2\) gives

\[
\frac{d\gamma}{dN_2} = \frac{RT\alpha}{N_1 e^{-\gamma_1/RT} + N_2 e^{-\gamma_2/RT}} \left[ e^{-\gamma_1/RT} - e^{-\gamma_2/RT} \right]
\]

(6)

Now Gibbs adsorption isotherm for ideal solutions can be written as

\[
\frac{d\gamma}{dN_2} = -\frac{RT}{\alpha} \frac{\gamma_2}{N_2}
\]

(7)

Combining equations 6 and 7
If now we let \( \gamma_1 - \gamma_2 = \delta \), then \( \delta \) becomes

\[
\Gamma'_2 = N_2 \frac{e^{-\gamma_2 a/kT}}{N_1 e^{-\gamma_1 a/kT} + N_2 e^{-\gamma_2 a/kT}}
\]

(8)

It is evident from equation 9 that if \( \delta > 0 \), then \( \gamma_1 > \gamma_2 \) and \( \Gamma'_2 > N_2 \); and if \( \delta = 0 \), then \( \Gamma'_2 = 0 \); and finally if \( \delta = \infty \), then \( \Gamma'_2 = 1 \).

Consequently the component with the lower surface tension is positively adsorbed at the grain boundary. Furthermore, if the solution is non-ideal, with positive deviations from Raoults Law, the surface excess of component 2 will be greater than that predicted by equation 9.

From equation 5 it can be seen by inspection that the temperature coefficient of adsorption will depend on the values of \( \gamma_1 \) and \( \gamma_2 \). Both \( \gamma_1 \) and \( \gamma_2 \) are defined by general relations of the type

\[
\gamma_1 = \gamma_0 - B_1 T \quad \text{and} \quad \gamma_2 = \gamma_0 - B_2 T
\]

(10)

where \( \gamma_0 \) = surface tension at temperature zero

\( T \) = temperature

\( B_1, B_2 \) = constants

The variation of \( \gamma \) with temperature will depend on the explicit nature of equations 10, and it is clear that the temperature coefficient of adsorption can be either positive or negative.
B. General Literature on Adsorption Effects

Although no great body of literature exists concerning adsorption effects in metals the possible existence of such phenomena has been used to explain anomalous behavior in metals in the past. As early as 1939 Benedicks, referring to the work of Gibbs, suggested that concentration variations within metallic grains could be produced by positive or negative adsorption of dissolved elements. He used this theory to explain the influence of aluminum on grain growth in steel, assuming the aluminum nitride was concentrated by this mechanism at the grain boundaries of the steel. Phillips and Brick considered this a factor in polycrystalline alloy equilibria and produced experimental evidence to support their contention that relative amounts of grain boundary areas influenced the solubility limits in solid phases. Their work shows that the larger the grain size in polycrystalline metals the greater will be the solid solubility. Weist noted that single crystals retained larger amounts of solute than polycrystalline metals, thereby inferring some effect due to grain boundaries. Later some experiments were performed on solid solutions of copper in zinc, in which actual analyses were made of the bulk solid solution and also of grain boundary material. The latter was obtained by coating the material, cutting away the area over the grain boundaries, and etching electrolytically to obtain a definite quantity of alloy. Composition
differences so obtained led to the conclusion that the concentration of the solid solution differs between the grain interior and the grain boundary.

In the classical "bubble raft" experiment a great deal of light was shed on the nature of grain boundary formation. These experiments showed that bubbles which were markedly smaller or larger than the average tended to segregate at the boundaries. Such evidence lends credence to the idea that impurity atoms in a metal tend to segregate at the boundaries. King and Chalmers theorized that the grain boundary is a region where atoms are not arranged on a regular crystalline lattice, and, that because of this diffusion occurs here more readily than anywhere else in the system. Also the grain boundary is a region where large foreign atoms fit more readily than within the crystal lattice of the grains. In the normal diffusion process, therefore, foreign atoms tend to remain at the boundaries; thus the concentration of impurities is higher than in the grains themselves.

The embrittlement of copper by bismuth is well known, and it was proposed that a thin film of elementary bismuth at the grain boundaries of the alloys was responsible. Ting-Sui Ke, using this work as a basis for some internal friction experiments, showed logically that bismuth at the copper grain boundaries was the likely embrittling mechanism. However, the energy peaks associated with the bismuth showed that not enough elementary bismuth was present at
the majority of the grain boundaries to influence the grain boundary viscosity. Nevertheless, it was pointed out that bismuth need not be present in the elementary form to cause the embrittlement.

Solid solutions of lead and bismuth have been studied by Chalmers, et al. using radioactive bismuth. The alloys were examined for segregation of the polonium resulting from the decay of bismuth. From these experiments crystal boundary segregation was established. Polonium was present in concentrations of only about one atom per $10^{10}$ bismuth atoms, but autoradiographs of the bicrystal specimens showed that despite the low concentration polonium segregates at the crystal boundaries. More recent work by Thomas and Chalmers has shown that the amount of polonium in the grain boundaries depends on the orientation of the crystals adjacent to the boundary and the temperature at which equilibrium is attained. Furthermore the concentration of polonium in the boundaries decreases rapidly with annealing temperature, i.e., polonium exhibits a negative temperature coefficient of adsorption. At high annealing temperatures segregate persists only in the high-angle boundaries. Puttick and King noted the effect of impurities while studying boundary slip in bicrystals of tin. Irregular grain boundary slip was correlated with differences in boundary appearance after straining. In turn these differences in appearance were thought to be due to the presence of impurities which collected at the grain boundaries during solidification.
Miekk-Oja\textsuperscript{16} studied the segregation of iron and phosphorus in 70:30 brass alloys by noting the effect of their differing amounts and combinations on grain growth in the alloys. His work points out that even very small amounts of impurities have a decisive influence on grain growth and final grain size, which can only be accounted for by assuming grain boundary segregation. In these experiments the anomalies in grain size versus temperature curves and the observed occurrence of discontinuous grain growth are better accounted for by the varying partition of impurity atoms between grain boundary and lattice than by submicroscopic precipitations.

Quite recently McLean\textsuperscript{17} investigated the embrittlement of copper-antimony alloys. It had been suggested in previous work\textsuperscript{18} on brass-antimony alloys that the microscopically visible film around the grains was actually an antimony film which was responsible for the observed brittleness. Furthering this study, McLean showed that the same brittleness was present in copper-antimony alloys where no grain boundary film was observed under the microscope. However, the "phase contrast" microscope showed the identical "ridge and trough" boundaries previously found in brittle copper-bismuth alloys and associated with an excess grain boundary concentration of bismuth.\textsuperscript{19,20}

Perryman\textsuperscript{21} investigated the effect of iron content and heat treatment on the grain boundary attack of aluminum by hydrochloric
acid and sodium hydroxide. The wide grooves formed at the grain boundaries during the attack were explained by the assumption that iron segregates to the grain boundaries in solid solution.

Several authors have quite logically explained many of the known phenomena concerning temper-brittleness in steel by assuming the positive adsorption of carbon at the austenite grain boundaries during the austenitizing treatment. \textsuperscript{3,22,23} Using this theory Spretnak and Speiser\textsuperscript{3} propose that the embrittling phase in temper brittleness is a thin shell of martensite around the prior austenite grains. These authors cite further examples of possible grain boundary effects in this publication. Among these are the embrittlement of molybdenum by carbon and oxygen, overheating and burning in steels, sensitizing of austenitic stainless steels to intergranular corrosion, general effects on the kinetics of nucleation in solid-solid reactions, and the boron hardenability effect.

C. Specific Literature on Adsorption Effects in Boron Steels

The literature with respect to the specific high temperature effects to be investigated in this study is somewhat sparse. Grange and Garvey\textsuperscript{24} were the first authors to consider the possibility of nonhomogenous distribution of boron in austenitic iron. They proposed that boron atoms are preferentially located at the austenite grain boundaries before transformation and act to inhibit nucleation at the grain boundaries by some mechanism.
These authors also investigated the effect of austenitizing temperature on the hardenability of boron steels. Their results, graphically represented, are reproduced in Figure 1. The observation that short periods of heating at high temperature could decrease the hardenability effect due to boron was attributed to a possible unfavorable distribution of boron in austenite produced by these conditions. To explain the effect of austenitizing temperature on boron hardenability it was stated that at relatively low austenitizing temperatures, undissolved particles remain which could contain some carbon and boron atoms. Thus austenitizing temperatures too low for the solution of such particles might lead to decreased hardenability at least in higher carbon steels. However, it was further postulated that higher austenitizing temperatures might lead to unfavorable distribution of the boron atoms and result in less hardenability.

The unique metallographic test for boron was first discussed in this study. The constituent observed in the grain boundaries as a network precipitate was postulated by these authors to be a boron compound. They assumed that the grain boundary enrichment in boron atoms could result in some precipitation of this boron compound. Finally, it was observed in this study that homogenization of boron treated steels could completely eliminate the boron effect. This occurrence was attributed to the possible conversion of boron into an ineffective form by chemical combination
Figure 1. Influence of austenitizing temperature upon the hardness of small, air cooled (normalized) samples of a low-alloy steel with and without boron. Held 15 minutes at the austenitizing temperature (After Grange and Garvey).
with another element or elements.

As previously stated Spretnak and Speiser\textsuperscript{3} proposed a grain boundary mechanism to explain the non-homogenous distribution of boron in austenite and treated the subject in some thermodynamic detail. They explained the temporary loss of hardenability in connection with the proposed positive adsorption of boron. It is presumed that the high austenitizing temperature builds up the boron content in solid solution at the vicinity of the grain boundaries. On cooling down the boron precipitate forms from the solid solution which becomes supersaturated as a result of the temperature change. The particles thus formed present additional nucleating surfaces and decrease the relative hardenability.

Some recent work at Battelle Memorial Institute\textsuperscript{25} on the mechanism of the boron hardenability effect has led to the conclusion that boron concentrates at lattice imperfections. Since the imperfections are concentrated at the grain boundaries a nonhomogenous distribution of boron is postulated in accordance with Figure 2 reproduced from this study. The results of Battelle's hardenability studies suggest that increasing the boron content in a steel increases the boron concentration at the grain boundaries as shown in the figure.

Further observations by these workers; namely, that

a. Increasing the austenitizing temperature results in a decrease in hardenability, and the lower the boron
Figure 2. Schematic representation of boron concentration at the grain boundary as a function of boron content of the steel (After Simcoe, Elsea, and Manning).

B<sub>1</sub> < B<sub>2</sub> < B<sub>3</sub> < B<sub>4</sub>
B = 0.0002% boron
B<sub>1,2,3,4</sub> - Boron content of various steels
A - Boron concentration for minimum grain boundary energy at subcritical transformation temperature and maximum hardenability effect.
P - Boron concentration which will produce boron precipitate at the subcritical transformation temperature.

Boundary Concentration

Distance from Grain Boundary
content of the steel the higher the austenitizing temperature must be before the loss of hardenability is encountered,

b. The temperature to which a steel must be heated before the constituent can be developed at the grain boundaries decreases as the boron content increases, and

c. A boron steel must be heated to a relatively high temperature before the boron constituent can be developed at the grain boundaries,

suggest that boron concentrates at the grain boundaries with increasing austenitizing temperature as shown in Figure 3, also reproduced from this study.

It is suggested that on quenching a boron steel from a high austenitizing temperature the distribution of boron originally established is retained to the transformation temperature. Then if this grain boundary concentration of boron exceeds that amount which results in the minimum grain boundary energy, a loss in boron effect results.

Adair, Spretnak, and Speiser have measured the relative interfacial tension between austenite grains in AISI 8640 and AISI 86840 steels at two different temperatures. Their results indicate that boron lowers the interfacial tension between gamma grains and
Figure 3. Schematic representation of boron concentration at the grain boundary as a function of austenitizing temperature (After Simcoe, Elsea, and Manning).

\[ T_1 < T_2 < T_3 \]
\[ T_3 \approx 2000^\circ F. \]

\( T_{1,2,3} \) - Austenitizing temperatures

A - Boron concentration for minimum grain boundary energy at subcritical transformation temperature and maximum hardenability effect.

P - Boron concentration which will produce boron precipitate at the subcritical transformation temperature.
that the decrease is greater at the higher temperature. However, the magnitude of the decrease is shown to be statistically insignificant with regard to the hardenability effect. The results obtained indicate positive adsorption of boron in austenite.

Insofar as the effect of boron on grain growth in the austenite phase is concerned, considerable differences of opinion exist. Grange and Garvey\textsuperscript{24} reported that boron, as well as certain other elements in Grainal, reduced the effect of aluminum in inhibiting grain growth in steel. Vinarov, on the other hand, found finer grain structures in boron steels than in nonboron steels under normal austenitizing conditions. More recently workers at Battelle Memorial Institute\textsuperscript{29} found that addition of boron to alloy steels prevented the sporadic grain growth customarily observed in aluminum killed steels.
III. EVALUATION OF EXPERIMENTAL TECHNIQUES

First consideration is given to the possibility of getting direct evidence of grain boundary effects in boron steels. The autoradiographic detection of small concentrations of solute made radioactive by neutron irradiation suggests itself. Such a technique has been successfully employed by Chalmers, et al.,\textsuperscript{13,14} using alloys of bismuth in lead. Paraggi, Kohn, and Doumere\textsuperscript{29} report successful detection of boron in steel by this method but only at compositions of 0.01\% boron and more. Workers at Battelle Memorial Institute also tried to employ this method using commercial boron steel compositions.\textsuperscript{30} Briefly, the method centers around the reaction

\[ \text{B}^7 + n \rightarrow \text{Li}^7 + \text{He}(\alpha) \]

The alpha particles are detected by autoradiographic means. Apparently the major problems encountered concern the irradiation source for thermal neutrons and the mechanics of exposing and stripping the special film. The high neutron flux that must accompany the processes is also accompanied by heavy gamma radiation which darkens the film and makes the results ambiguous. No significant results were obtained by this method. Still another direct approach consists of examination of grain boundaries and surfaces of metallographically prepared boron steel specimens at the high magnifications obtainable with electron microscopy. This also has
been done with no results. The close examination and evaluation of cleavage fractures in typical boron steels was also fruitless. It appears, then, that the direct approaches to establishing grain boundary effects in boron steels have been exhausted, to no avail.

It was felt that this problem might logically be studied by other means. Such means involve the design of critical experiments to measure the effect of boron on properties which might be subject to variation because of grain boundary effects. This immediately suggested a study of grain growth characteristics and grain boundary migration in pertinent alloys. A further study of the theoretical aspects of grain growth, the details of which are presented later in the thesis, supports the idea of such an experiment.

Another valid type of experiment involves the measurement in polycrystalline materials of properties whose values depend on the bulk of the grains, being negligibly influenced by grain boundaries. One such property is the lattice parameter measured by x-ray diffraction. The value of the lattice parameter reflects the average conditions which obtain over a relatively large number of atoms in a fixed crystalline lattice, and is therefore mainly dependent on bulk grain material. Measurement of lattice parameter variation over the austenite range of temperatures in iron with and without boron should give evidence of concentration variations in the bulk grain material if adsorption effects are significant.
Another experiment based on the concept just outlined involves thermoelectric measurements. The thermoelectric properties of a metal, while complex, depend basically on the mean free path of the electrons. The mean free path is greatly influenced by impurities and consequently by their variation. Basically then, an experiment akin to the x-ray diffraction experiment would be to measure the variation of thermo-electric power in gamma iron with and without boron in the hope of detecting concentration variations induced by adsorption effects. A subsequent section deals with more detailed theoretical considerations of thermoelectricity.

Grange and Garvey have described in some detail a unique metallographic test for boron in which a characteristic constituent can be developed in the austenite grain boundaries. The very occurrence of this phenomenon suggests grain boundary enrichment of boron. Accordingly, an investigation of the occurrence of this boron constituent and its variation with austenitizing temperature should be fruitful in delineating grain boundary effects.

A final experiment to complete this phase of research concerns itself with an investigation of the reported permanent loss of boron hardenability effect after a homogenizing heat treatment.

During the course of this work an experiment based on the same conceptions presented above was completed by workers at another laboratory. The damping capacity of a base steel composition with and without boron was measured, since this property is apparently
sensitive to structural changes. Curves of damping capacity versus temperature showed a very slight difference in internal friction between the steels. The authors state that this may be caused by boron in the austenite grain boundaries.
IV. MATERIALS

Since this work was designed to evaluate specific effects of boron in iron, it was decided to prepare high purity iron and iron alloy ingots for use in the study. To this end one-pound ingots of pure iron, an iron-boron alloy, an iron-carbon alloy, and an iron-boron-carbon alloy were prepared. The base material used was electrolytic iron, the composition of which is given in Table I.

The vacuum induction furnace and its gas purification train, used to prepare the materials for experimentation, is shown in Figure 4. The furnace itself is of brass construction with all connections having o-ring seals. An opaque fused silica furnace tube is used, while alumina extraction thimbles serve as the stool to hold the melting crucible, radiation shielding, and melting crucibles. The vacuum system comprises a high capacity mechanical pump in series with an oil diffusion pump and a liquid nitrogen trap. A Phillips tube and gauge are used to measure the vacuum. The work coil can be moved vertically during melting to provide for directional solidification and eliminate piping. Power for the furnace is supplied by an Ajax mercury-arc gap unit. Although high purity argon was used in atmosphere melting a purification train was provided to further reduce impurities. The gas was passed through columns of anhydrous calcium sulfate and phosphorus pentoxide.
# TABLE I

**TYPICAL ANALYSIS FOR ELECTROLYTIC IRON**

<table>
<thead>
<tr>
<th>Element</th>
<th>Weight, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>0.010</td>
</tr>
<tr>
<td>Mn</td>
<td>0.010</td>
</tr>
<tr>
<td>P</td>
<td>0.003</td>
</tr>
<tr>
<td>S</td>
<td>0.004</td>
</tr>
<tr>
<td>Si</td>
<td>0.003</td>
</tr>
<tr>
<td>Ni</td>
<td>0.030</td>
</tr>
<tr>
<td>Cu</td>
<td>0.030</td>
</tr>
<tr>
<td>Co</td>
<td>0.007</td>
</tr>
<tr>
<td>Sn</td>
<td>0.005</td>
</tr>
<tr>
<td>V</td>
<td>0.003</td>
</tr>
<tr>
<td>Al</td>
<td>0.002</td>
</tr>
<tr>
<td>Cr</td>
<td>0.015</td>
</tr>
<tr>
<td>Mo</td>
<td>0.015</td>
</tr>
<tr>
<td>Ag</td>
<td>0.002</td>
</tr>
<tr>
<td>O</td>
<td>0.200</td>
</tr>
</tbody>
</table>
Figure 6. Induction furnace and gas purification train.
to remove moisture and then through titanium turnings to reduce the oxygen and nitrogen content. A Hoskins combustion furnace operating at 840°C holds the titanium turnings.

The initial step in the preparation of the pure iron ingot was to melt the chips of electrolytic iron which had been washed in acetone and dried. A vacuum of about \(1 \times 10^{-5}\) mm of Hg was obtained after which the charge was melted and held molten for several minutes. This step serves to reduce the relatively high carbon content of the base iron. After cooling the ingot was removed from the furnace and surface machined. The second melting of the cleaned ingot was done under dry hydrogen in order to reduce the oxygen content. High purity hydrogen was passed through the columns of anhydrous calcium sulfate and phosphorus pentoxide prior to being used in the furnace chamber. The furnace was evacuated using the mechanical pump and then flushed with hydrogen. This cycle was repeated twice. The third cycle was performed under the full vacuum and after flushing, a flow of hydrogen under a slight positive pressure was maintained. After melting the charge was again held molten for several minutes and then allowed to solidify under the flow of hydrogen. Cooling below the solidification point was done in vacuum. Again, the finished ingot was surface machined prior to being remelted. For the high purity iron ingot the third and final melt was done under high vacuum to insure complete
hydrogen removal. The preparation of the high purity iron alloys differed only from the above procedure in that the final melt was done under a purified argon atmosphere. Chemically pure carbon and boron were obtained for alloying additions. To insure complete solution of the additions the twice-melted iron ingots were drilled to provide a receptacle for the carbon and/or boron. After placing these alloying additions in the hole provided in the ingot the hole was repacked with the iron drillings. As before, the alloyed ingots were surface machined after melting. Prior to being chemically analysed each ingot thus prepared was homogenized for approximately four hours at 1000°C under a pressure of 2 x 10^-5 mm of Hg. A quantitative spectrographic analysis was obtained on the pure iron ingot and in addition oxygen, nitrogen, and carbon were determined by the vacuum-fusion method. The results of these analyses are given in Table II. Semi-quantitative spectrographic analyses were performed on the alloy ingots while quantitative determinations of the alloy additions were obtained. These analyses are shown in Table III.

The homogenized ingots were then subjected to the following sequence of fabrication treatments: forging to 5⁄8 inch bars, swaging to 0.300 inch rounds, and drawing to 0.025 and 0.010 inch wire. A temperature of 1000°F was used in the forging operations, whereas both the swaging and wire drawing operations were done at room temperature. Portions of each ingot were retained in the swaged condition for experimental use.
<table>
<thead>
<tr>
<th>Element</th>
<th>weight, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn</td>
<td>0.005</td>
</tr>
<tr>
<td>Si</td>
<td>0.010</td>
</tr>
<tr>
<td>Cu</td>
<td>0.0005</td>
</tr>
<tr>
<td>Ni</td>
<td>less than 0.005</td>
</tr>
<tr>
<td>Cr</td>
<td>less than 0.010</td>
</tr>
<tr>
<td>V</td>
<td>less than 0.010</td>
</tr>
<tr>
<td>Mo</td>
<td>less than 0.005</td>
</tr>
<tr>
<td>Al</td>
<td>less than 0.001</td>
</tr>
<tr>
<td>Sn</td>
<td>less than 0.001</td>
</tr>
<tr>
<td>P</td>
<td>less than 0.0005</td>
</tr>
<tr>
<td>Co</td>
<td>less than 0.010</td>
</tr>
<tr>
<td>Ca</td>
<td>less than 0.0005</td>
</tr>
<tr>
<td>C</td>
<td>0.0078</td>
</tr>
<tr>
<td>O</td>
<td>0.0023</td>
</tr>
<tr>
<td>N</td>
<td>0.0080</td>
</tr>
</tbody>
</table>

* Carbon, oxygen, and nitrogen were determined by vacuum fusion analysis. Courtesy of Westinghouse Electric Corporation.*
### TABLE III

**SEMI-QUANTITATIVE SPECTROGRAPHIC ANALYSES OF IRON ALLOYS**

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Major more than 10%</strong></td>
<td>Fe</td>
<td>Fe</td>
<td>Fe</td>
</tr>
<tr>
<td><strong>Low .1 - 1%</strong></td>
<td>None</td>
<td>None</td>
<td>None</td>
</tr>
<tr>
<td><strong>Very low .01 - .1%</strong></td>
<td>None</td>
<td>None</td>
<td>None</td>
</tr>
<tr>
<td><strong>Very low-trace .005 - .05%</strong></td>
<td>Si</td>
<td>Si, Al</td>
<td>Si</td>
</tr>
<tr>
<td><strong>Trace less than .01%</strong></td>
<td>Mn, Ti</td>
<td>B, Fe</td>
<td>Cu, As</td>
</tr>
<tr>
<td></td>
<td>Cu, As</td>
<td>Mn, Ti</td>
<td>Ni, Sb</td>
</tr>
<tr>
<td></td>
<td>Ni, Sb</td>
<td>Cu, As</td>
<td>Cr, Pb</td>
</tr>
<tr>
<td></td>
<td>Cr, Al</td>
<td>Ni, Sb</td>
<td>V, Sn</td>
</tr>
<tr>
<td></td>
<td>V, Pb</td>
<td>Cr, Pb</td>
<td>Mo, Zr</td>
</tr>
<tr>
<td></td>
<td>Mo, Sn</td>
<td>V, Sn</td>
<td>Co, Zn</td>
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<tr>
<td></td>
<td>Co, Zr</td>
<td>Mo, Zr</td>
<td>Bi</td>
</tr>
<tr>
<td></td>
<td>Bi, Zn</td>
<td>Co, Zn</td>
<td>Ti</td>
</tr>
<tr>
<td><strong>Boron</strong></td>
<td>0.0053</td>
<td></td>
<td>0.0021</td>
</tr>
<tr>
<td><strong>Carbon</strong></td>
<td>0.30</td>
<td></td>
<td>0.29</td>
</tr>
</tbody>
</table>

* Boron analyses by spectrographic method.

** Carbon analyses by a combustion method.
For certain portions of the work, typical commercial steels were used. These materials were supplied by the Republic Steel Corporation, Canton, Ohio, and corresponded to AISI 8640 and AISI 86B40 compositions. Both materials were taken from the same base heat the boron being added to a portion of the heat as Grainal No. 79. The composition and treatment of these materials is shown in Table IV.
TABLE IV

ANALYSIS OF REPUBLIC STEEL CORPORATION HEAT E-32720

Heat had base analysis of AISI 8640; special ingot treated with Grainal No. 79. 5A represents base analysis; 3A represents base plus four pounds per ton of Grainal No. 79.

<table>
<thead>
<tr>
<th></th>
<th>C</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
<th>Si</th>
<th>Ni</th>
<th>Cr</th>
<th>Mo</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>E32720-ladle</td>
<td>.39</td>
<td>.85</td>
<td>.015</td>
<td>.019</td>
<td>.31</td>
<td>.53</td>
<td>.48</td>
<td>.23</td>
<td></td>
</tr>
<tr>
<td>3A-Grainal No. 79</td>
<td>.395</td>
<td>.89</td>
<td>.31</td>
<td>.54</td>
<td>.48</td>
<td>.25</td>
<td>.0013</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5A-base</td>
<td>.396</td>
<td>.88</td>
<td>.31</td>
<td>.54</td>
<td>.47</td>
<td>.25</td>
<td>.0000</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
V. GRAIN GROWTH STUDIES

A. Background

Many excellent reviews of boundary migration and grain growth theory appear in the literature. The substance of the elementary theory is that the primary driving force for grain growth is the decrease in grain boundary interfacial energy which accompanies an increase in grain diameter. Harker and Parker\textsuperscript{31} suggested an atomistic mechanism for boundary migration. Later Beck\textsuperscript{32} derived an equation of the form

$$\frac{dD}{dt} = \frac{A\sigma}{D}$$

where

- \(D\) = average grain diameter
- \(t\) = time of anneal
- \(\sigma\) = interfacial free energy of grain boundaries
- \(A\) = constant at any temperature

which implies that isothermal grain growth can be described by considering the rate proportional to the interfacial free energy per unit volume. Burke\textsuperscript{33} considered the boundary migration rates proportional to their curvatures and derived the same equation on the assumption that the rate of grain growth is proportional to the average migration rate. Fullman\textsuperscript{34} points out however that the following assumptions are made in all derivations of elementary theory:
1. During the grain growth process the grain boundary mobility and interfacial free energy are constant,

2. Inclusions have no influence on grain boundary migration, and

3. Grain boundary free energy is the only driving force present.

Such assumptions lead only to fair approximations of the true behavior. Any quantitative measurement of grain growth must account for the error introduced by these assumptions.

Experimental results of isothermal grain growth studies are usually interpreted in light of a theoretical equation derived in the following manner. As a first approximation, it is assumed that the total grain boundary surface area per unit volume of metal is inversely proportional to the average grain diameter, i.e.,

$$S = c' \cdot \frac{l}{D}$$

where

- $S$ = total grain boundary surface area
- $D$ = average grain diameter

Furthermore the boundary surface energy per unit volume is proportional to the surface area and if $dD/dt$ is assumed to be proportional to the instantaneous surface energy, then

$$\frac{dD}{dt} = c" \cdot \frac{1}{D} \quad \text{or} \quad D \cdot dD = c" \cdot dt$$
Upon integration this leads to

\[ D = ct^{\frac{1}{2}} \]

where \( D \) = average grain diameter
\( t \) = time of anneal

Grain growth in metals frequently obeys a relationship of the form \( D = kt^n \) where in general \( n \) is less than \( \frac{1}{2} \). Experimentally the value of \( n \) varies greatly with both materials and temperature. The manner in which temperature affects the rate of grain growth can be described by an activation energy if the process is elementary in nature. The fact that \( n \) does vary with temperature prevents the description of the process by a single activation energy and points to more complex phenomena. Thus, Fullman\(^3\) points out that if one accepts the hypothesis that the major driving force for grain growth is the decrease in grain boundary free energy, then the problem of understanding the variation of activation energy with grain size is identical to understanding why \( n \) varies with temperature and why it is not always equal to \( \frac{1}{2} \).

A study of the factors which may influence \( n \) includes the effects of inclusions, changes in grain boundary free energy, adsorption of impurities at grain boundaries, orientation, polygonization, and strain. Again, Fullman\(^3\) has discussed each of these effects in detail and where possible has examined them quantitatively. In this treatment it is shown that decreases in grain boundary free energy during grain growth should not be chiefly responsible for
the small values of \( n \) observed. This treatment further shows that even though the adsorption of solute atoms at the grain boundaries does not appear to alter the surface energy significantly and thereby influence the grain growth exponent, such an occurrence can still have a substantial effect on grain boundary mobility which tends to decrease \( n \) by a large relative amount. Inclusions, strains, and preferred orientations depend on the degree to which each is present for their effects on \( n \), while it appears that polygonization will have little effect under any circumstance. With this background as a framework, a study of the isothermal grain growth characteristics of the iron-carbon and iron-carbon-boron alloys described previously was undertaken.

B. Experimental Method

A system analogous to that described by Miller and Day\textsuperscript{35} for heat etching steel specimens in a highly purified hydrogen atmosphere was used in this study. The equipment is pictured in Figure 5 and further described schematically in Figure 6.

The whole of the purification train coming before the heat etching furnace is chiefly for the removal of oxygen and water vapor from the gas. Electrolytically purified hydrogen is first bubbled through sulfuric acid and a column of drierite to remove water vapor and then through a column of soda lime for carbon
dioxide removal. Next the gas is subjected to two repetitive cycles consisting of passing it over platinized asbestos at 1000°F and thence through columns of activated alumina and phosphorus pentoxide in series. The function of the furnaces containing the platinized asbestos is to reduce oxygen to water vapor which is then absorbed in the ensuing portions of the train. Two furnace shells from Hoskins 20 volt - 50 ampere furnaces were fitted with Alundum liners previously wound with 0.064 inch nichrome wire. Inconel tubes (3/4 inch) were packed with platinized asbestos, inserted into the above furnaces, and these were then the completed furnaces used in the purification system. These furnaces were wired through 110 volt - 15 ampere rheostats for control purposes. The vertical heat etching furnace consists of the shell from a Hoskins Hevi-Duty (Type 303A) 110 volt - 5 ampere furnace, a replacement Alundum liner wound with 0.061 inch Kanthal wire, and a one-inch diameter Inconel tube 36 inches in length. This furnace tube is fitted with copper cooling coils on each end. A mercury quenching bath, contained in a water-cooled steel pot, seals the lower end of the furnace tube while the upper end is fitted with a push rod which carries the specimen to be treated. This push rod operates through an o-ring seal which is gas tight when the rod is clamped in place by means of a brass retaining ring and screw fitted brass nut provided for the purpose. The wiring of the heat etching furnace includes a 220 volt - 15 ampere
Figure 5. Heat-etching furnace and hydrogen purification train.
Legend for Figure 6

1. Sulfuric acid
2. Drierite
3. Soda lime
4. Platinized asbestos furnace
5. Activated alumina
6. Phosphorus pentoxide
7. Platinized asbestos furnace
8. Activated alumina
9. Phosphorus pentoxide
10. Mercury quenching bath
11. Push rod specimen holder
12. Control and recording thermocouples
13. Kanthal furnace windings
Figure 6. Schematic drawing of heat-etching furnace and hydrogen purification train.
rheostat and a Pyrovane controller with a temperature range of 0-1400°C. A closed-end stainless steel tube is fitted into the furnace adjacent to the heating zone and contains both the control and the measuring thermocouples (alumel-chromel).

In operation a specimen 4 inch long is taken from a ¼ inch rod and one face is threaded internally to fit the push rod while the opposite face is given a high polish. The polishing technique consisted of hand polishing through the 4-0 grit paper using kerosene on the papers followed by wet polishing on duck cloth saturated with alumina and final vari-speed polishing on velvet using a suspension of red rouge in water. A polished specimen is then washed with acetone and placed on the end of the push rod in the furnace. The rod is then raised in the tube until the specimen is about in the center of the tube area covered by the upper cooling coils. Nitrogen is then bubbled through the entire system until the air is displaced. The two platinized asbestos furnaces are then allowed to heat to 1000°F. When these furnaces are up to temperature hydrogen is switched into the system until the nitrogen is displaced. At this point the hydrogen flowing from the system is ignited and allowed to burn continuously. Power is then supplied to the heat etching furnace and the controller set at the desired temperature. When the furnace is controlling at temperature, the specimen and push rod are lowered into the hot zone of the furnace. After the desired time for heat etching the
push rod and specimen are plunged into the mercury bath. Nitrogen
is again switched into the system and allowed to completely dis­
place the hydrogen before the system is opened to the atmosphere
and the specimen removed. The results obtained using this method
are depicted in the microstructures of Figures 7-11. These
photo-micrographs depict a series of iron-0.30% carbon alloy
specimens which have been heat etched at 1900°F for times ranging
from 15 minutes to 4 hours according to the method just described.

Isothermal grain growth studies were made at temperatures
of 1750, 1850, and 1900°F for times ranging from 15 minutes to
4 hours. The average grain size analysis of the heat etched
specimens was based on the grain count as obtained from six photo­
grahic fields. Each specimen was examined under a metallurgical
microscope at a magnification that would produce about 100 grains
in a 5 x 7 inch field. Six exposures were made at random over the
surface of the specimen. The negatives obtained were placed over
a light source and the grain structure revealed by the heat etching
was traced in india ink directly on the negative. The number of
grains per negative could then be easily obtained by manual counting.

The system used to count the grains can best be described by

\[
total \text{ number of grains} = x + \frac{1}{2}y
\]

where \( x \) = number of whole grains in field

\( y \) = number of grains intersected by
the field boundary.
Figure 7. Specimen heat-etched for 15 minutes at 1900°F.
Figure 8. Specimen heat-treated for 30 minutes at 1900 F.
Figure 1. Specimen heat-etched for 1 hour at 1900°F.
Figure 10. Specimen heat-etched for 2 hours at 1900°F.
Figure 11. Specimen heat-etched for 4 hours at 1900°F.
By using the following equation the average grain size is then determined:

\[ D = \frac{1.075}{M} \sqrt{\frac{A}{N}} \]

where

- \( D \) = average grain diameter
- \( M \) = magnification
- \( A \) = area of field
- \( N \) = average number of grains in field.

This equation is based on a regular hexagon shape where \( D \) is the distance between parallel edges of the hexagon.

Initially it was hoped that this work could be carried out using the high-purity iron and iron-boron alloys. However, exploratory tests showed that grain growth in the gamma phase for the pure iron is extremely rapid and the heat etched structure obtained was somewhat ambiguous. After the decision was made to use the carbon containing alloys which had been prepared, an attempt was made to recrystallize the forged and swaged structures prior to testing. Such recrystallizing heat treatments in the alpha range (600-700°F) led to sporadic grain growth and consequently a highly nonhomogenous grain structure. However, it was determined that recrystallization took place in these specimens at the test temperatures in less than one minute and led to fairly homogenous grain structure. The recrystallized alpha grain size after this time was of the order of .001 mm. Accordingly the as-swaged specimens were used as starting material in this experiment.
C. Results and Discussion

Figures 12 and 13 are the plots of average grain diameter versus time of anneal for each of the alloys studied. These data were analyzed in terms of the grain growth equation

\[ D = kt^n \]

where \( D \) = average grain diameter  
\( t \) = time of anneal  
\( k, n \) = constants

According to this equation a plot of log \( D \) versus log \( t \) should give a straight line with slope \( n \) and intercept log \( k \). This of course is based on the assumption that the initial grain size is negligible in comparison to grain sizes encountered on annealing and also that the time for recrystallization is negligible in comparison to the annealing times used. Both of these assumptions appear valid in the examination of this data.

Figures 14 and 15 show the data plotted according to the above scheme. It is seen that the experimental data do reasonably fit a straight line on this plot. Further it is apparent that the slope of the curves increases continuously for the iron-carbon alloy over the range of temperatures studied whereas it decreases continuously for the iron-carbon-boron alloy studied.

In order to refine the data, a least squares analysis was performed on the assembled data points and the best equation to
Figure 12. Isothermal grain growth characteristics of high purity iron - 0.3% carbon alloy.
Figure 13. Isothermal grain growth characteristics of high purity iron - 0.29% carbon-0.0021% boron alloy.
Figure 11. Isothermal grain growth characteristics of high purity iron - 0.3% carbon alloy.
Figure 15. Isothermal grain growth characteristics of high purity iron - 0.29% carbon- 0.0021% boron alloy.
fit each set of data points was determined. A tabulation of these
data is given in Table V.

While little physical significance as such can be attributed
to $n$, one interpretation is evident as shown by Beck.\textsuperscript{32} Differentiation of the equation $D = kt^n$ gives

$$\frac{dD}{dt} = nktn^{-1}$$

If this equation is divided through by $D = kt^n$, then

$$n = \frac{\frac{dD}{dt}}{D/t}$$

This is equivalent to saying that $n$ is the ratio of the instantaneous grain growth $dD/dt$ to the average growth rate $D/t$. It should be remembered that the average growth rate is actually $(D-Do)/(t-tr)$ where $Do$ is the initial grain size after recrystallization and $tr$ is the time for recrystallization. Obviously the quantity reduces to $D/t$ where $Do$ and $tr$ are negligible. That $n$ should have such significance is obvious from the geometry of the type of plot shown in Figures 12 and 13.

For the present study the equations of the straight lines of Figures 11 and 15 have been differentiated to obtain rates of grain growth. These values are tabulated in Table VI. Examination of these data shows that at a given time the rate of grain growth increases with temperature for the iron-carbon alloy while the rates at comparative times decrease with temperature for the iron-
TABLE V

EQUATIONS FOR THE ISOTHERMAL GRAIN GROWTH OF AN IRON-0.3% CARBON ALLOY AND AN IRON-0.29% CARBON-0.002% BORON ALLOY AT VARIOUS TEMPERATURES

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Temperature, °F</th>
<th>Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe-0.3C</td>
<td>1750</td>
<td>$D = 0.046t^{0.097}$</td>
</tr>
<tr>
<td>Fe-0.3C</td>
<td>1850</td>
<td>$D = 0.043t^{0.14}$</td>
</tr>
<tr>
<td>Fe-0.3C</td>
<td>1900</td>
<td>$D = 0.036t^{0.21}$</td>
</tr>
<tr>
<td>Fe-0.3C-.002B</td>
<td>1750</td>
<td>$D = 0.042t^{0.14}$</td>
</tr>
<tr>
<td>Fe-0.3C-.002B</td>
<td>1850</td>
<td>$D = 0.061t^{0.11}$</td>
</tr>
<tr>
<td>Fe-0.3C-.002B</td>
<td>1900</td>
<td>$D = 0.076t^{0.086}$</td>
</tr>
</tbody>
</table>
**TABLE VI**

EQUATIONS FOR THE RATE OF ISOTHERMAL GRAIN GROWTH OF AN IRON-0.3\% CARBON ALLOY AND AN IRON-0.29\% CARBON-0.0021\% BORON ALLOY AT VARIOUS TEMPERATURES

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Temperature, °F</th>
<th>Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe-0.3C</td>
<td>1750</td>
<td>( \frac{dD}{dt} = -0.93 )</td>
</tr>
<tr>
<td>Fe-0.3C</td>
<td>1850</td>
<td>( \frac{dD}{dt} = -0.86 )</td>
</tr>
<tr>
<td>Fe-0.3C</td>
<td>1900</td>
<td>( \frac{dD}{dt} = -0.79 )</td>
</tr>
<tr>
<td>Fe-0.29C-0.002B</td>
<td>1750</td>
<td>( \frac{dD}{dt} = -0.86 )</td>
</tr>
<tr>
<td>Fe-0.29C-0.002B</td>
<td>1850</td>
<td>( \frac{dD}{dt} = -0.89 )</td>
</tr>
<tr>
<td>Fe-0.29C-0.002B</td>
<td>1900</td>
<td>( \frac{dD}{dt} = -0.91 )</td>
</tr>
</tbody>
</table>
carbon-boron alloy. The increase of n with temperature is probably chiefly a thermal effect since it has been shown in a few cases that the value of n extrapolates to its theoretical value of \( \frac{1}{3} \) at the melting point. The decrease of n with temperature, however, indicates that grain boundary migration is being deterred by some mechanism and the deterring action increases with increasing temperature. In this instance it is to be noted that the addition of boron to the iron-carbon alloy causes first a relative increase in grain growth rate followed by a continuous decrease in growth rate with temperature increase. Further, the absolute grain size at corresponding temperatures is always greater in the boron alloy than it is in the non-boron alloy.

It seems likely that the decreasing value of n with increasing temperatures observed for the boron alloy reflects the increasing adsorption of boron at the grain boundaries with increasing temperatures. Microscopic examination of the heat etched specimens failed to show any visible inclusions. Nevertheless one possible explanation might involve the formation of boron nitride at the lower temperature. The removal of these elements from solution in the boron alloy could account for the larger grain size and higher initial value of n. Decreasing values of n with temperature increases would reflect dissociation of some boron nitride at higher temperatures with accompanying effects on grain growth. Because of the small concentrations of boron and nitrogen used here
a reaction between the two would probably involve the assumption of grain boundary enrichment of both elements. In general too little is known about the reaction between boron and nitrogen and about recrystallization and the initial stages of grain growth in the alloys as used here to come to any definite conclusions. Any other effects due to orientation, strain, etc. should be constant in these two alloys which were similar in all respects save the addition of boron to one. Fundamentally then it appears that the effects observed point strongly to grain boundary adsorption as their cause.

The question remains as to what the fundamental mechanism which causes a continuous decrease in the rate of boundary migration must be. Most authors agree that the adsorption of either soluble or insoluble impurities at the grain boundaries will substantially account for this effect. Some insight to the mechanism may be gained by determining an "activation energy" for the process on the basis of experimental data obtained.\textsuperscript{37} In certain instances such activation energies may be related to known activation energies for self-diffusion or for diffusion of known impurities in the system.

The simplest way to obtain activation energies is to plot the log annealing time necessary for the average grain size to increase from a starting grain size \(D_0\) to a selected final standard grain size \(D\) as a function of the reciprocal of the annealing temperature. There is applicable an expression of the form
\[ \ln \frac{t_2}{t_1} = \frac{Q}{R} (\theta_2 - \theta_1) \]

where \( t_1 \) = time of anneal to grain size \((D-D_0)\) at temperature \( T_1 \),

\( t_2 \) = time of anneal to grain size \((n-D_0)\) at temperature \( T_2 \), and

\( Q \) = activation energy for reaction process.

It should be stated that the above treatment involves an elementary process and is not valid for any other. The variation of \( n \) with temperature in the grain growth process shows a complex mechanism not definable by a single activation energy. Hence such quantities are meaningless except in that they indicate orders of magnitude.

The data of this experiment have been treated in accordance with the above and the results are shown in Figure 16. The activation energies for grain growth calculated from this plot are 98 kcal/mol for the iron-carbon alloy and 160 kcal/mol for the iron-carbon-boron alloy where the value of constant grain size was chosen as 0.09 mm. These values compare favorably with those obtained by Miller \(^{35}\) which were of the order of 100 kcal/mol. The activation energy for the diffusion of carbon in gamma iron is given as 28-34 kcal/mol and that for the self diffusion of gamma iron is given as 48 kcal/mol. Further, it can be assumed, as has been suggested, \(^{38}\) that the diffusivity rates of boron and carbon in iron are comparable. Then by comparison it would appear that diffusion or atomic mobility is not the rate controlling factor in the grain growth mechanism of this system. Whatever the mechanism
Figure 16. Annealing times to reach grain size of 0.09 mm in iron-0.3% carbon and iron-0.29% carbon-0.0021% boron alloys.
may be it would still appear that the adsorption of boron to the grain boundaries has an important effect on its functioning.
VI. X-RAY DIFFRACTION STUDIES

A. Background

The basic concepts underlying the x-ray diffraction studies of lattice parameters in the gamma phase of iron have been briefly considered in a previous section dealing with evaluation of experimental techniques. Thermal expansion data for pure iron over the gamma temperature range have been fairly well established by x-ray diffraction techniques. It was presumed for purposes of this study that the introduction of boron in small concentrations would have a measurable effect on the thermal expansion of iron, and further that detectable variations of comparative thermal expansion values might be interpreted in light of concentration variations that might be induced by adsorption effects. Axon and Hume-Rothery have concluded that lattice parameters in solid solution are influenced by the following four factors:

1. the relative volume per valency electron in crystals of the solvent and solute,

2. the relative radii of the ions of solvent and solute,

3. effects due to the overlap of Brillouin zones, and

4. the difference between solvent and solute in the
electrochemical series.
Whatever the effects of the interplay of these factors in determining the effect of boron on the iron lattice, it is clear that the slopes of the thermal expansion curves for iron and an iron-boron alloy should be parallel if no redistribution of solute atoms is encountered. This assumes that the effect of temperature on variations of electron configuration and electron concentration due to the solution of small concentrations of boron in iron will be negligible.

B. Experimental Method

The materials used in this study were 0.010 inch wires of each of the high purity materials prepared for this work. Initially diffraction patterns were obtained on each of these materials at room temperature. A 114 mm Norelco powder type x-ray diffraction camera was used for this work. After centering of the wire specimen and loading the camera it was externally wrapped with a heavy cotton packing material and aluminum foil to provide thermostating. A thermometer was inserted adjacent to the camera body and temperature readings were taken every five minutes during the exposure. Under these conditions temperature variations were limited to ±0.1°C. The best room temperature exposures were obtained using unfiltered cobalt radiation with exposure lengths being about one hour. Film reading was done on standard equipment and the extrapolation method of Nelson and Riley140 was used to obtain the precision lattice constants. In this method the values of lattice...
parameters determined from each line on the film are plotted against the function

\[ \frac{1}{2} \left( \csc \Theta + \Theta^{-1} \right) \cos^2 \Theta \]

where \( \Theta \) = Bragg reflection angle corresponding to each line.

The value of lattice parameter extrapolated to zero Bragg angle is then the most precise value. The Nelson and Riley function is supposedly applicable over a larger range of back reflection angles and is thus more useful where the number of such reflections are limited. Other extrapolation functions were tried but the one chosen seemed preferable. Lattice parameters, corrected to 20°C, as determined by this method are shown in Table VII. Both the alloys containing boron show a decrease in lattice parameter relative to pure iron whereas the alloy containing carbon alone shows no variation of lattice parameter referred to pure iron. Thus there appears to be a possibility that effective amounts of boron are in solution in iron at room temperature.

The high temperature, vacuum camera selected for the high-temperature lattice parameter study and its accessory equipment is pictured in Figures 17-19. A schematic diagram of the camera body alone is shown in Figure 20. This equipment is located in the Experiment Station at The Ohio State University. The cylindrical camera body is made of brass and fitted with internal copper cooling coils. The body is split with two halves joined by an o-ring seal. Platinum wound resistor coils are mounted in the
TABLE VII

LATTICE PARAMETERS OF PURE IRON AND SOME IRON ALLOYS AT 20°C *

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Parameter (corrected to 20°C), Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>2.8665</td>
</tr>
<tr>
<td>Fe-.005%B</td>
<td>2.8662</td>
</tr>
<tr>
<td>Fe-0.3%C</td>
<td>2.8665</td>
</tr>
<tr>
<td>Fe-0.29%C-.002%B</td>
<td>2.8664</td>
</tr>
</tbody>
</table>

* Unfiltered cobalt radiation, thermostatted camera.
stationary lower half and removable top portion. The specimen mount comes up through the lower coil and the thermocouple comes down through the upper coil so that it is placed just at the tip of the specimen during operation. The film holder fits over the assembly as shown. Both the exit and entrance tube forming the slit system are removable and join to the camera body through O-ring seals. A thin cellophane sheet is glued over the entrance slit to provide a vacuum seal and the exit tube is provided with a leaded glass shield coated with fluorescent compound. Test temperatures up to 1200°C are easily attained and the temperature is controlled to ±2°C with the aid of a power input stabilization unit. Vacuums of the order of 2 x 10⁻⁵ mm of Hg were maintained using a high capacity mechanical fore pump in series with an oil diffusion pump. Vacuum measurements were supplied by an ion gauge.

In operation the wire specimens are cut to an accurate length of 3/16 inch and mounted on the topaz mounting rod with the aid of a dab of alundum paste. The specimen is aligned vertically prior to the drying of the cement. Final eccentricity adjustments are made through a series of cams and are done by a trial and error method. When the alignment is completed the camera is assembled and evacuated. Power is then supplied to the coils and the camera brought up to temperature slowly. Exposures are then made for the desired time. In this study unfiltered cobalt radiation was used and exposure times of approximately 1½ hours were necessary.
Legend for Figures 17-19

A. Mechanical vacuum fore pump
B. Ammeter
C. Powerstat
D. Input power supply stabilizer
E. Control panel for ion-thermocouple vacuum gauge
F. Control panel for power and water supply
G. Oil diffusion pump
H. Water pan
J. X-ray camera
K. Portable potentiometer
L. Thermometer for temperature correction
Figure 17. Vacuum pump and power stabilization unit used with the high-temperature X-ray diffraction camera. (See legend before Figure 17 for description of lettered items).
Figure 16. Control panels and diffusion pump used with the high-temperature X-ray diffraction camera. (See second before figure 17 for description of lettered items).
Figure 19. High-temperature X-ray diffraction camera (See legend before Figure 17 for description of lettered items).
1. Stupakoff fittings.
2. Steel holder for alumina thermocouple tubing.
3. Two hole alumina thermocouple tubing.
4. Alumina sample holder.
5. Brass plate.
6. Alumina tubing.
7. Topaz rod.
8. Thumb screw.
11. Film holder.
13. Film.
16. Beryllium foil 0.012 inch thick.
17. O-rings.
18. Brass post.
20. Steel shaft.
22. Garlock closure, Model 51.
23. Pulley.
Legend for Figure 20 (continued)

24. washer.
25. Brass plate.
27. Brass shell.
28. X-ray beam trap assembly.
29. Collimator assembly.
30. Base support-beam trap end.
31. Base support-collimator end.
32. Thumb screws.
33. Steel springs.
34. Platinum, Platinum-10% Rhodium thermocouple.
Figure 20. Schematic diagram of a high-temperature x-ray diffraction camera.
Some preliminary work was done on testing wires of varying thickness and different initial conditions. Wire sizes of 0.003, 0.005, and 0.010" diameter were exposed to determine if sufficient differences in accuracy of measurement were involved because of diminishing line width. The smaller diameter wires were very difficult to handle mechanically and alignment in particular was impractical. Within the accuracy obtainable in the film reading method used the 0.010 inch wires were found satisfactory and accordingly used throughout the test. In general such tests on high purity materials are complicated by grain growth. Initial experiments on fully annealed wires indicated that certain reflections would be absent and that the resulting pictures would be so spotty as to prevent accurate measurements. Under the conditions of this experiment the face-centered lattice reflections obtained correspond to the following half planes: (111), (200), (220), (311), (222), and (400). The corresponding values of \( h^2 + k^2 + l^2 \) are 3, 4, 5, 11, 12, and 16. Of these the reflections represented by 3 and 4 are front reflections and are practically useless in lattice parameter determination. With the annealed wires it was extremely difficult to record the 11 and 22 reflections and the remaining two tended to be spotty. This effect was obviated to a large degree by the use of cold drawn samples which recrystallized in the camera during the heating up period. Even under these circumstances, however, it was frequently necessary to make as
many as three exposures to obtain the necessary reflections in one complete enough to insure sufficiently accurate results when read. In several instances the extrapolation data was obtained from a combination of two exposures. The measurements were limited to the high purity iron and the iron-boron alloy. Here again the extrapolation method of Nelson and Hiley, previously described, was used in calculating the lattice parameters. Previous work with the camera used indicated that parameter measurements in this temperature range were accurate to ±0.0005 Å.

C. Results and Discussion

Figure 21 presents the data obtained for the thermal expansion of the iron and iron-boron alloy studied. A presumptive notion of the expected behavior of the thermal expansion of the iron-boron alloy relative to that for pure iron was developed as shown in Figure 22 (a). This was based on the assumption that boron would be in interstitial solid solution in gamma iron. As a result of this condition, an expansion of the lattice was expected. Further, if the boron were randomly distributed in the gamma iron, over the temperature range of the test, the thermal expansion curve of the iron-boron alloy could be expected to be a mirror to the curve for pure iron. The occurrence of adsorption would be indicated if the
Figure 2.1. Gamma phase lattice parameter of pure iron and an iron-0.005% boron alloy.
(a.) Expected Behavior

(b.) Observed Behavior

Figure 22. Schematic representation of the effect of boron on the expected and observed behavior of the thermal expansion of pure iron.
thermal expansion curve of the alloy approached that for pure iron as shown in the figure. The observed behavior plotted in Figure 21 has been redrawn schematically in Figure 22(b) for comparison purposes. Obviously, the addition of boron to the pure iron causes a contraction of the lattice. The thermal expansion curve for the alloy is divided into two sections, a and b, in Figure 12(b). The portion of the curve marked a is better understood by reference to the Fe - Fe₃B equilibrium diagram of Moiride, Spretnak, and Speiser. In this diagram, at a 0.005% boron concentration, a two phase field exists between 536°C and about 1025°C. Above 1025°C all the boron is in solution in austenite. The observed constant slope portion of the thermal expansion curve for the iron-0.005% boron alloy must then represent the solution of Fe₃B. Along the portion of the curve marked b, the tendency is for the lattice parameter of the alloy to converge to that for pure iron. This behavior can be plausibly explained by concentration variations within the grains as previously surmised, i.e., the positive adsorption of boron in austenite, increasing with increasing temperature.

The lattice contractions observed when boron is added to iron indicate that boron atoms occupy substitutional positions in both the alpha and gamma phases. Moiride, Spretnak, and Speiser considered the probable types of boron solid solution in iron. On the basis of the relative size of the boron atoms and the inter-
interstitial and substitutional holes in the lattice they predicted a substitutional solid solution of boron in alpha iron. Never and Mueller indicated the observation of a lattice contraction in their studies on the iron-boron system. More recently, Ebersnas obtained a parameter contraction in an alpha solid solution of boron in iron comparable to that observed in the present study. While the evidence thus points to boron being substitutional in alpha iron it has previously been assumed that boron is interstitial in gamma iron. Davis, Irish, and Garwill observed that the rate of diffusion of boron was comparable to that of carbon in the study of decarburized zones of commercial steels. From this observation they surmised that boron, like carbon, occupies interstitial positions in the gamma iron lattice. Later, uslay, wave, and Wells established more precisely that the diffusion rates of carbon and boron in gamma iron were about the same. A similar type, "it all predict an interstitial type of solid solution based on calculations involving the dependence of solubility on the energy required to introduce a boron atom into either an interstitial or substitutional position. The solubility, however, was not a certain that indicated the necessity for high temperature diffusion studies to resolve the problem.

Not enough is known about diffusion mechanisms to speculate on the seeming incongruity presented by the diffusion data and x-ray diffraction data. One possibility suggesting itself is that the
strain energy which boron introduces into the substitutional position of the face centered lattice may be of the same order of magnitude as the energy necessary to fit the atom into an interstitial position. In addition to diffusing by a process which the mechanism, then, the diffusivity of boron atoms may be enhanced by the ability to "tunnel" through interstitial positions. This is equivalent to saying that even though the majority of boron atoms occupy substitutional positions in the face centered cubic lattice, at any given instant a certain portion of them may be found in interstitial sites. This explanation could account for the comparable diffusion rates of boron and carbon in vanadium.
VII. THERMOELECTRIC STUDIES

A. Background

The basis for the study of the thermoelectric characteristics of iron and some of its alloys was derived from the work of Gaspard, set forth in a recent publication, where it was found that the thermoelectric power of an impure metal is extremely sensitive to small variations in solute concentration. It is suggested that the thermoelectric power of iron must be sensitive to the distribution of carbon and boron within the gamma grains. Thus at temperatures just above the transformation temperature, a solute distributed homogeneously throughout the gamma solid solution could be expected to have some significant effect on the thermoelectric power relative to pure iron. If the solute were absorbed to the grain boundaries with increasing temperature it was expected that the thermoelectric power would change over and above any changes associated with boron in iron, since its value should depend on the size of the grain boundaries. That this should tend to occur for the reasons given earlier is evident from their discussion in other areas.

Thermoelectric phenomena in metals are the result of some complex interrelation between heat conductivity, and electrical conductivity. On the next and electrical conductivity of the
Electrons in a metal depend on the mean free path of the electrons in the metal. The collisions which limit the free path of the electrons are primarily those between the electrons and the fixed ions composing the crystal lattice. Detailed investigations of these collisions made by electrons show that such collisions are due only to the displacement of ions from their equilibrium positions by impurities and temperature motion. For the lattice without impurities, it is shown that the number of collisions per unit time is proportional to the temperature. The effect of impurities is to cause a constant temperature independent contribution to the number of collisions per unit time. Since the mean free path is inversely proportional to the number of collisions, 

$$l = \frac{\lambda_0}{a + T}$$

where \(\lambda_0 = \text{constant}\)

\(T = \text{temperature}\)

\(a = \text{constant}\)

The temperature independent constant \(a\) is highly dependent on the amount of impurity in the metal.

In order to derive a theoretical equation describing the ordinary optical effect, Mayer and Wigner treat the electrons in a metal as a gas of mechanically independent particles. Application of a temperature gradient or an electric field to the metal disturbs the equilibrium of the electron gas and the number of electrons per unit of momentum, i.e., the distribution function must be.
determined under the perturbing influence. Taking into account the exclusion principle, the Maxwell-Boltzmann collision equation with the proper distribution function is solved to determine the rate of transport of both the charge through the metal. The electric potential difference between the two ends is then given as,

\[ 
\psi = \phi(A) - \phi(B) = \frac{\pi^2 k^2}{3 e} \int_0^T \left( \frac{l}{\mu_a} \left( 1 + \frac{\mu_a l'}{l} \right) - \frac{l}{\mu_b} \left( 1 + \frac{\mu_b l'}{l} \right) \right) \, dT \]

where \( \phi(A) - \phi(B) \) = Volta potential between metals A and B,

- \( T \) = temperature
- \( \mu \) = chemical potential
- \( l' \) = derivative of mean free path
- \( l \) = mean free path, and
- \( \pi, k, e \) = constants

a and b subscripts refer to the metals A and B.

By differentiating the above expression an equation for the thermoelectric power is obtained. Thus

\[ \frac{d\psi}{dT} = \frac{\pi^2 k^2}{3 e} T \left\{ \left( \frac{1}{\mu_a} + \frac{l'}{l} \right) - \left( \frac{1}{\mu_b} + \frac{l'}{l} \right) \right\} \]

If one treats the chemical potentials as temperature independent, the relation between the thermoelectric power and mean free path is evident.
Thus any effects of an added solute on the thermoelectric power of a pure material should be reflected in a change of slope of the curve of emf generated versus temperature. Effects such as might be introduced by solute adsorption should be shown apparent by comparison of the slope of this curve for the alloy with the slope of the curve for the pure material.

3. Experimental Method

The discussion above suggests the technique to be used for experimental verification. The materials used were 0.010 inch wires from each of the purity grade ingots prepared. These wires were fully annealed (4 hours at 1000°C) and thoroughly cleaned prior to use. Test thermocouples were formed using these wires and chemically pure platinum wire. The thermoelectric force of each of these couples was then measured over the austenitic range of temperatures up to 1200°C. Duplicate tests showed the results to be reproducible.

The vacuum system and accessories used in this experiment are shown in the photographs of Figures 23 and 24, and again in the schematic drawing of Figure 2. The furnace shell, water jacket, and vacuum system were constructed with copper and brass tubing while the cold trap was made from stainless steel. The power leads to the heating coil are stainless steel rods secured to the furnace.
Figure 23. Vacuum furnace for thermoelectric studies.
Figure 24. Measuring instruments used in thermoelectric studies.
Legend for Figure 25

1. Diffusion pump.
2. Mechanical pump.
3. O-ring seal.
4. Stainless steel flask.
5. Liquid nitrogen trap.
6. O-ring seal.
7. Phillips tube to vacuum gauge.
8. Radiation shields.
9. Platinum, Platinum-10% Rhodium Thermocouple.
10. Test thermocouple.
12. Stupakoff seals.
15. Baffles.
16. Rowerstat lends.
17. O-ring seal.
18. Water ports.
Figure 2S. Schematic diagram of vacuum furnace used in thermoelectric studies (see legend for description of numbered items).
bottom through Stupakoff seals. In a similar way the brass furnace cover contains four Stupakoff seals which serve as thermocouple wire ducts. The furnace cover, which is removed to insert the test thermocouples, is fastened on an o-ring seal by twelve screw bolts. The heating coil made of 0.050 inch molybdenum wire is wound around four reinforced alundum posts equally spaced within stainless steel rings at the top and bottom. This unit is held together by four molybdenum rods fastened to the rings and insulated from the coil by alundum tubing. The sample holder is a molybdenum rod threaded into a stainless steel bar which is secured by pins on the top ring. Screwed onto the end of the molybdenum rod is a tantalum block drilled to take a welded thermocouple and also to force fit the test wires. The latter was accomplished by means of a drilled hole and an undersized tantalum peg. The wires were twisted and then force fitted between the hole and the peg. These thermocouple wires were led from the tantalum block to the furnace cover and through the seals, being fastened with a drop of solder, thence to a cold junction of mercury in an ice water bath and finally to the respective measuring instruments. The coil itself was entirely protected from the inner furnace shell and the specimen wires by molybdenum sheet radiation shields and baffling. The inner baffling protected the thermocouples from alternating current pickup.
Temperature readings from the standardized Platinum, Platinum-13% Rhodium thermocouple were taken using a Leeds and Northrup semi-precision potentiometer capable of reading $10^{-6}$ volts, and test thermocouple temperature readings were recorded on a Leeds and Northrup Type K-2 precision potentiometer sensitive to $10^{-7}$ volts. Vacuums of the order of $2 \times 10^{-5}$ mm of Hg were maintained at test temperatures using a Welsh mechanical fore pump in series with a three stage oil diffusion pump and liquid nitrogen cold trap. Power at 220 volts is brought into the system through a relay to the vacuum pump heating element and to the furnace heating coil. A Pressuretrol switch is provided in the cooling water circuit which functions to cut off the power if the cooling water pressure should reach a dangerously low level. Power to the furnace coil is regulated by a powerstat transformer and the pressure of the system is indicated by a Phillips vacuum gauge.

After the system had been assembled the wires were heated in vacuum to approximately 1200°C and held at this temperature until no changes in the emf produced by the couples could be detected. The power input to the system was then reduced by a small amount and the emf's again allowed to come to equilibrium. This procedure was repeated, recording the two sets of equilibrium emf data, until the austenite temperature range had been covered. This was easily detected by a discontinuity in the emf versus temperature plot. The experiment was repeated for each of the test
thermocouples and then repeated from the beginning, using the previously tested wires, to insure reproducibility. As previously stated the results were reproducible within small experimental variations.

C. Results and Discussion

The results of these tests are shown in Figures 26-29. Data are plotted for the range of temperatures representing the gamma phase in these iron alloys. Curves are presented for the thermo-electric force and the thermoelectric power of each of the couples tested. The curves of thermoelectric power were derived from the curves of thermoelectric force by a method of graphical differentiation.\(^7\) These plots show that the independent addition of boron or carbon, as well as the addition of a combination of the two, to iron lowers the thermoelectric force of iron measured against platinum. The effect of carbon in this respect is greater than that of boron and the effect of the combination of the two elements causes the greatest lowering of the thermoelectric force. Further, in the temperature range just above transformation, the thermoelectric power of iron measured against platinum is decreased by the addition of carbon, boron, and the combination of both. The addition of boron alone appears to have the greatest effect and that of carbon the least. with increasing temperatures in the
Figure 26. Characteristic thermoelectric force curves for thermocouples of iron versus platinum and iron-0.005% boron versus platinum.
Figure 27. Characteristic thermoelectric force curves for thermocouples of iron-0.3% carbon versus platinum and iron-0.29% carbon-0.0021% boron versus platinum.
Figure 28. Thermoelectric power curves of iron versus platinum and iron-0.005% boron versus platinum over the austenite temperature range derived from the Volta potential.
Figure 29. Thermoelectric power curves of iron-0.3% carbon versus platinum and iron-0.29% carbon-0.0021% boron versus platinum over the austenite temperature range derived from the Volta potential.
gamma range each of the alloys tend to assume values of thermo-electric power equal to that of the pure iron.

To interpret this data reference is made to the previously derived equations of this section. For three metals A - platinum, B - iron, and C - iron-boron, combinations of the potential difference equations lead to

$$\psi = \phi(c) - \phi(a) = \frac{4\pi^2 k^2}{3} e^{\frac{T_e}{T}} \left( \frac{1}{\mu_c} + \frac{\ell c}{\lambda N_0T} \right) \left( \frac{1}{\mu_b} + \frac{\ell b}{\lambda N_0T} \right) dT$$

(3)

In this equation the temperature dependent expressions for the mean free path have been substituted. The constant $a$ represents the boron impurity atoms which cause a decrease of mean free path in this alloy. If we assume changing concentrations with increasing temperature in the boron alloy $a$ is no longer a temperature independent constant, and

$$\psi = f(T, a) \text{ so that } \frac{d\psi}{dT} = \frac{\partial \psi}{\partial T} + \frac{\partial \psi}{\partial a} \frac{da}{dT}$$

Differentiating equation (3) term by term gives

$$\frac{d\psi}{dT} = \frac{4\pi^2 k^2}{3} e^{\frac{T_e}{T}} \left( \frac{1}{\mu_c} + \frac{\ell c}{\lambda N_0T} \right) \left( \frac{1}{\mu_b} + \frac{\ell b}{\lambda N_0T} \right)$$

(4)

and

$$\frac{d\psi}{da} = \frac{4\pi^2 k^2}{3} e^{\frac{T_e}{T}} \left[ \frac{\ell c}{\lambda N_0T} \left( \frac{\partial \mu_c}{\partial a} + \frac{\ell c}{\lambda N_0T} \right) \left( \frac{\partial \mu_b}{\partial a} + \frac{\ell b}{\lambda N_0T} \right) \right]$$

$$- \left[ \left( \frac{1}{\mu_c} \frac{\partial \mu_c}{\partial a} + \frac{\ell c}{\lambda N_0T} \right) \left( \frac{1}{\mu_b} \frac{\partial \mu_b}{\partial a} + \frac{\ell b}{\lambda N_0T} \right) \right] dT$$

(5)
The last term of the equation for \( \frac{\partial u}{\partial a} \) drops out because pure iron is independent of \( a \). Hence \( \frac{\partial u}{\partial T} \) is controlled by the remaining expressions. By inspection it appears that the quantities in the second term of \( \frac{\partial u}{\partial a} \) are in the nature of second-order terms and hence small. The major factor in the second term of \( \frac{\partial u}{\partial T} \) is the differential \( \frac{da}{dt} \) and since it is expected that any adsorption effects will be very small it appears that the second term of \( \frac{\partial u}{\partial T} \) is negligible. Hence the expected behavior of the thermoelectric power of these alloys can be predicted from the expression for \( \frac{\partial u}{\partial T} \). As a good approximation \( \mu_c \) may be considered equal to \( \mu_b \). Then, under these circumstances the entire behavior depends on the ratios 

\[
\frac{\mu_c}{N_c/\alpha + T} \quad \text{and} \quad \frac{\mu_b}{N_b/\alpha + T}
\]

Obviously the former ratio will always be larger than the latter which is to say that \( \frac{\partial u}{\partial T} \) is always positive. The difference between the slopes of the curves being always positive means that they cannot cross. Further we see by inspection that as \( a \) decreases, the slopes of the two lines should converge. The condition for the positive adsorption of boron, increasing with increasing temperature, is that \( a \) should constantly decrease as the temperature increases. Thus the expected behavior for positive adsorption would be that the slopes of the emf versus temperature curves for iron
and an iron-boron alloy should converge, tending to become parallel but never crossing. This, of course, is the behavior shown by the experimental data. As expected the effects are small but significant. Examination of the thermoelectric force curve for the iron-0.005\% boron alloy shows that it bears a strong resemblance to the curve of lattice parameter versus temperature. The slope of the thermoelectric force curve for iron-0.005\% boron between 900°C and 1025°C again reflects the solution of boron in gamma iron. Above this temperature the slope changes, as shown, can be interpreted as adsorption effects. Whether the small differences in slope shown for the iron-carbon alloy are a temperature effect alone or also reflect adsorption effects introduced by carbon is problematical. Again too little is known about the ternary system to interpret the very slight changes that are evident. In any case it appears that the comparison of the data for pure iron and the iron-0.005\% boron alloy can be interpreted as positive adsorption effects of boron in solution in austenite, increasing with increasing temperature.
VIII. METALLOGRAPHIC STUDIES

A. Background

Grange and Garvey have discussed a unique metallographic test for boron. Whenever heat treatment of a steel containing a small percentage of boron results in increased hardenability, a characteristic constituent can be formed in the microstructure which cannot be found in steels not containing boron. Grange and Garvey obtained this constituent by heating in the vicinity of 2000°F and rapidly cooling to a subcritical temperature where ferrite forms at the austenite grain boundaries on holding. The constituent which is bead-like and more or less continuous in outlining the prior austenite grains appears in the ferritic areas. It was pointed out that the amount of boron constituent increases with increasing boron content and seems to be influenced by the carbon content. The authors speculated that boron atoms were concentrated at the grain boundaries at the high austenitizing temperatures and precipitation of the constituent occurred on rapidly cooling to the sub-critical transformation temperature. Under the circumstances leading to the phenomenon described above, it appeared that a study of the variation of boron constituent with austenitizing temperature might be a sensitive means of establishing the possible occurrence of surface adsorption of boron in austenite.
B. **Experimental Method**

The atmosphere heat-treating equipment used in this work is basically that employed in the previously outlined grain growth studies and shown in Figures 4-6. Temperatures of about 2350°F could be attained by this Kanthal wound furnace and this was sufficient for the present study. However, modifications had to be made in the gas purification train and the quenching bath. Since the short, high-temperature austenitizing treatments had to be done in argon it was necessary to use titanium chip furnaces, operating at 1000°C, in the place of the furnaces containing platinized asbestos. This treatment removes the major portion of nitrogen and water vapor from the argon. The experiment also requires a quenching bath that operates at constant sub-critical temperatures. After experimenting with various methods of meeting this requirement it was decided to replace the mercury seal in the system with a rubber stopper closure while simultaneously providing an independent salt quenching bath which could be moved into the required position for the quenching operation. The salt bath used was of the modified chloride type (borax added), held in welded stainless steel pots and heated to the required temperature in a Hoskins FD104 pot furnace.

The material used in this study was a portion of a commercial heat of AISI 8640 steel supplied by the Republic Steel Company.
Table IV gives the analysis of this heat of steel. Cylindrical specimens \( \frac{1}{4} \) inch in diameter and \( \frac{3}{4} \) inch long were drilled and threaded to fit the push rod in the furnace. The technique employed was to bring the austenitizing furnace to temperature, immerse the specimen and hold at temperature for ten minutes, and then simultaneously remove the bottom stopper of the heating tube and quench the specimen into a salt bath held at constant sub-critical temperature. After sufficient holding time to insure transformation the specimen was removed and cooled in an air blast.

Initially sporadic results were obtained in the effort to obtain the boron precipitate because of the extreme sensitivity of these steels to deboronization. In order to circumvent this tendency each of the specimens to be used was nickel plated just prior to testing. This was done simply with the aid of a nickel anode, a nickel plating bath, and a standard 6 volt battery. The composition of the nickel plating bath was as follows:

<table>
<thead>
<tr>
<th>Compound</th>
<th>Weight, grams/gal</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nickel Sulfate, ( \text{NiSO}_4 )</td>
<td>680</td>
</tr>
<tr>
<td>Ammonium Chloride, ( \text{NH}_4\text{Cl} )</td>
<td>93</td>
</tr>
<tr>
<td>Boric Acid, ( \text{HBO}_3 )</td>
<td>113</td>
</tr>
<tr>
<td>Hydrogen Peroxide, ( \text{H}_2\text{O}_2 )</td>
<td>2</td>
</tr>
</tbody>
</table>

The hydrogen peroxide was added to wet the sample. Prior to plating each specimen was etched in hydrochloric acid and cleaned in an
alkali solution composed of 30 grams of sodium carbonate (NaCO₃), 15 grams of tri-sodium phosphate (Na₃PO₄), 7.5 grams of sodium hydroxide (NaOH), and one liter of water. Both the specimen, as cathode, and the nickel anode were suspended in the heated plating solution (50°C) and the circuit completed through a six volt battery and variable resistor. Good, adherent plates of any desired thickness were obtained in this manner. As an additional precaution in preventing deboronization as well as decarburization graphite powder was heaped on the plated specimen during the heat treatment. With these precautions dependable and reproducible results were obtained.

It was necessary to make a preliminary study of the temperature and time of holding in the subcritical transformation range in order to obtain optimum conditions for developing the boron constituent. An austenitizing temperature of 2000°F was chosen and subcritical quenching temperatures were varied from 1050°F to 1250°F with holding times at these temperatures varying from five minutes to one hour. Below 1125°F, the structures were acicular in nature and the boron constituent could not be detected under the microscope. Above this temperature the boron constituent was easily developed in a ferrite network, and the amounts of ferrite developed after complete transformation did not vary appreciably up to 1250°F. Transformation in all cases seemed to be complete after about one-half hour. On this basis a temperature of 1200°F
and a holding time of one hour was chosen for the subcritical
treatment. A further study of the constituent was made using an
austenitizing temperature of 2000°F and a subcritical transformation
temperature of 1200°F with holding times from 30 seconds to one
hour. Figure 30 is the microstructure of AISI 8640 steel and is
shown for comparison purposes. Figures 31, 32, 33, and 35 depict
the progress of isothermal transformation at 1200°F in the
companion AISI 8630 steel studied. Note that the boron consti­
tuent was present in the first proeutectoid ferrite that formed at
the shortest holding time. Increases in the amount of constituent
are evident up to the time the transformation appears complete at
about one-half hour. Further holding up to times of one hour failed
to show a change in amount or disposition of the boron constituent.
Further study showed that the coarsening temperature for this steel
was about 1800°F. Detection of the boron constituent using
austenitizing temperatures below this figure was very difficult.
Grange and Garvey also recognized that grain coarsening was necessary
if the boron constituent were to be developed. Undoubtedly grain
size is of importance in increasing the boron concentration at the
grain boundaries.

The critical experiment consisted of heat treating specimens
in increments of 100 degrees from 1800°F to 2200°F for ten minutes,
quenching into a constant temperature salt bath at 1200°F and holding
for one hour before removal and cooling in an air blast. Each
Figure 30. Microstructure of AISI 8640 steel specimen, austenitized for 10 minutes at 2000°F, quenched to 1200°F and transformed isothermally for 1 hour.
Figure 31. Microstructure of AISI 86340 steel specimen. Austenitized for 10 minutes at 2000°F, quenched to 1200°F and transformed isothermally for 30 seconds.
Austenitized for 15 minutes at 2000°F, quenched to 1200°F and transformed isothermally for 30 seconds.
specimen so treated was sectioned, polished, etched with picral and viewed under the microscope at magnifications from 1000X to 1500X. The typical microstructure obtained at heating temperatures of 1800, 2000, and 2200°F are shown in Figures 31-36. The evaluation of the relative amount of boron constituent developed in the grain boundaries at the various temperatures involved the measurement of grain size, the size and distribution of the constituent, and the relative amounts of grain boundary area covered by the constituent in each of the specimens. Grain size determinations were made by comparison with ASTM charts. The size, distribution, and boundary coverage of the boron particles were determined microscopically at 1250X with the aid of a filar eyepiece and an oil immersion objective lens. Particle size and distribution were estimated by measuring the diameter and distance between approximately 500 particles in randomly distributed patches of constituent throughout the specimens. To estimate the grain boundary coverage, an average of 50 randomly chosen fields per specimen were evaluated.

C. Results and Discussion

The result of each of the independent measurements outlined above is shown in Table VIII. A factor representing the relative amount of boron constituent present in each of the variously treated specimens is assigned based on the interdependence of the quantities
Figure 3. Microstructure of AISI 86B40 steel specimen. Austenitized for 10 minutes at 1800°F, quenched to 1200°F and transformed isothermally for 1 hour.
AISI 86400  Peral Etch  7.0X

Figure 3. Microstructure of AISI 86400 steel specimen, Austenitized for 10 minutes at 2000°F, quenched to 1200°F and transformed isothermally for 1 hour.
Figure 36. Microstructure of AISI 8640 steel specimen. Austenitized for 10 minutes at 2200°F, quenched to 1200°F and transformed isothermally for 1 hour.
measured, e.g., the amount of boron constituent varies directly with the size, distribution, and grain boundary coverage of the particles but inversely with the grain size. The factors obtained also appear in Table VIII.

From the results of the semi-quantitative measurements made, it appears that some three times as much boron constituent is present in the specimen heat treated at 2200°F as is present in the specimen heat treated at 1800°F. The obvious interpretation of these data is that boron must be concentrating at grain boundaries in increasing amounts with increasing temperatures.

An interesting aspect of the formation of boron constituent has been reported recently. Specimens of a plain carbon steel were heated to 2000°F and quenched to 1600°F prior to subcritical transformation. By varying the time of holding at 1600°F the constituent could be removed from the microstructure. Thus where the quench was interrupted but no time of holding at the intermediate temperature allowed the constituent formed in a normal manner. However, after holding the specimen for approximately one hour at the intermediate temperature, no constituent could be developed. A further observation along the same lines was made during this present investigation. Samples of AISI 86540 steel having been heated at temperatures from 1800°F to 2200°F were allowed to cool at a rate of about 20°F per minute until a temperature of 1600°F was reached. The specimens were then quenched
TABLE VIII

STATISTICAL ANALYSIS OF THE BORON CONSTITUENT FORMED IN SPECIMENS OF AISI 86B40 STEEL UNDER CONDITIONS OF VARYING HEAT TREATMENT

<table>
<thead>
<tr>
<th>Temperature of austenitizing treatment, °F</th>
<th>Average particle diameter, units</th>
<th>Average particle concentration number/unit</th>
<th>Average grain diameter, mm</th>
<th>Fraction of the grain boundary covered</th>
</tr>
</thead>
<tbody>
<tr>
<td>1800</td>
<td>0.050</td>
<td>5.9</td>
<td>0.051</td>
<td>0.23</td>
</tr>
<tr>
<td>1900</td>
<td>0.050</td>
<td>7.0</td>
<td>0.072</td>
<td>0.37</td>
</tr>
<tr>
<td>2000</td>
<td>0.049</td>
<td>8.0</td>
<td>0.101</td>
<td>0.75</td>
</tr>
<tr>
<td>2100</td>
<td>0.052</td>
<td>8.4</td>
<td>0.101</td>
<td>0.81</td>
</tr>
<tr>
<td>2200</td>
<td>0.051</td>
<td>9.1</td>
<td>0.122</td>
<td>0.95</td>
</tr>
</tbody>
</table>

Factors listed below are computed using the data at 1800°F as a base.

\[\begin{align*}
1900°F \text{ factor} & = \frac{7.0}{5.9} \cdot \frac{0.051}{0.072} \cdot 0.37 = 1.35 \\
2000°F \text{ factor} & = \frac{8.0}{5.9} \cdot \frac{0.051}{0.101} \cdot 0.75 = 2.23 \\
2100°F \text{ factor} & = \frac{8.1}{5.9} \cdot \frac{0.051}{0.101} \cdot 0.81 = 2.53 \\
2200°F \text{ factor} & = \frac{9.1}{5.9} \cdot \frac{0.051}{0.122} \cdot 0.95 = 2.62 
\end{align*}\]
to 1200°F and transformed. In each case the boron constituent was still present in the microstructure. An example of this is shown in Figure 37. In one instance after holding for one-half hour at 1600°F subsequent to slow cooling and prior to subcritical transformation, the boron constituent was still present in the microstructure although in much less quantity. This occurrence points to the possibility of the boron constituent being formed at temperature. It has also been observed in this laboratory that what appears to be boron constituent can be formed after long periods of isothermal holding at relatively low temperatures. The best example of this occurred as the result of an experiment to measure boron solubility in a high purity iron-carbon alloy. In this instance the original specimen was a "sandwich" whose core was an iron-0.77% carbon alloy and whose outer layers were iron-4% boron alloy. In an effort to saturate the core with boron the sandwich was equilibrated in argon at 900°C and quenched after 100 hours for metallographic examination. The examination revealed the presence of boron constituent. At this point the core was considered saturated and a boron analysis yielded 0.0025%. This occurrence further strengthens the belief that the boron constituent may form at temperature.

During the course of this work, several attempts were made to develop the boron constituent in high purity iron-boron alloys. In each case the alloy without carbon failed to develop the constituent. This appears to correlate with the data obtained by Darken,
Figure 37. Microstructure of AISI 86B40 steel specimens. Austenitized for 10 minutes at 2000°F, slowly cooled to 1600°F, quenched to 1200°F and transformed isothermally for 1 hour.
et al.\textsuperscript{18,19} on the phase equilibria in the ternary iron-carbon-boron system. This work establishes the presence of a boron-cementite at temperatures in the austenite range of this system. Boron apparently substitutes for small amounts of carbon in this compound. It is probable, then, that the observed boron constituent is a boron-cementite compound.
IX. EFFECT OF PROLONGED HEATING AT HIGH TEMPERATURE

A. Background

It has been observed by Grange and Garvey that the homogenization of boron-treated steels could lead to complete elimination of the hardenability effect caused by boron. The experimental technique leading to this conclusion involved the heating of steel specimens with and without boron at 2350°F for 24 hours. To prevent oxidation and decarburization the specimens were encapsulated under vacuum in silica tubes. This observation of permanent deterioration of boron effect was noted in both a 0.63% plain carbon steel and a 0.25% carbon low alloy steel, both of which had been treated with ferroboron and homogenized at 2350°F for 24 hours. In another series of boron-treated steels which had been homogenized for shorter times, the effect was to reduce but not completely eliminate the boron effect. Under these circumstances, it was presumed that longer heating times would cause permanent deterioration of boron effect in this series of steels also. Since the characteristic grain boundary constituent could not be formed in any of these steels after homogenization, it was concluded that possibly boron was being converted into an ineffective form through chemical combination resulting from prolonged heating at high temperatures. Should the permanent loss of hardenability caused by boron, as described, be
a real effect, it is important to establish the relationship of temperature of homogenization to the kinetics of the deterioration.

B. Experimental Method

A series of experiments to establish the data described above was contemplated. Prior to this, however, an attempt was made to reproduce the results just described. For this purpose the commercial lots of AISI 8640 and Grainal-treated AISI 86340 steels previously described were used. Hardenability evaluation was on the basis of the hardness of normalized sections. Grange and Garvey\textsuperscript{24} pointed out that these steels are air hardening to some extent and such a technique can be used. For these tests the specimens were held for 20 minutes in a salt bath at 1600°F and then cooled in still air.

Several evacuated silica capsules containing pairs of the test steels were made up and heated for 24 hours at 2350°F. A number of failures occurred among these capsules, but evaluation of the specimens successfully treated indicated a complete deterioration of the boron effect. Examination of the surface of the treated specimens, however, showed that some reaction, probably with the silica tube, had taken place since none of them were bright. One further test was made at 2350°F for 12 hours using a pair of specimens wrapped in tantalum foil prior to encapsulation. These specimens appeared bright after treatment, and their hardenability
evaluation showed that no deterioration had taken place.

Since these steels are extremely sensitive to deboronization at high temperatures and particularly at long times of holding, the experimental observations raised some doubt as to the real occurrence of the permanent deterioration effect. To resolve this question, an experiment was undertaken in which the high-temperature portion of the treatment was completed in vacuum. To accomplish this the vacuum heat treating furnace used in the thermoelectric experiments and shown in Figures 23-25 was modified in order to withstand the high temperatures of this test. The molybdenum wound resistance coil had to be supported on a frame whose entire construction consisted of molybdenum parts. Further all the metal accessory equipment inside the furnace shell not already made of molybdenum was replaced in kind with this metal. With this equipment a temperature of 2,140°F was obtained and held under a pressure of 5 x 10^{-5} mm of Hg for 24 hours. The pair of steel specimens were suspended in the furnace and heated simultaneously. Temperature was measured with a standardized Platinum, Platinum-13% Rhodium thermocouple, the value of whose millivoltage at 2,140°F was extrapolated from the standardization equation good up to 2,200°F. The error in temperature reading under these conditions should be negligible.

C. Results and Discussion

The complete evaluation of these specimens is shown in Table IX. The hardness values attained by each steel after normalizing,
both before and after the prolonged high temperature treatment, remain the same. Figures 38-40 show typical microstructures of AISI 52100 specimens at various points in the heat treatment. Figure 38 shows the normalized structure (20 minutes at 1600°F and air cooled) prior to the high temperature treatment to consist of some ferritic areas in a matrix of lower transformation products. Figure 40 shows the structure of this same steel normalized in the same manner except subsequent to the high temperature treatment. The two microstructures appear approximately equivalent as might be expected since their hardness values are also equivalent. The intermediate micrograph shown in Figure 39 merely shows the structure of this alloy after it had been subjected to the high temperature treatment and cooled in vacuum with the furnace power off. A comparable series of microstructures for specimens of AISI 8640 appear in Figures 41-43. Note, however, that due to the increased hardenability caused by the addition of boron to the base steel composition the normalized structures both before and after the high temperature treatment are basically martensitic. This again is substantiated by the higher hardness level in these specimens which again are about the same despite the intervening heat treatment.

It would appear then that no permanent loss of boron hardenability effect occurs, at least in these Grainal-treated steels.
TABLE IX

HARDENABILITY EVALUATION OF COMMERCIAL AISI 8640 AND AISI 86340 STEELS BEFORE AND AFTER PROLONGED HEATING

<table>
<thead>
<tr>
<th>Heat Treatment</th>
<th>Hardness Values, R_c</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>AISI 86340</td>
</tr>
<tr>
<td>As Received</td>
<td>25</td>
</tr>
<tr>
<td>20 minutes at 1600°F, air cool</td>
<td>18</td>
</tr>
<tr>
<td>24 hours at 2400°F, 20 minutes at 1600°F, air cool</td>
<td>47</td>
</tr>
</tbody>
</table>
Figure 37. Microstructure of normalized specimen of AISI 6645 steel before homogenization heat treatment.
Figure 39. Microstructure of furnace cooled specimen of 4140 steel after the homogenization heat treatment.
Figure 10. Microstructure of normalized specimen of AISI 3640 steel after homogenization heat treatment.
Figure 41. Microstructure of normalized specimen of AISI 9680 steel before homogenization heat treatment.
AISI 36340 3010X

Figure 42. Microstructure of furnace cooled specimen of AISI 36340 steel after homogenization heat treatment.
Figure 43. Microstructure of normalized specimen of AISI 8650 steel after homogenization heat treatment.
X. CORRELATION AND DISCUSSION OF EXPERIMENTAL RESULTS

Taken together the results of the experiments involving grain growth, thermoelectric power, high temperature x-ray diffraction, and metallography indicate that boron in solution in gamma iron is surface active with respect to that phase. Furthermore it appears that the temperature coefficient of adsorption is positive, i.e., the concentration of boron in the grain boundaries increases with increasing temperature in the austenite temperature range. This behavior may very well be an integral part of the mechanism by which boron increases the hardenability of steels.

It is widely agreed that boron exerts its effect on hardenability in steels by decreasing the rate of nucleation of pro-eutectoid ferrite or upper bainite thereby delaying the start of the austenite transformation. The effective mechanism could be one of altering the energy conditions at the interfaces or one of modifying the kinetics of transformation, or it could involve a combination of both. It has been pointed out that should the solution of boron in gamma iron decrease the gamma-gamma interfacial energy more than it does the alpha-gamma interfacial energy then the conditions for decreased rate of nucleation of pro-eutectoid ferrite are met. However, work in this laboratory on the measurement of gamma-gamma interfacial energies showed that even though boron apparently does decrease the available energy at this interface, the
decrease is so small as to be statistically insignificant insofar as its effect on the hardenability mechanism is concerned. The results of the above experiment were qualitatively interpreted as being the probable result of positive adsorption of boron in austenite. Under these conditions it would appear that the kinetic factor is at least the more important in the operative boron hardenability mechanism. Further since boron is known to exert its effect only by delaying the start of the austenite decomposition to pro-eutectoid ferrite and not its completion, the effect is apparently restricted to the grain boundaries, where such transformation normally begins. It is probable, therefore, that the grain boundary enrichment as a result of positive adsorption results in a critical grain boundary concentration of boron which is effective in delaying the start of transformation. Having once surmounted the barrier thus presented, the transformation proceeds unhampered by the average boron concentration in the bulk of the grain.

The observed temporary loss of hardenability is also probably concerned with the positive adsorption of boron in gamma iron. It has been shown that there is a correlation between the appearance of the boron constituent and the loss of hardenability. Thus in the work at Battelle Memorial Institute, it was shown that hardenability could be fully restored in specimens heated at high austenitizing temperatures merely by quenching from the high temperature to the optimum austenitizing temperature and holding for a
sufficient time before the quench to room temperature. The boron constituent, observed when the holding times were insufficient, completely disappeared when the full hardenability was restored by this isothermal treatment. Here it is likely that the excess of boron in the grain boundaries at the higher temperature is precipitated, as the observed constituent, when the temperature is lowered and the interfaces thus created present further nucleating sites for the transformation. If the temperature coefficient of adsorption of boron is positive, the hardenability should decrease with increasing temperature because of the further excess of new nucleating surfaces formed prior to the transformation. This, of course, is observed.

Finally it must be concluded that the reported permanent deterioration of hardenability caused by boron is erroneous, at least insofar as steels treated with Grainal are concerned. Such work should be repeated with steels that have been treated with ferro-boron.
XI. BIBLIOGRAPHY


49. Private Communication.

50. Private Communication.

I, Robert M. Goldhoff, was born on September 3, 1920, in Cincinnati, Ohio. My primary education was obtained in the public schools of Cincinnati, and my secondary education at Western Hills High School, Cincinnati, Ohio.

I graduated from the co-operative school of Engineering and Commerce, University of Cincinnati, in 1943 with the degree Bachelor of Chemical Engineering. In April, 1943 I was taken into the U. S. Army and served in the Ordnance Department until 1946. After discharge I was employed by the Dayton Malleable Iron Company until 1949. At this time I returned to the University of Cincinnati and in 1950 received the degree Master of Science in Metallurgy. After graduation I was employed by the Battelle Memorial Institute until 1953 when I accepted the position of Research Associate in the Department of Metallurgy, The Ohio State University. At the same time I enrolled in the Graduate School where I fulfilled the requirements for the degree Doctor of Philosophy in Metallurgy.