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TECHNICAL REPORT 54-150

**THE EFFECT OF BORON ON THE RELATIVE
INTERFACIAL TENSION OF GAMMA IRON**

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THE OHIO STATE UNIVERSITY

APRIL 1954

WRIGHT AIR DEVELOPMENT CENTER

WADC TECHNICAL REPORT 54-150

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April 1954

Aeronautical Research Laboratory
Contract No. AF18(600)-94
RDO No. 477-645B

Wright Air Development Center
Air Research and Development Command
United States Air Force
Wright-Patterson Air Force Base, Ohio

FOREWORD

This report was prepared by the Department of Metallurgy of the Ohio State University as an activity of the Ohio State University Research Foundation under USAF Contract AF18(600)-94. This research and development project is identified as RDO No. 477-645B, "Metallurgy of Boron in Iron and Steel." The project was administered under the direction of the Metallurgy Research Branch, Aeronautical Research Laboratory, Directorate of Research, Wright Air Development Center, with Mr. James W. Foynter acting as project engineer.

ABSTRACT

The effect of boron on the relative interfacial tension of gamma iron in two commercial steels is studied by means of thermal etching techniques. In each case, boron effects a measurable reduction in interfacial tension, although the differences in the average groove angles measured do not appear to be statistically significant. The data indicate a positive temperature coefficient for adsorption of boron to the grain boundaries. In the range of 0.20 to 0.40 percent, carbon has essentially no effect on the degree of reduction of the interfacial tension by boron.

PUBLICATION REVIEW

This report has been reviewed and is approved.

FOR THE COMMANDER



LESLIE B. WILLIAMS
Colonel, USAF
Chief, Aeronautical Research Laboratory
Directorate of Research

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I INTRODUCTION

There are sufficient arguments and evidence^{1,2,3,4} to indicate that boron should be adsorbed to existing austenite grain boundaries during the austenitizing treatment. Accordingly, it is possible that boron contributes to the hardenability of heat treatable steels by the reduction of the interfacial energy of austenite grain boundaries, at which sites are nucleated heterogeneously the decomposition products of austenite. Such a reduction in interfacial energy would reduce the total energy that can be borrowed in these heterogeneous nucleation processes and thus retard the initiation of transformation.

This investigation was undertaken to attempt to determine the effect of boron on this interfacial tension in commercial steels. It was realized that in the present state of knowledge, only relative values of the interfacial tension of gamma iron could be estimated. However, it is believed that such a study, despite its deficiencies, is justified to determine if boron produces a measurable effect on the interfacial tension and the relative magnitude of this effect, thus establishing whether or not boron is "surface active" in iron (i.e., if boron is significantly adsorbed to grain boundaries).

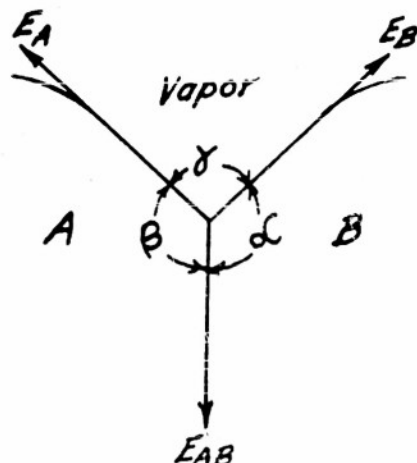
II REVIEW OF PREVIOUS WORK

The mechanism of thermal etching was used in this investigation to allow the austenite grain boundaries to develop grooves, the angles formed being the equilibrium shape for each temperature used. Concerning this mechanism, Shuttleworth⁵ believes that atomic migration over the surface of the metal is the principal factor leading to the formation of thermal etch patterns. Evaporation of atoms from the surface is another contributing cause, more important at high temperatures than at low, but the activation energy for an atom to evaporate is much greater than that required for an atom to migrate over the surface. The presence of an inert gas surrounding the sample may assist the formation of boundary grooves and other markings, as the evaporating atoms are reflected back by the gas molecules. This process of evaporation and condensation would lead eventually to the same surface configuration as that produced by atomic migration. In a vacuum, the absence of gas molecules would prevent condensation of evaporated atoms; the resulting process would be a stripping of atomic layers, which of itself would not produce boundary grooves.

Olney⁶ believes, however, that in the early stages of thermal etching, the loss of atoms by evaporation may well be greater at the boundaries, i.e., at points initially of high energy than at the exposed grain surfaces.

Under these conditions, not until the equilibrium surface has formed will the stripping of atomic layers take place uniformly over the metal surface.

Regardless of the mechanism, Shuttleworth⁵ and Greenough and King⁷ regarded the phenomena of thermal etching as an adjustment of a surface to minimum free energy. If we heat etch a metal sample, we would find the following surface configuration:



E_A = free energy of Surface A

E_B = free energy of Surface B

E_{AB} = free energy of interface between A and B

The relationship between interfacial energies and respective angles is given by

$$\frac{E_A}{\sin \alpha} = \frac{E_B}{\sin \beta} = \frac{E_{AB}}{\sin \gamma} \quad (1)$$

If the assumption is made that the free energy of a grain surface is independent of the orientation, then equation (1) reduces to

$$E_{AB} = 2E_S \cos \frac{\gamma}{2} \quad \text{where } E_S = E_A = E_B \quad (2)$$

If equation (2) is applied to an austenitic region, then

$$E_{\text{interfacial}} = 2E_{Fe} \cos \frac{\gamma}{2} \quad (3)$$

If the value of $\gamma_{\gamma\alpha}$, the surface tension of gamma iron, is known or can be calculated, then the interfacial energy can be calculated by determining the value of the equilibrium austenite groove angles formed by thermal etching.

In seeking a practical method for determining the austenitic grain boundary groove angles, the methods of microtopography described by Chalmers⁸ were investigated. It was thought that this method could not be accurately adapted to this work, since the groove angles were so small and the necessary equipment was not immediately available.

Buttner, Udin, and Wulff⁹ found the absolute interfacial energy of gold by heat etching fine wires and examining the groove angles formed by a goniometer attachment to a metallurgical microscope. Considerable error was found in determining the positions of the light spot traversing the heat etched groove. This method was not considered to have sufficient accuracy for it was thought that the differences in the groove angles for the steels used would be small. Also, this method requires the use of wires while only cylindrical samples were available in this investigation. Hess¹⁰ states that at the present time some method of optical measurement of the groove angles is the most applicable. This includes liquid-solid configurations, interfaces and viewing of nearly 120° junctions of grain boundaries.

In the work of Greenough and King⁷ on the grain boundary energy of silver, they used a method of measuring the groove angles consisting of plating pure silver on the heat etched surface and sectioning normal to the surface to obtain the shape of the groove; the angle was measured by mechanical means or from photomicrographs. They also used a revolving stage on a microscope with a small light beam, similar to the apparatus used by Buttner, Udin, and Wulff.⁹ After investigating a method of plating the steel samples, the method of nickel plating and sectioning normal to the heat etched surface was chosen as the one most suited to this problem. Also, Bailey and Watkins¹¹ thermally etched polycrystalline specimens of copper in various atmospheres at two different temperatures. They then prepared metallographic sections normal to the etched surface and, assuming that the groove angle was constant for any given condition of thermal etching, found a value for this angle by measuring a selection of the smallest groove angles seen in the section. They found that the angles were smaller at the lower temperatures, which is to be expected.

Dann and Lionetti¹² determined the effect of orientation on grain boundary energies by growing crystals of silicon ferrite, with 3.5 percent silicon, of different orientations forming almost a 120 degree junction. They found that a difference in orientation of 30 degrees and below showed a sharp drop in the relative surface tensions. This is to be expected to

a certain extent, since at zero orientation difference the grain boundary would disappear. Also, Aust and Chalmers¹³ found that in tin the energy of the crystal boundary was not independent of the orientation of the neighboring crystals. This was true for orientation differences of 6 degrees and below. Above this value, the energy was essentially the same for varying orientations. This work was done on seed crystals of varying orientations and the angles were measured at grain junctions. Dunn, Daniels, and Belton¹⁴ in determining the effect of orientation on the relative grain boundary energies in silicon iron, found results similar to the work done previously by Dunn and Lionetti.¹² They found that there was a rapid rise in grain boundary energies up to orientation differences of 30 degrees.

Ikenye and Smith¹⁵ measured dihedral angles between joining grains in aluminum and copper alloys by allowing tin rich liquid layers to form at grain junctions. After annealing, they measured the dihedral angle formed by the tin by using a micrometer eyepiece mounted on a metallograph. The distributions of the dihedral angles were determined for various amounts of cold work and annealing time. Using these values, they found relative interfacial energies for changes in temperature and composition. The shape of the distribution plots was not too different from distribution plots found in this investigation.

Sears¹⁶ developed a method from which he determined the absolute interfacial energy for copper. He polished one end of a cylinder of OFHC copper, placed it in a furnace, and covered the polished end with lead dust. After heating 8 hours at 800 degrees C, the cylindrical samples were cooled, copper plated, sectioned, and polished normal to the lead surface. The dihedral angles were calculated from the lengths and thicknesses of the lenticular lead drops. Finding the values of these angles consistent, he determined the absolute interfacial free energy for copper-copper.

The publication, "Imperfections in Nearly Perfect Crystals,"¹⁷ groups together methods of evaluating surface and interfacial tensions. These methods consist of measuring angles formed by grain junctions, interfaces between solid and liquid metals or compounds, and those angles formed by thermally etched grain boundary grooves. Each has advantages over the other, depending on the materials being studied. Van Vlack¹⁸ measured the energy of the interface between two immiscible liquids, copper and copper sulfide, by the capillary method, then equilibrated this surface with gamma iron and ultimately determined the grain boundary energy. The calculated value of the interfacial tension for gamma iron was 850 dynes per centimeter. This value will be used later in calculating the relative surface tension of gamma iron, as suggested by Smith.¹⁹

III EXPERIMENTAL PROCEDURE

The thermal etching of specimens was conducted in a vacuum furnace designed to operate up to 1900°F at pressures of 10^{-6} mm of mercury or

less. The vacuum was adequate to prevent any discernible oxidation of the steel specimens. Temperatures were measured by means of a platinum-platinum, 13% rhodium thermocouple.

After thermal etching at the desired temperature and time and cooling in vacuum to room temperature, the etched surface of the specimen was nickel plated to preserve the grain boundary grooves during the metallographic sectioning of the specimen necessary in measuring groove angles. The electroplating bath consists of nickel sulphate, 680 grams/gal; ammonium chloride, 93 grams/gal; boric acid, 113 grams/gal. The operating conditions of the plating process are the following: current density, 30 amps/sq ft; temperature, 50-60°C; pH of 5.6 to 5.9. Hydrogen peroxide was used as a wetting agent for the sample. An alkaline cleaning solution was used, composed of 30 grams of sodium carbonate, 15 grams of tri-sodium phosphate and 7.5 grams of sodium hydroxide in one liter of water. A typical nickel plated grain boundary groove is illustrated in Figure 1.

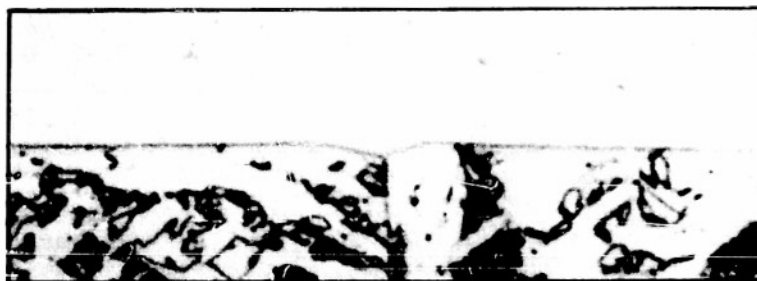


Figure 1. Typical Grain Boundary Groove Produced by Thermal Etching. 1500X - Nital Etch

The nickel-plated specimens were mounted in bakelite so that the plated, heat-etched surface was perpendicular to the anvil of the mounting press. Thus, when the mounted sample was polished, the polished surface was perpendicular to the surface previously heat etched. These mounted specimens were polished by standard metallographic techniques and etched in three percent nital. After examining the surface, the specimen was repeatedly ground and polished to expose many grain boundary grooves for measurements.

A magnification of 1500X was used in measuring the angle formed by the grain boundary grooves. A filar eyepiece was used to measure both the

width and depth; the angle was then calculated by trigonometric relations. To minimize errors of the instrument and those due to the eye, five values of the width and depth were taken and averaged to give the value of the width and depth for each groove measured. One hundred grooves were measured for each sample to give a distribution of the angles and give a good estimate of the average value of the groove angle for each sample.

In this investigation, two sets of steels were used to obtain the requisite data. The matching steels were produced by splitting the heat, i.e., the base steel was divided and boron was added to half the heat in the form of Grainal No. 79. The steels and their compositions, supplied by The Republic Steel Corporation, are listed in Table I.

TABLE I

Steel Compositions

<u>Type</u>	<u>C</u>	<u>Mn</u>	<u>P</u>	<u>S</u>	<u>Si</u>	<u>Ni</u>	<u>Cr</u>	<u>Mo</u>	<u>B</u>
AISI 8740	0.396	0.88	0.015	0.019	0.31	0.54	0.47	0.25	0.00
AISI 87B40	0.395	0.89	0.015	0.019	0.31	0.54	0.48	0.25	0.0013
AISI TS 8117	0.198	0.81	0.018	0.029	0.23	0.26	0.41	0.11	0.00
AISI TS 81B17	0.200	0.81	0.018	0.029	0.23	0.26	0.41	0.11	0.0011

It was found that at a temperature of 1830°F, 8 hours were required to produce an equilibrated surface; heat etching at temperatures of 1600°F and 1650°F required 24 hours to produce the desired equilibrated surface. The AISI 87B40 and AISI 8740 steels were heat etched at both 1830° and 1600°F; the AISI TS 8117 and AISI TS 81B17 steels were heat etched at 1650°F, the recommended austenitizing temperature. The samples employed were discs 3/4 inch in diameter and 3/4 inch thick. One end of the specimen was tapped to fit the sample holder of the furnace. The other end of the disc was carefully polished prior to thermal etching.

IV EXPERIMENTAL RESULTS

Figure 2 is a bar graph of frequency of occurrence versus groove angle in degrees, showing the distribution of the groove angles for boron steel AISI 87B40 heat etched at 1830°F. The mean value of the groove angle is shown to be 147.13°.

The bar graph of Figure 3 shows the distribution of groove angles for boron-free steel AISI 8740, also heat etched at 1830°F. The mean value of the groove angle is shown to be 145.93°. Comparing Figures 2 and 3, we see that the mean austenitic groove angle for the boron steel is 1.2° greater than the mean groove angle for the boron-free steel.

Distribution of Groove Angles
for Boron Steel AISI 87B40
Heat Etched at $1830 \pm 5^\circ \text{F}$.

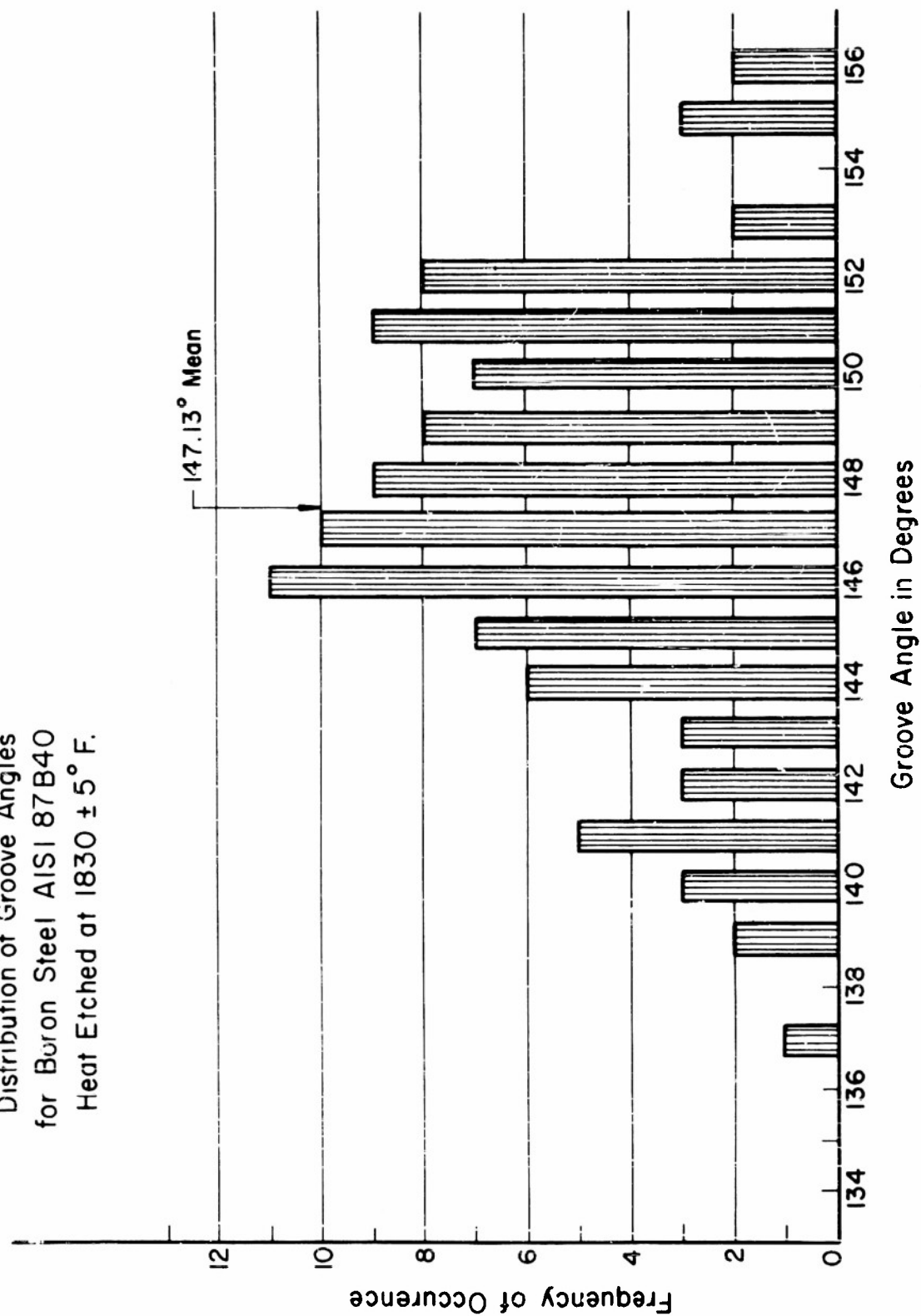


Figure 2

Distribution of Groove Angles
for Boron Free Steel AISI 8740
Heat Etched at $1830 \pm 5^\circ \text{F}$.

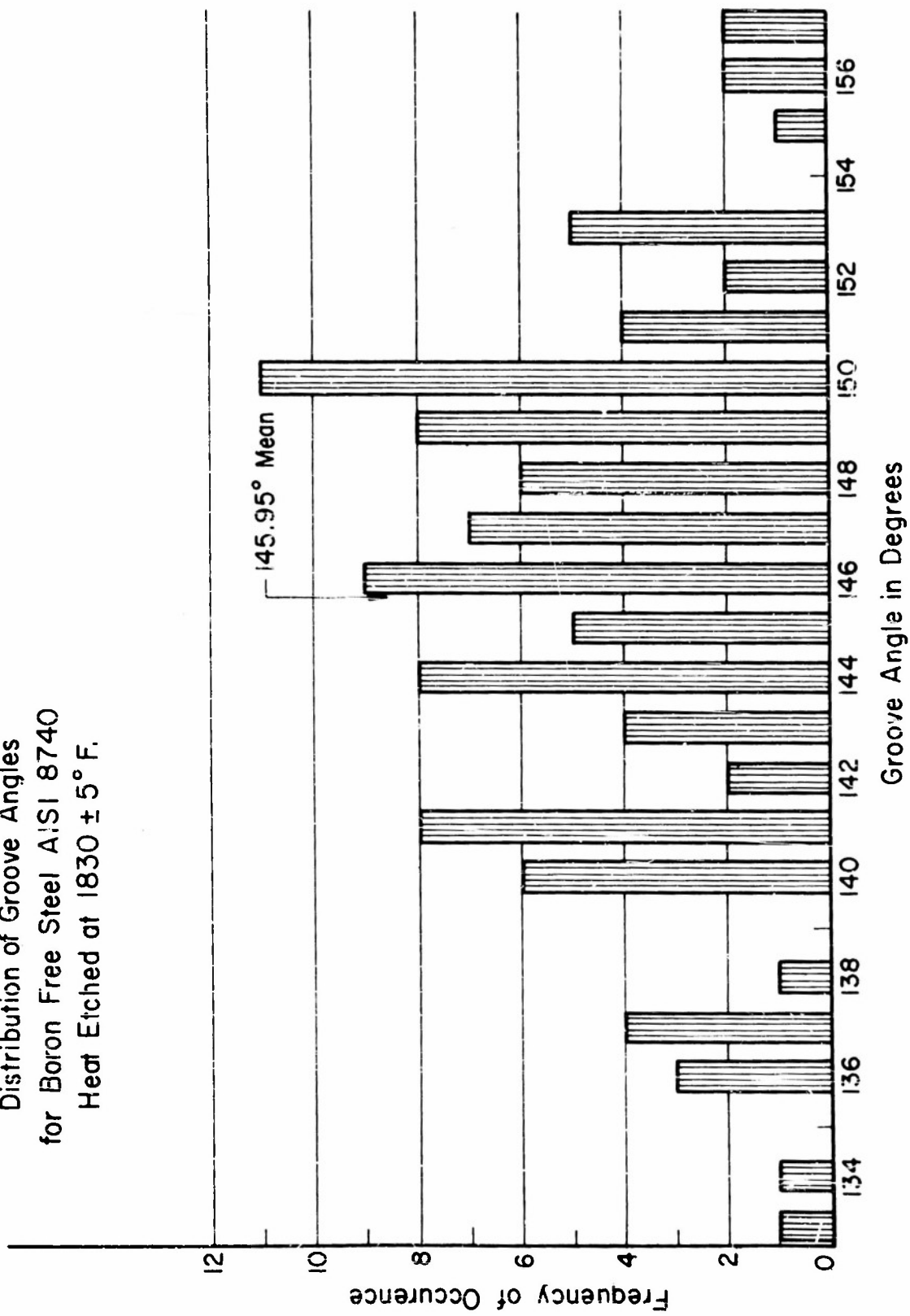


Figure 3

Figure 4 is a bar graph showing the distribution of groove angles for boron steel AISI 87B40 heat etched at 1600°F. The mean value of the angle is indicated as 144.20°. The bar graph in Figure 5 shows the distribution of groove angles for boron-free steel AISI 8740 also heat etched at 1600°F. The mean value is shown to be 143.49°. Comparing the graphs of Figures 4 and 5, we see that the mean austenitic grain boundary groove angle of the boron steel is 0.71° greater than the mean groove angle for the boron-free steel.

Figure 6 is a bar graph indicating the distribution of austenitic groove angles for boron steel AISI TS 81B17 heat etched at 1650°F. A mean value for the groove angle is shown to be 144.28°. The bar graph of Figure 7 shows the distribution of groove angles for boron-free steel AISI TS 8117 heat etched at 1650°F. The mean value for the groove angle is shown to be 143.42°. Comparing the distribution plots of boron and boron-free steels of Figures 6 and 7, we see that the mean groove angle of boron steel is 0.86° greater than the mean angle for boron-free steel.

To determine the statistical significance of the differences observed for the groove angles of the boron and boron-free steels, the standard deviation, σ , was calculated by using the expression

$$\sigma = \sqrt{\frac{\sum X_i^2}{N} - \bar{X}^2} \quad (4)$$

where σ is the standard deviation, X_i is the individual values of the angles, N is the total number of angles measured, and $\bar{X}$ is the mean value for the groove angle. Also, in comparing boron and boron-free steels, we need to know σ_D , the standard deviation of the difference of means. σ_D was calculated by the expression

$$\sigma_D = \sqrt{\frac{\sigma_B^2}{N_B} + \frac{\sigma_{BF}^2}{N_{BF}}} \quad (5)$$

where σ_B is the standard deviation for boron steel, N_B the total angles measured for the boron steel, and σ_{BF} and N_{BF} are the similar values for the boron-free steel. The values of these sigmas and the difference of the means for boron and boron-free steels treated similarly are tabulated in Table II, where $\bar{X}_B$ and $\bar{X}_{BF}$ are the mean values of the groove angles for the boron and boron-free steels respectively.

Distribution of Groove Angles
for Boron Steel AISI 87B40
Heat Etched at $1600 \pm 5^\circ \text{F}$.

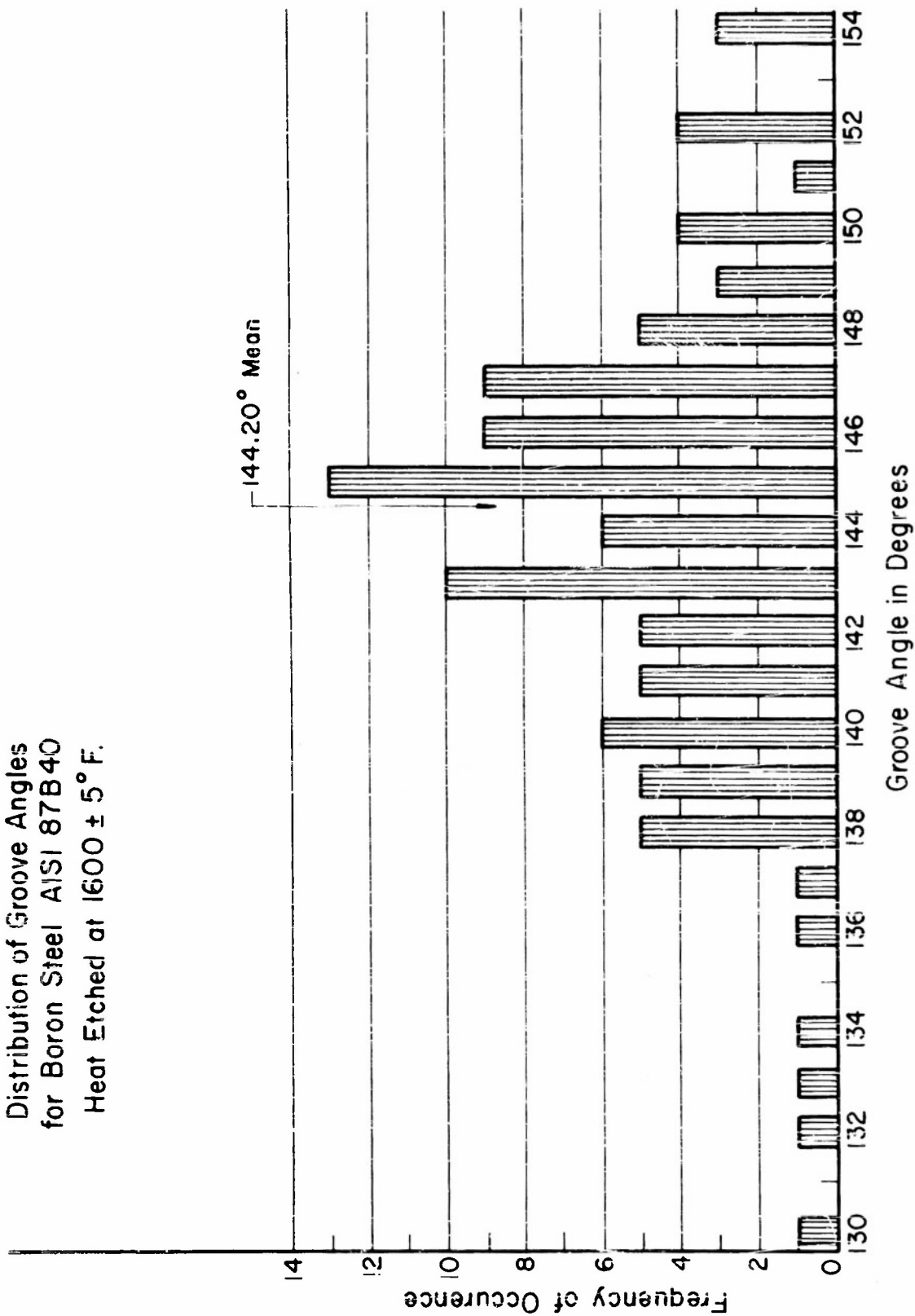


Figure 4

Distribution of Groove Angles
for Euron Free Steel AISI 8740
Heat Etched at $1600 \pm 5^\circ \text{F}$.

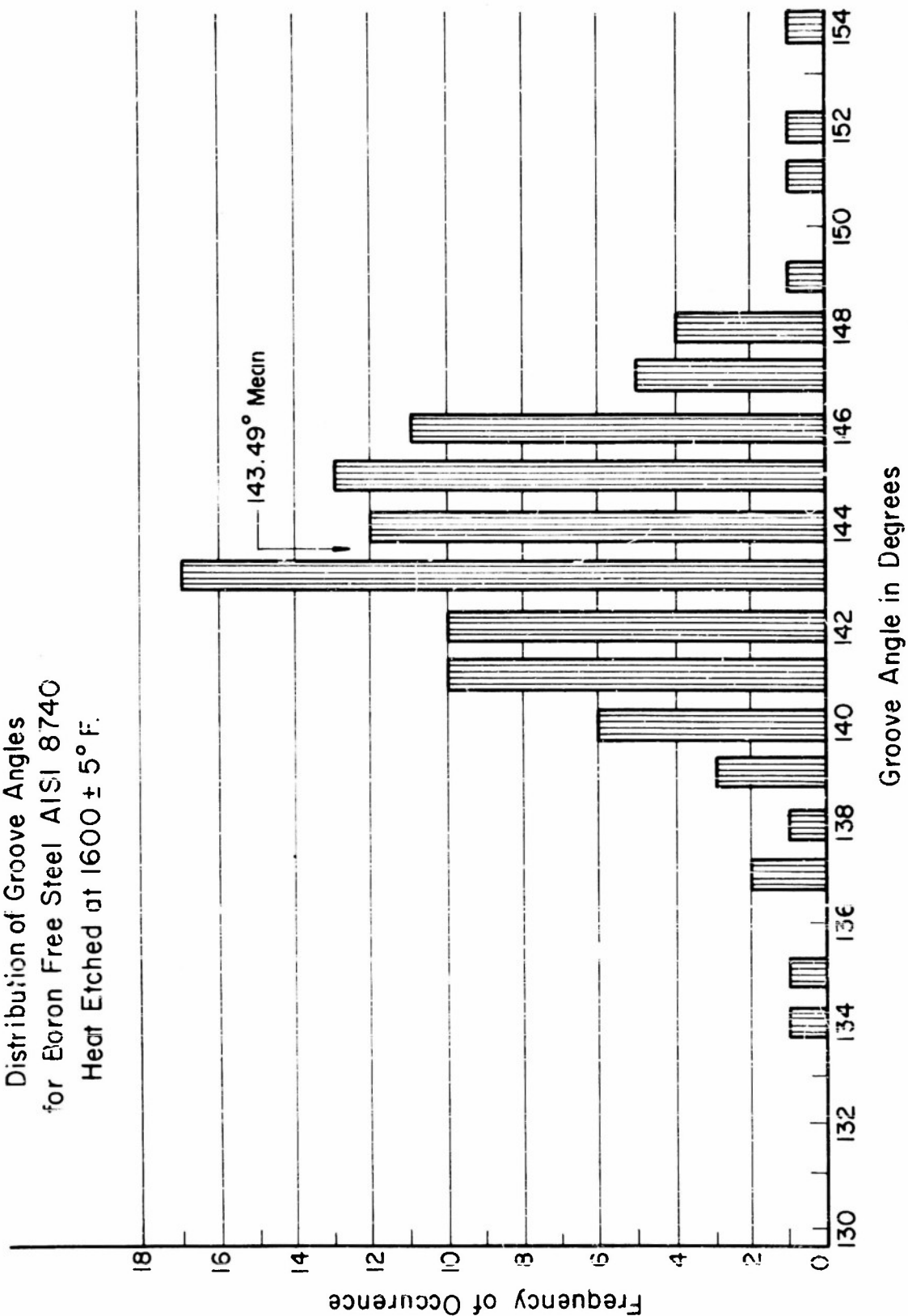


Figure 5

Distribution of Groove Angles
for Baran Steel AISI TS 81B17
Heat Etched at $1650 \pm 5^\circ\text{F}$.

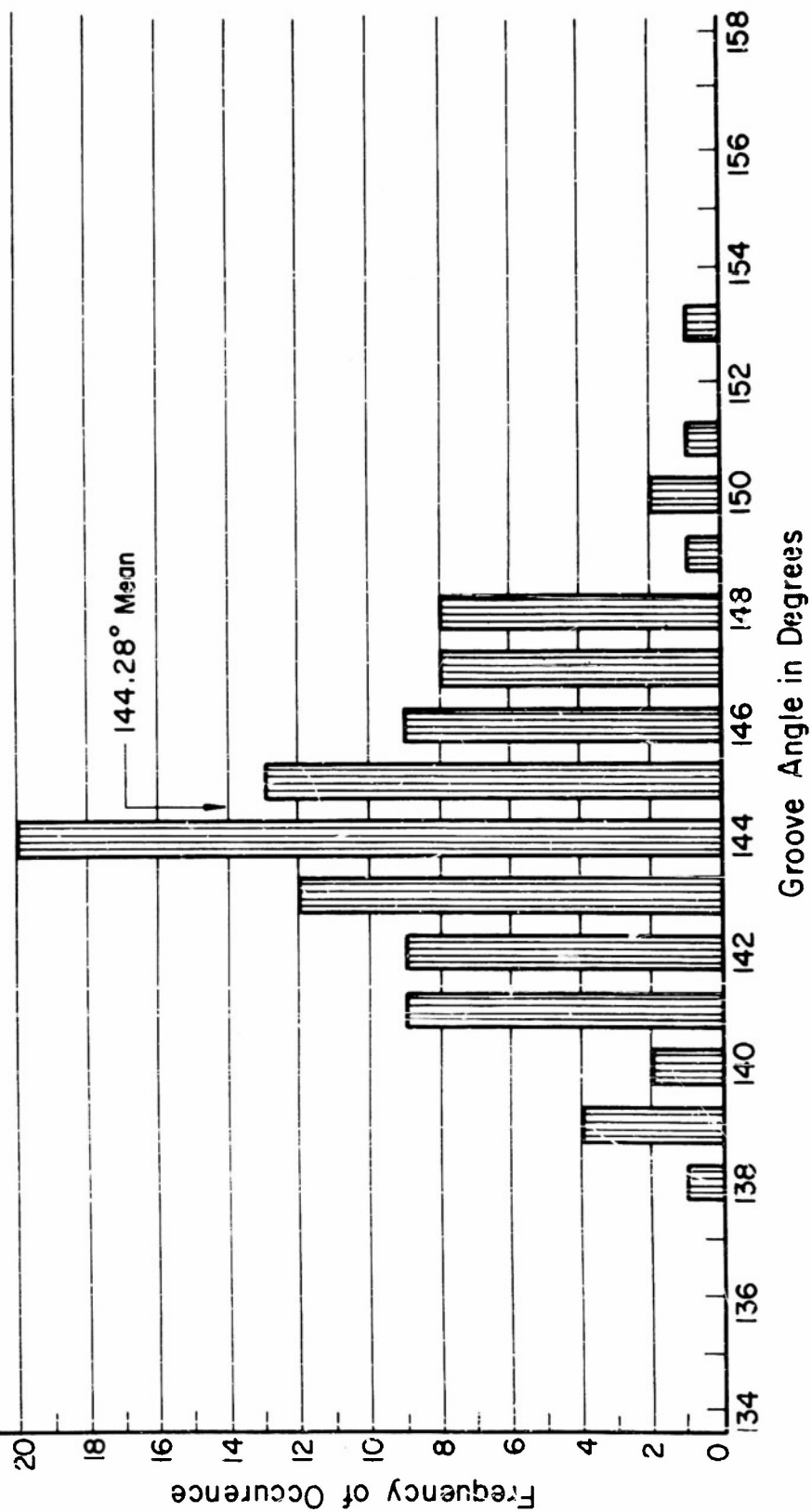


Figure 6

Distribution of Groove Angles
for Boron Free Steel AISI TS 8117
Heat Etched at $1650 \pm 5^\circ\text{F}$.

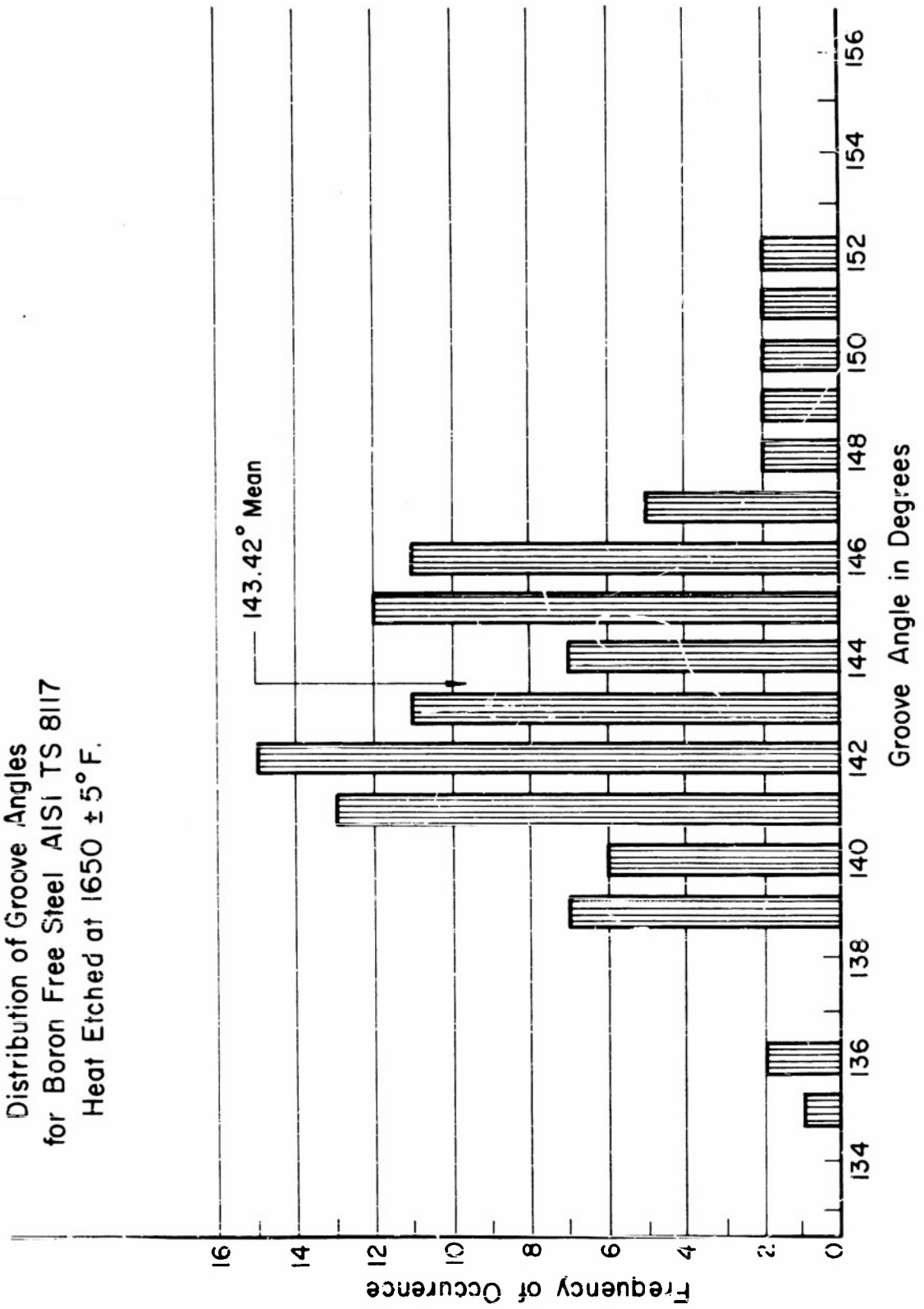


Figure 7

TABLE II

Steel	Temperature of Heat Etching	Mean Groove Angle	σ	σ_D	$3 \sigma_D$	$\bar{x}_D - \bar{x}_{HT}$
AISI 87B40	1830°F	147.13°	4.349	0.669	2.067	1.20
AISI 8740	1830°F	145.93°	5.346			
AISI 87B40	1600°F	144.20°	4.765	0.573	1.719	0.71
AISI 8740	1600°F	143.49°	3.184			
AISI TS 81B17	1650°F	144.28°	2.770	0.427	1.281	0.86
AISI TS 8117	1650°F	143.42°	3.274			

V DISCUSSION

It is appropriate now to discuss the sampling problem in measuring the groove angles of the steels studied. If we section through a cylindrical sample of a polycrystalline metal to view dihedral angles, we have the possibility of (1) rotation of the angles about an axis through the sample normal to the top surface and (2) rotation of the angles about an axis perpendicular to the axis of the sample, i.e., parallel to the top surface. It is inherent in forming the groove angles, by heat etching the top surface, not to have rotation of type (2) above. Grooves are formed only by those grain boundaries in the plane of the top surface and any curvature of the grain beneath the surface will not affect the shape of the groove. (A typical depth of a groove is less than a micron, compared to a typical grain circumference of 150 microns.) Thus, in forming the grooves, type (2) rotation is eliminated. By sectioning normal to the heat etched surface, this type of rotation is not introduced into the results of groove angle measurements. If both types of rotation were present, we would expect a spread of 0° to 180° for the groove angles. Since the results show a total spread of 24°, which is considerably less than a 0° to 180° spread, it is evident that we have only type (1) rotation in the sampling problem.

By polishing the samples on the side, we obtain a plane of view containing the shape of the grooves at the steel-nickel interface. This arbitrary trace can intersect the grooves at positions other than normal, which would not give the true angle. Steps were taken to minimize the error in sectioning by (1) measuring only those grooves whose angles had the smallest values (a range of angles of true to 180° is possible by such sectioning; wide, shallow grooves were not measured), (2) measuring only those grooves which were completely symmetrical. Ideally, a perpendicular section of the groove is desired; otherwise, the angle would be enlarged. Thus we see that the typical 24-degree spread contains both varying values

of the groove angle itself and the spread of properly sectioning the groove for measurement of the angle. Also the fact that small orientation differences affect the value of the interfacial tension is not considered to be of great importance. From equation (3), if the interfacial energy was greatly reduced, the groove angle would be quite large; large angles were not contained in those measured. For these reasons plus the fact that width and depth measurements were averaged for each angle, the accuracy of the work is considered to be adequate. Distribution plots obtained compare favorably in shape with those found for gold by Buttaer, Udin, and Wulff.⁹

As suggested by Smith,¹⁹ for the sake of having numerical values to compare, the value for the surface tension of γ iron was calculated by substituting Van Vlack's¹⁸ value of 850 dynes per centimeter for the interfacial tension of γ iron and the value of the experimentally determined groove angles in equation (3). It is realized that this value will not be the true value, for the iron used for the 850 dynes per cm value was saturated with copper and copper sulfide, and also we assume that the surface tension does not change with varying orientation of adjoining grains and that boron has no effect on the surface tension.* However, the calculated value of 1544 dynes per cm for the surface tension of γ iron will allow relative comparisons to be made between boron and boron-free steels.

Substituting the calculated value of E_s and the mean groove angles in equation (3), the calculations of E_{int} and the percent reduction of E_{int} by boron in steels similarly treated are shown in Table III on the following page.

We notice from Table II, for all the steels investigated, that the difference in the means of the groove angles is not statistically significant, i.e., it is possible that the difference could be due to chance variation only. However, the differences of means are not considerably less than $3\sigma_p$, and considering the consistency of the data obtained, the

* Since the normal boron adsorption effect in austenite appears to be a solid solution effect, it is reasonable to assume that the degree of adsorption at a given temperature is limited by the boron solubility at that temperature. With this same limitation on both interfacial boundaries and free surfaces, it would appear that the effect percentage-wise is greater on the interfacial tension than on surface tension and the effects measured are likely a reflection of decrease of interfacial tension relative to the surface tension. It is expected that both values are influenced by the presence of boron.

TABLE III

Steel	Temperature of Heat Etching	Mean Groove Angle	Γ_{int}^*	% Reduction
AISI 87B40	1830°F	147.13°	873.3	3.5
AISI 8740	1830°F	145.93°	904.5	
AISI 87B40	1600°F	144.20°	949.3	1.9
AISI 8740	1600°F	143.49°	966.9	
AISI TS 81B17	1650°F	144.28°	947.1	2.3
AISI TS 8117	1650°F	143.42°	969.0	

*Estimated values

significance of the differences of means might be considered borderline. From the estimations of interfacial tensions, listed in Table III, the reduction of the interfacial tension by boron is small, about 2 percent for normal austenitizing temperatures. The significance of this small reduction of interfacial tension is uncertain. An estimate of the significance of such a reduction in interfacial energy is made difficult by lack of the absolute gamma-alpha interfacial tension, shape factor of the nucleus and the correct strain energy term to be used. The overall effect would be to increase slightly the term involving the work of nucleation, which appears in the probability factor in the classical expression for rate of nucleation. This term in general is mainly influenced by the temperature, giving increasing probability of nucleus formation with decreasing temperature. Qualitatively, this reduction in interfacial tension does not appear to be sufficient to affect significantly the kinetics of nucleation. However, if the work of nucleation is reduced to a considerable extent by the pre-existing gamma interface, this effect might be significant.

Since the reduction of interfacial tension was measured at concentrations of one boron atom in 20,000 iron atoms, it does not seem logical that such low concentrations at the grain boundaries could cause a measurable effect. It is more logical that this reduction is caused by boron being adsorbed at the austenite grain boundaries. The amount of boron adsorbed should be limited by the solubility of boron at the temperature used. The concentrations of boron can thus be increased to one boron atom in 6000 iron atoms at the normal austenitizing temperature. Thus, it seems that only by positive adsorption of boron in gamma iron can boron concentrations be increased to a value that is responsible for the measurable reduction in the interfacial tension.

By comparing the steels AISI 87B40 and AISI 8740 with the AISI TS 81B17 and AISI TS 8117 steels, treated at their normal austenitizing

temperatures, the results indicate that carbon composition has little effect on the reduction of the interfacial tension of austenite by boron. The slight increase in the difference of the means of the 0.20 percent carbon steels over the 0.40 percent carbon steels is not significant, and may be due to increased adsorption of boron at the grain boundaries because of the slightly higher temperature used in heat etching.

Interesting consequences are found when reviewing the results obtained. The data show that the interfacial tension of austenitic grain boundaries is greater at lower temperatures, indicated by smaller values found for the groove angles at the lower temperatures. This is considered to be in agreement with previous thoughts on boundary energies, i.e., the interfacial energy is lower at higher temperatures and theoretically reduces to zero at the critical point.

After accepting the fact that positive adsorption of boron in gamma iron appears to be responsible for the measurable reduction in interfacial tension, we are concerned with the temperature coefficient of adsorption. A positive coefficient would indicate increased adsorption with increasing temperature; a negative coefficient would indicate decreased adsorption with increasing temperature. The results of this investigation indicate that the temperature coefficient of adsorption for boron in gamma iron is positive. This is exemplified by the fact that differences in the groove angles of boron and boron-free steels at the lower temperatures used are approximately one-half the differences in the angles at the higher temperatures. These results are of interest in the work now being done by others to determine the nature of adsorption of boron in austenite.

VI. CONCLUSIONS

From the results of this investigation, and the procedures used, the following specific conclusions are reached:

- (1) The method of heat etching, plating, and sectioning normal to the plated surface to measure groove angles formed is a satisfactory one in determining the interfacial tension of grain boundaries, provided a value for the surface tension of the solid is known.
- (2) While the differences of the mean groove angles for boron and boron-free steels are not statistically significant, the values of $(\bar{\gamma}_B - \bar{\gamma}_{BF})$ and $3\phi_p$ are close enough to indicate the possibility of a slight decrease in the interfacial tension of austenite by boron additions to steels.
- (3) Since the boron concentrations are so low, the fact that we can measure a reduction in the interfacial tension is explained by boron showing positive adsorption in gamma iron; the experimental results indicate that the temperature coefficient of adsorption for boron in gamma iron is positive.

(4) The carbon content, in the range of 0.20 to 0.40 per cent, has essentially no effect on the degree of reduction of the interfacial tension of gamma iron by boron.

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