THE EFFECT OF CATHODIC AND
PRESSURE-DIFFUSED HYDROGEN ON THE
HARDENABILITY OF SOME PLAIN CARBON
STEELS

Thesis for the Degree of Ph. D.
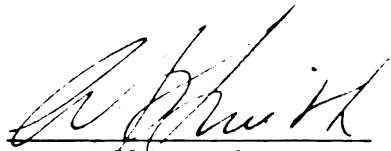MICHIGAN STATE UNIVERSITY
Douglas J. Harvey
1955

**This is to certify that the**

**thesis entitled**

The Effect of Cathodic and Pressure-Diffused Hydrogen

on the Hardenability of Some Plain Carbon Steels

**presented by**

Douglas Jack Harvey

**has been accepted towards fulfillment**
**of the requirements for**

Ph.D.      degree in Metallurgical Eng.

Major professor

Date  November 28, 1955

O-169

# THE EFFECT OF CATHODIC AND PRESSURE-DIFFUSED

# HYDROGEN ON THE HARDENABILITY OF SOME

# PLAIN CARBON STEELS
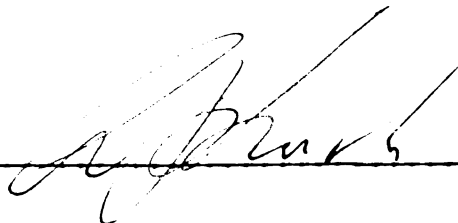
By

Douglas J. Harvey

AN ABSTRACT

Submitted to the School of Advanced Graduate Studies of
Michigan State University of Agriculture and Applied
Science in partial fulfillment of the requirements
for the degree of

DOCTOR OF PHILOSOPHY

Department of Metallurgical Engineering

Year 1955

Approved _____

Douglas J. Harvey

## ABSTRACT

In this work steels are hydrogenized using two methods: cathode charging, and heat-treating from a hydrogen atmosphere. The hardenabilities of specimens cathodically charged before heat-treating are compared to the hardenabilities of uncharged specimens. It is concluded that the amount of hydrogen obtained from cathode charging (estimated to be 5 to 7 milliliters per 100 grams) does not measurably affect the depth of hardening. Specimens are austenitized in hydrogen at 15 atmospheres, and quenched. These pressure-hydrogenated specimens show a greater depth of hardening than identical specimens heated in 1 atmosphere of nitrogen. Hardenability is measured by the method of symmetrical U-curves. In this work three steels are used ranging in carbon content from 0.33 percent to 0.50 percent. Some conclusions drawn are: (1) Hydrogen in amounts on the order of 15 milliliters per 100 grams has a small but definite effect on the hardenability of steel. (2) The increase in hardenability brought about by hydrogen content is negligible in commercial heat-treating practice, as the hydrogen content of steel is ordinarily very low. (3) The hardenability increase brought about by hydrogen appears not to change with carbon content (as in the

case

prod

Douglas J. Harvey

case of boron).  Also, some observations concerning hydrogen-

produced cracks are discussed.

THE EFFECT OF CATHODIC AND PRESSURE-DIFFUSED

HYDROGEN ON THE HARDENABILITY OF SOME

PLAIN CARBON STEELS


By

DOUGLAS J. HARVEY


A THESIS

Submitted to the School of Advanced Graduate Studies of
Michigan State University of Agriculture and Applied
Science in partial fulfillment of the requirements
for the degree of


DOCTOR OF PHILOSOPHY


Department of Metallurgical Engineering


1955

ode c

harde

are c

concl

(esti

urab

hyd

ena

spe

me

th

to

ar

b

i

c

# ABSTRACT

In this work steels are hydrogenized using two methods: cathode charging, and heat-treating from a hydrogen atmosphere. The hardenabilities of specimens cathodically charged before heat-treating are compared to the hardenabilities of uncharged specimens. It is concluded that the amount of hydrogen obtained from cathode charging (estimated to be 5 to 7 milliliters per 100 grams) does not measurably affect the depth of hardening. Specimens are austenitized in hydrogen at 15 atmospheres, and quenched. These pressure-hydrogenated specimens show a greater depth of hardening than identical specimens heated in 1 atmosphere of nitrogen. Hardenability is measured by the method of symmetrical U-curves. In this work three steels are used ranging in carbon content from 0.33 percent to 0.50 percent. Some conclusions drawn are: (1) Hydrogen in amounts on the order of 15 milliliters per 100 grams has a small but definite effect on the hardenability of steel. (2) The increase in hardenability brought about by hydrogen content is negligible in commercial heat-treating practice, as the hydrogen content of steel is ordinarily very low. (3) The hardenability increase brought about by hydrogen appears not to change with carbon content (as in the

cáse o

produc

case of boron).  Also, some observations concerning hydrogen-

produced cracks are discussed.

# ACKNOWLEDGMENTS

# TABLE OF CONTENTS

# LIST OF TABLES

## LIST OF FIGURES

FIGURE                                                              Page

will o

that t

ertie

of c

in a

sm

ter

th

c

# INTRODUCTION

For several years it has been known that the element iron will occlude hydrogen. It has also been recognized for some time that the absorption of hydrogen will greatly affect the physical properties of a steel. Since hydrogen definitely occurs in steel, it should, of course, be considered an alloying element even though its presence in any significant amount may be temporary. Hydrogen atoms are so small that they can diffuse freely through the iron lattice even at temperatures as low as -78°C. (1). Because of this active diffusion, the hydrogen content of a steel may change in a very short period of time.

There is very little information available concerning the solubility of hydrogen in steel. However, there is reliable information on the solubility of hydrogen in iron. The difference between hydrogen solubility in iron and in plain carbon steel is probably quite small. There is some experimental evidence to support this belief (2).

Results of Sieverts' early work concerning the solubility of hydrogen in iron are shown in Figure 1 (3). This work agrees well with four other more recent investigations (4, 5, 6, 7).
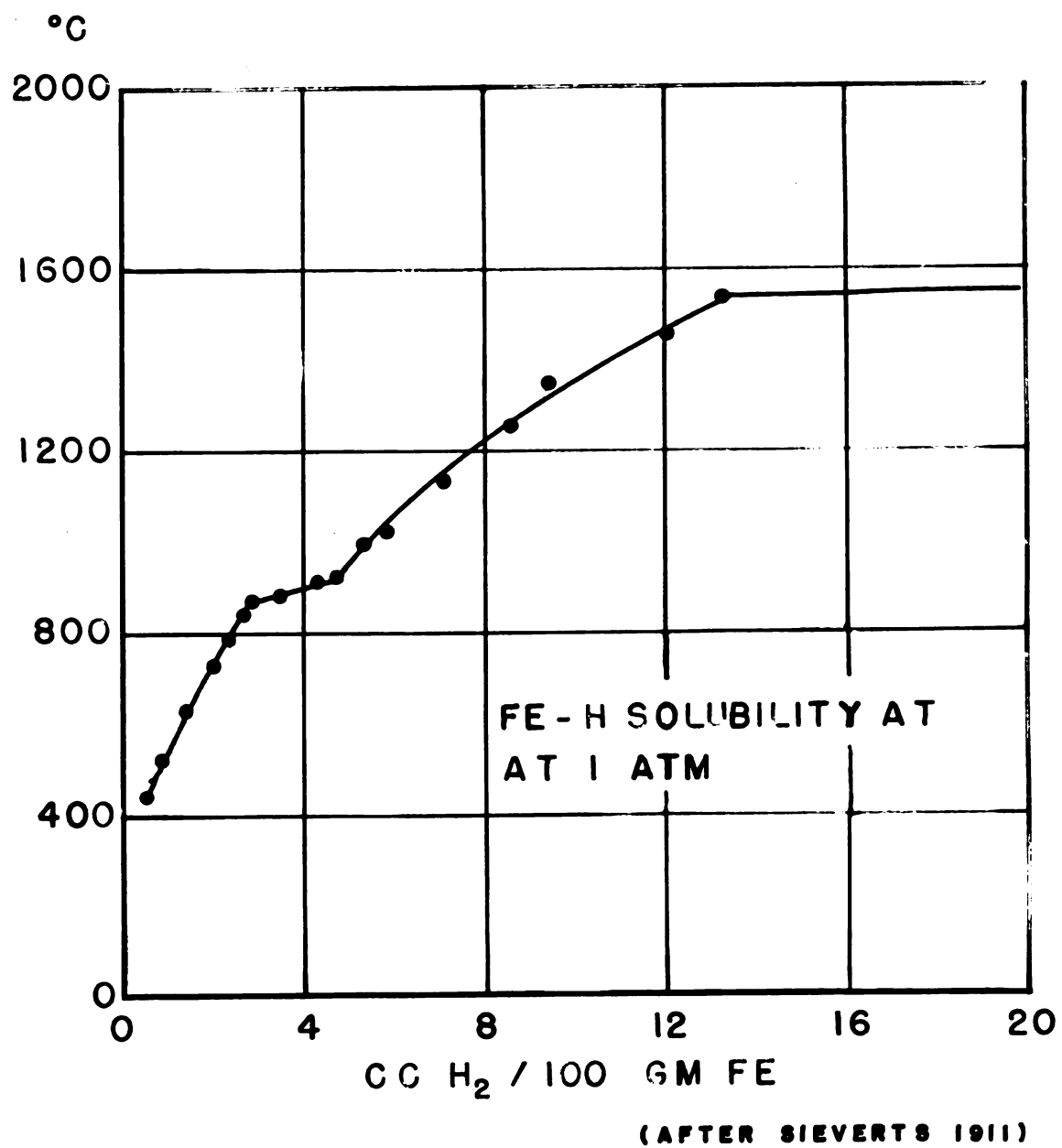
Figure 1. Fe-H solubility at 1 atmosphere.

Solubility curves prepared by Zapffe using the above work are shown in Figure 2. The similarity between this and Sieverts' work can be seen by comparing the curve for 1 atmosphere in Figure 2 with the curve shown in Figure 1.

Sieverts and his colleagues confirmed that hydrogen dissolves atomically (8), and that the solubility varies with the pressure according to the following relationship (9):

$$[H] = K'(PH_2)^{1/2}$$

where $[H]$ is the hydrogen concentration, P is the pressure, and K' is a constant.

The solubility curves for pressures above and below 1 atmosphere shown in Figure 2 were calculated using this formula. Also, data for the curves below 400° C. were similarly estimated, since no experimental data are available for the lower temperatures (10).

There is some evidence that the hydrides FeH, $FeH_2$, and $FeH_3$ exist at low temperatures (below 300°F.) (11). Also, Simons and Ham (12) attempted to explain the diffusion of hydrogen on the basis of hydride formation. Another investigator (13) observed a thin white constituent in the area near cracks which had been caused by hydrogen. This material was believed to be a hydrogen-rich phase, but no definite evidence such as an identification of the
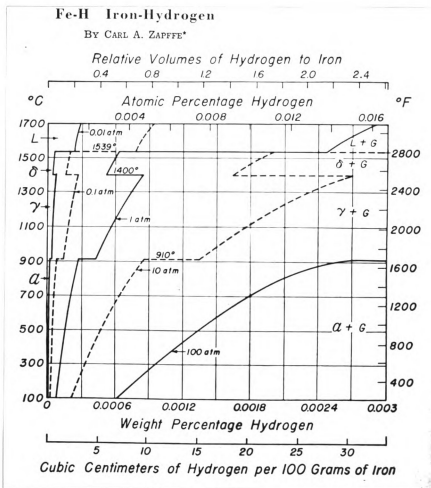
Figure 2. Iron-hydrogen.

supposed compound was offered. In fact, there is doubt that any stable hydrides exist.

Under certain conditions hydrogen may be present in iron and steel in quantities that considerably exceed equilibrium amounts. This overcharging may occur when a metal is exposed to cathodic or chemically liberated monoatomic hydrogen. It may also occur when a cold-worked metal is exposed to gaseous hydrogen (14). A metal may acquire amounts of hydrogen considerably above the solubility limit by rapidly changing conditions of temperature or pressure. For example, if molten iron is saturated with hydrogen and then allowed to solidify rapidly and to cool at room temperature, the resulting product will contain a quantity of hydrogen several times the equilibrium amount. The overcharging in this case results from the increased solubility of hydrogen in liquid iron over solid iron and the increase in solubility brought about by high temperatures. Similar results may be obtained by heating a sample of iron in high-pressure hydrogen. This high-pressure hydrogeneration technique was used by Hobsen and Sykes to study the effect of hydrogen on the ductility of low-alloy steel (15). A hydrogen content of 7.6 milliliters per 100 grams was obtained by heating a steel specimen for two hours at 600° C. in a hydrogen pressure of 56 atmospheres.

It is widely accepted that hydrogen dissolves interstitially in iron and steel. It is also possible that hydrogen finds its way into dislocations or other lattice defects. Evidence for this is furnished by the ability of cold-worked metals to absorb a greater amount of gas than similar annealed metals. According to Hagg (16), to form an interstitial alloy, the ratio of the atomic diameter of the interstitial solute atom to the solvent atom must be less than 0.59, and the solvent must be one of the transition metals. It is generally believed that there are only four elements with small enough atoms to dissolve interstitially in iron (which, of course, is a transition metal) (17). The four interstitial elements are hydrogen, boron, carbon, and nitrogen.

For several years many investigators have carefully studied the qualitative and quantitative effects of the various alloying elements on the hardenability of steel. At the present time the hardenability effects of most elements found in steel can be expressed in terms of a multiplying factor (18). This factor depends on the behavior and the percentage of the element. Hydrogen remains as one of the recognized important elements found in steel for which little or no hardenability information is available.

Among the interstitial elements the influence of carbon is well documented. Boron has been found to have a very pronounced effect

on the hardenability of steel even though the addition is very small. According to Grange and Garney (19), a boron content as low as 0.001 percent will give the maximum hardenability effect. The multiplying factor for this quantity of boron is approximately 1.5 (20). This means that 0.001 percent boron is equivalent to 0.1 percent molybdenum or 0.3 percent chromium. The effect of boron reaches a maximum, as does the influence of carbon in the presence of boron (21). It has been established that nitrogen will aid in the stabilization of austenite in stainless steels. For instance, the nickel content of 18-8 may be partly replaced by nitrogen (22). It might be expected then that nitrogen would arrest the austenite transformation in ordinary carbon steels and thus have an effect on hardenability. However, this has not been proven because of certain difficulties such as low solubility and compound formation (23). In the light of the influence of the other interstitial elements it seems entirely possible that the element hydrogen might have an effect on the stability of austenite or on the hardenability of steel.

There is a limited amount of information concerning the influence of hydrogen on the transformation of austenite (24, 25, 26). This information will be discussed in detail in the second part of this report.

# HYDROGEN AND STEEL

## Solubility

As stated previously, the equilibrium solubility of hydrogen in iron varies as the square root of the hydrogen pressure and increases with temperature. M. Armbruster (27) made a study of the solubility of hydrogen in iron, nickel, and certain steels. This work indicated that the solubility-pressure relation of

$$S = p^{1/2}$$

applies to certain steels as well as to iron. In addition, it was found that the relation between temperature and solubility for solid iron can be expressed as follows:

$$\text{Log } (S/p^{1/2}) = -(1454/T) + 1.946$$

where S is solubility in micromoles of hydrogen per 100 grams of iron, T is the absolute temperature, and p is pressure in millimeters of mercury. With a change of constants, this formula may be applied to steel. However, it was found that the solubility of hydrogen in low-alloy steels differs little from that of pure iron.

The hydrogen content of a steel may be expressed by atomic percentage, weight percentage, micromoles per 100 grams, relative volumes of hydrogen to iron, or cubic centimeters of hydrogen per

8

100 grams of steel. The methods of relative volumes and cubic centimeters per 100 grams seem to be the most popular.

Hydrogen may enter liquid steel and then become trapped when the steel solidifies, or may enter solid steel. It is generally believed that hydrogen enters solid steel as a charged atom. The charged atoms may be the result of cathodic deposition, a chemical reaction, or ordinary dissociation of the hydrogen molecule

## Hydrogen Entry Into Liquid Steel

One of the major sources of hydrogen in liquid steel is water. This may be water vapor or water of hydration of components in the furnace charge. Hydrogen may also be introduced into liquid steel by ferro-alloys, and slag-making constituents. Furnace fuels may be a source of hydrogen, since they introduce hydrogen and hydrocarbon into the furnace atmosphere.

Barraclough (28) found the hydrogen content of various steels sampled at tapping to vary from 4.6 to 10.3 milliliters per 100 grams. Barraclough's work indicated that the hydrogen content was more dependent upon the composition of the steel than on the kind of furnace or process used. However, he presented some evidence that indicated acid heats will have a slightly lower hydrogen content than basic heats of the same chemical composition.

Carney, Chipman, and Grant (29) reported in their work that the rate of solution of hydrogen into molten iron was very rapid. Only a few minutes were required for solution after hydrogen was introduced into the furnace atmosphere. The evolution of hydrogen from the molten metal was also rapid after removal of the hydrogen source from the furnace atmosphere. Mallett (30) found, in his investigation concerning the introduction of hydrogen into molten metal during arc welding, that the hydrogen content of the resulting weld metal can be closely estimated from an analysis of gases in the arc atmosphere. His work indicates that hydrogen in the arc atmosphere results from the water gas reaction:

$$CO + H_2O \rightleftharpoons CO_2 + H_2$$
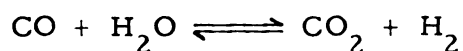
He also found that certain arc welding atmospheres contain as much as 40 percent hydrogen, which accounts for the high hydrogen content of some arc welds.

## Hydrogen Entry Into Solid Steel

In pickling operations, the hydrogen atoms may be furnished by the following reaction (31):

$$Fe + H_2SO_4 \longrightarrow FeSO_4 + 2H$$
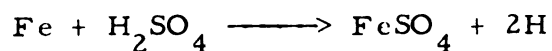
During the electrodeposition of a metal on steel there is an evolution of hydrogen ions on the steel surface. These hydrogen ions

readily enter the iron lattice. Deliberate cathodic charging will cause the solution of a quantity of hydrogen several times the equilibrium amount at room temperature. Cathodic charging has been used by several investigators in their study of the effect of hydrogen on the properties of metals.

It is believed by Smith (32) that steel will absorb hydrogen during heat-treatment from the steam reaction:

$$Fe + H_2O \longrightarrow FeO + 2H$$

The reaction:

$$Fe + 2H_2O \longrightarrow Fe(OH)_2 + 2H$$
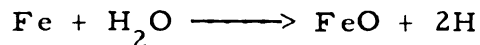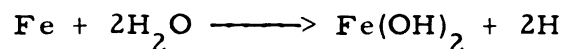
during rusting may cause the introduction of hydrogen into a steel.

Ordinary dissociation of the hydrogen molecule

$$H_2 \rightleftharpoons 2H$$
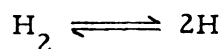
will produce atomic hydrogen for entry into steel placed in an atmosphere of hydrogen. The amount of dissociation, and consequently the amount of hydrogen absorbed, will depend upon the temperature and pressure. Since this reaction causes an increase in volume, an increase in pressure will lower the degree of dissociation. However, the dissociation is strongly endothermic and will be increased with high temperature. Giangue (33), using spectrographic data, calculated the dissociation values for hydrogen at various temperatures. Some of these values are given in Table I. It is evident

## TABLE I

### HYDROGEN DISSOCIATION
(from spectrographic data by Giangue)

| Degrees Fahrenheit | Percent Dissociation at 1 Atmosphere |
|---|---|
| 77 | $(1.8 \pm 6.6) \times 10^{-34}$ |
| 435 | $(4.4 \pm 6.7) \times 10^{-19}$ |
| 1335 | $(1.3 \pm 0.8) \times 10^{-7}$ |
| 2235 | $(9.5 \pm 3.4) \times 10^{-4}$ |
| 3135 | $0.086 \pm 0.011$ |
| 4035 | $1.31 \pm 0.13$ |
| 4935 | $8.1 \pm 0.65$ |
| 5830 | $29.7 \pm 1.1$ |
| 6740 | $63.3 \pm 2.2$ |
| 7630 | $95.7 \pm 0.1$ |

from this table that very little atomic hydrogen is available from dissociation for occlusion at room temperature. However, at higher temperatures there is a considerable amount available.

## Diffusion of Hydrogen in Steel

Barrer (34) states that a hydrogen atom may diffuse interstitially as a proton through the metal lattice. There seems to be little doubt that hydrogen atoms, which dissolve interstitially, diffuse through the interstices of the iron lattice (35). However, there is some doubt as to whether hydrogen atoms diffuse as protons (positively charged hydrogen atoms). X-ray data indicate a measurable amount of distortion of the ferrite lattice caused by the solution of hydrogen. If the hydrogen atoms dissolved as protons, there would be no such distortion of the iron lattice.

Smith (36) made the following remarks concerning the diffusion of hydrogen in iron:

> 1. Diffusion of hydrogen, at least in iron, occurs at the same rate, through single-crystals and polycrystalline mass.
> 2. Diffusion is not facilitated by grain boundaries but is hindered when they are very numerous. 3. Diffusion is at least approximately proportional to the square root of the impelling pressure difference. Like the similar relation for solubility, this probably fails for extreme conditions. [37]

It has also been observed that diffusion occurs at an accelerated rate through stressed metal.

Geller and Sun (38) calculated diffusion constants for iron and certain alloy steels. In general they found that alloy additions such as silicon, chromium, and nickel decrease diffusivity and that the diffusivity of hydrogen is much lower in gamma iron than in alpha iron at the same temperature. Another and more detailed investigation (39) gives further support to these principles.

### Effect of Hydrogen on Ductility and Impact Strength

The reduction of ductility is the most significant effect of the solution of hydrogen in iron and steel. Usually this reduction of ductility is proportional to the amount of hydrogen dissolved in the steel. However, at least one investigation (40) has shown that after a certain minimum ductility value is reached additional hydrogen has no further effect. The partial or almost complete effusion of hydrogen from the metal will be accompanied by a complete return of ductility. The loss of ductility caused by hydrogen occlusion is often commercially eradicated by annealing the steel for a period of time sufficient to remove a major portion of the hydrogen (41).

Sims and his colleagues (42) found that a 100 hour aging treatment at 400°F. was sufficient to return the ductility to a normal value and lower the hydrogen content from 0.28 to 0.04 relative volume in a cast carbon steel. The exact amount of hydrogen necessary

to cause embrittlement depends upon a number of factors such as composition, cleanliness, thermal history, and degree of segregation of hydrogen within the specimen (43).

In an investigation concerning the effect of hydrogen on the tensile properties of steel, Hobson and Hewitt (44) found that the significant factors are: "(1) Hydrogen content, (2) alloy type, (3) heat treatment, microstructure, and tensile strength, (4) previous history . . ., (5) rate and type of testing, (6) temperature (of testing), and (7) direction of stress." (45)

They also found that with amounts of hydrogen usually found in finished steel (1 to 4 milliliters per 100 grams) the effect on ductility at room temperature should not be severe unless the steel is hardened and very lightly tempered or extremely spheriodized.

## Underbead Cracking of Welds

The cracks that appear in the base metal adjacent to metal deposited by the metallic arc process are believed to result from hydrogen (46). There is fairly conclusive evidence that hydrogen is dissolved in the liquid metal during welding and then diffuses into the base metal (47). Most of this diffusion takes place when the zone near the weld is in the austenitic condition. Apparently by

some little-understood mechanism, this hydrogen dissolved in the base metal causes "underbead cracks."

Some of the characteristics of underbead cracks are as follows: (1) They increase with increasing hardenability. (2) They form at room temperature. (3) They require a period of time to form. (4) Martensite must be present. (5) The arc atmosphere must contain hydrogen (which is to say hydrogen must be present in the base metal) (48).

It appears that in some way, in a manner not completely explained, the hydrogen embrittles the untempered martensite which is then susceptible to cracking.

## Shatter Cracks or Flakes

The occurrence of an abnormal fracture appearance in a steel is often considered as evidence of the presence of hydrogen. These areas of abnormal fracture have been called by such names as flakes, snow flakes, or fish eyes. They are referred to as shatter cracks when the failure occurs during rolling or forging.

Segregation of hydrogen is believed to be an important factor in the formation of this type of fracture. Derge and Duncan (49) concluded that "thermal segregation" due to temperature gradients during cooling is a greater factor in the case of hydrogen distribution

than dendritic segregation during freezing. For example, samples from ingots air-cooled after pouring showed a greater degree of hydrogen segregation than similar ingots that were water-cooled. This higher hydrogen content of the center of the ingots is believed to be the cause of cracks during rolling or forging.

Sims (50) attributes the occurrence of fish eyes to the diffusion and segregation of hydrogen into voids or discontinuities in the steel. He explains that the hydrogen will diffuse into the voids and form hydrogen molecules $(H_2)$.

Carney, Chipman, and Grant (51) calculated that pressure as high as 218,500 pounds per square inch could be developed by virtue of hydrogen building up in these rifts or discontinuities in the steel. "It is postulated, therefore, that the molecular hydrogen present under high pressure in the cavities rushes into slip planes, as soon as slip starts, springs them apart and renders that part of the steel incapable of further plastic deformation." (52)

### Effect of Hydrogen on the Transformation of Austenite

In his work on hard-zone cracking of welds, Cottrell (53) noted that presence of this type of failure could be related to the temperature for completion of the austenite transformation during cooling. Since it had also been established that the presence of

hydrogen was necessary for the formation of this type of crack, Cottrell decided to study the effects of hydrogen on the transformation of austenite. Small specimens measuring 0.25 inch long by 0.225 inch outside diameter by 0.150 inch inside diameter were used. These small, thin specimens were charged cathodically, induction-heated, and then cooled by a blast of nitrogen. Simultaneous temperature and dilatation measurements were recorded. Figure 3, taken from Cottrell's work, illustrates his findings on the relationship between cooling time and transformation product, and cooling time and hardness. This diagram shows that, for a given cooling time, the hydrogen treatment had little effect on the final hardness, but the presence of hydrogen seems to increase the amount of martensite formed. In Cottrell's work the amount of martensite was estimated from dilatation. The work reported above also indicated that hydrogen has no effect on the $M_s$ temperature, but does have an effect on the end of transformation temperature. This effect is illustrated in Figure 4, taken from Cottrell's work. This work also indicated that, ''when the steel is supersaturated with hydrogen immediately before the dilation test, there are more pauses in the transformation to martensite, and the temperature for completion of transformation is lowered considerably for a given cooling rate.''

(54)
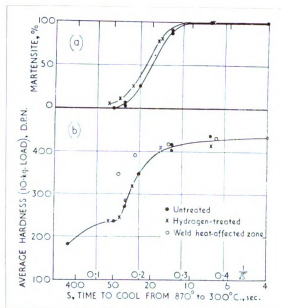
Figure 3. Relationship between cooling time and (a) transformation product, (b) hardness, for Mn-Mo steel (Cottrell).
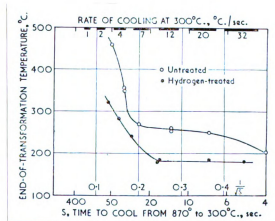


Figure 4. Relationship between end-of-transformation temperature and cooling time for Mn-Mo steel (Cottrell).
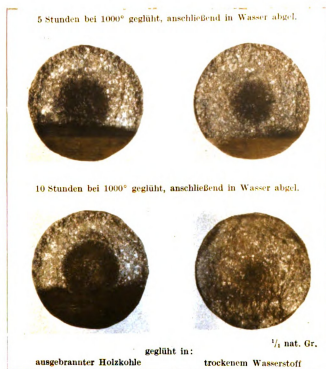
Figure 5. Influence of hydrogen on the depth of hardening on an unalloyed steel with 0.96 percent carbon, 0.13 percent silicon, and 0.28 percent manganese (by Houdremont and Heller).

Houdremont and Heller (55) reported that hydrogen had an effect on the hardenability of a steel containing 0.96 percent carbon. In this work specimens were heated for various periods of time in burned-out carburizer or wet hydrogen at 1 atmosphere. The results are shown in Figure 5. From these photographs taken from the work of Houdremont and Heller, it appears that the specimens heated in wet hydrogen hardened to a greater depth than the specimens heated in the burned carburizer. The specimens were all quenched in water. The photographs of the fractured specimens also indicate that ten hours in wet hydrogen give a greater depth of hardening than five hours. Harness U-curves presented in the work reveal that the specimens were seriously decarburized on the surface from the long periods of heating. Houdremont has also reported a portion of this work in a book (56).

# EXPERIMENTAL PROCEDURE AND RESULTS

## Cathode Charging

For this portion of the work, steel number 1 was used. The composition of this steel is given in Table II, and the microstructure is shown in Figure 6. In the first phase of this work, hardenability measurements were attempted using the Jominy end-quench method. Specimen A-1 was cathodically charged for twenty-five hours in a 20 percent solution of $H_2SO_4$. After charging, the specimen was rapidly heated in an agitated molten salt bath to 1550°F. It was determined experimentally that the temperature of the center of the 1 inch round bar would be within 10° of the temperature of the salt bath in three minutes. After heating, the specimen was transferred to the Jominy fixture and end-quenched. Specimen A-2 was heated in the same manner as Specimen A-1, but was uncharged. The resulting curves are shown in Figure 9.

These first results were encouraging, but inconclusive. Further work with this procedure indicated that the curves were not reproducible. This was attributed to the insensitiveness of the end-quench method. Apparently, if cathodic hydrogen had an effect on hardenability, it was too small to show distinctly by this method.

## TABLE II

### COMPOSITION OF STEEL USED
(percentages)

| Element | Steel Number | | |
|---|---|---|---|
| | 1 | 2 | 3 |
| Carbon .................... | 0.50 | 0.42 | 0.33 |
| Manganese ................. | 0.77 | 0.76 | 0.78 |
| Phosphorus ............... | 0.015 | 0.046 | 0.010 |
| Sulphur ................... | 0.038 | 0.034 | 0.026 |
| Silicon .................... | 0.20 | 0.27 | 0.21 |
| Nickel .................... | 0.04 | 0.07 | 0.05 |
| Chromium ................. | 0.04 | 0.20 | 0.09 |
| Molybdenum ............... | 0.05 | 0.06 | 0.05 |
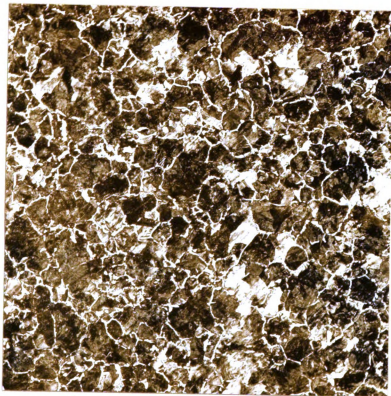
Figure 6. Steel No. 1, nital etch, 100X.
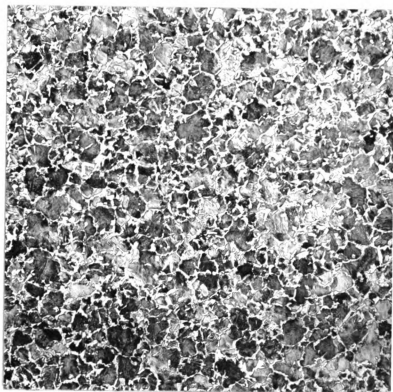
Figure 7.  Steel No. 2, nital etch, 100X.
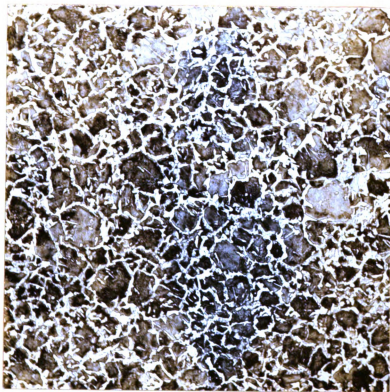
Figure 8.  Steel No. 3, nital etch, 100X.
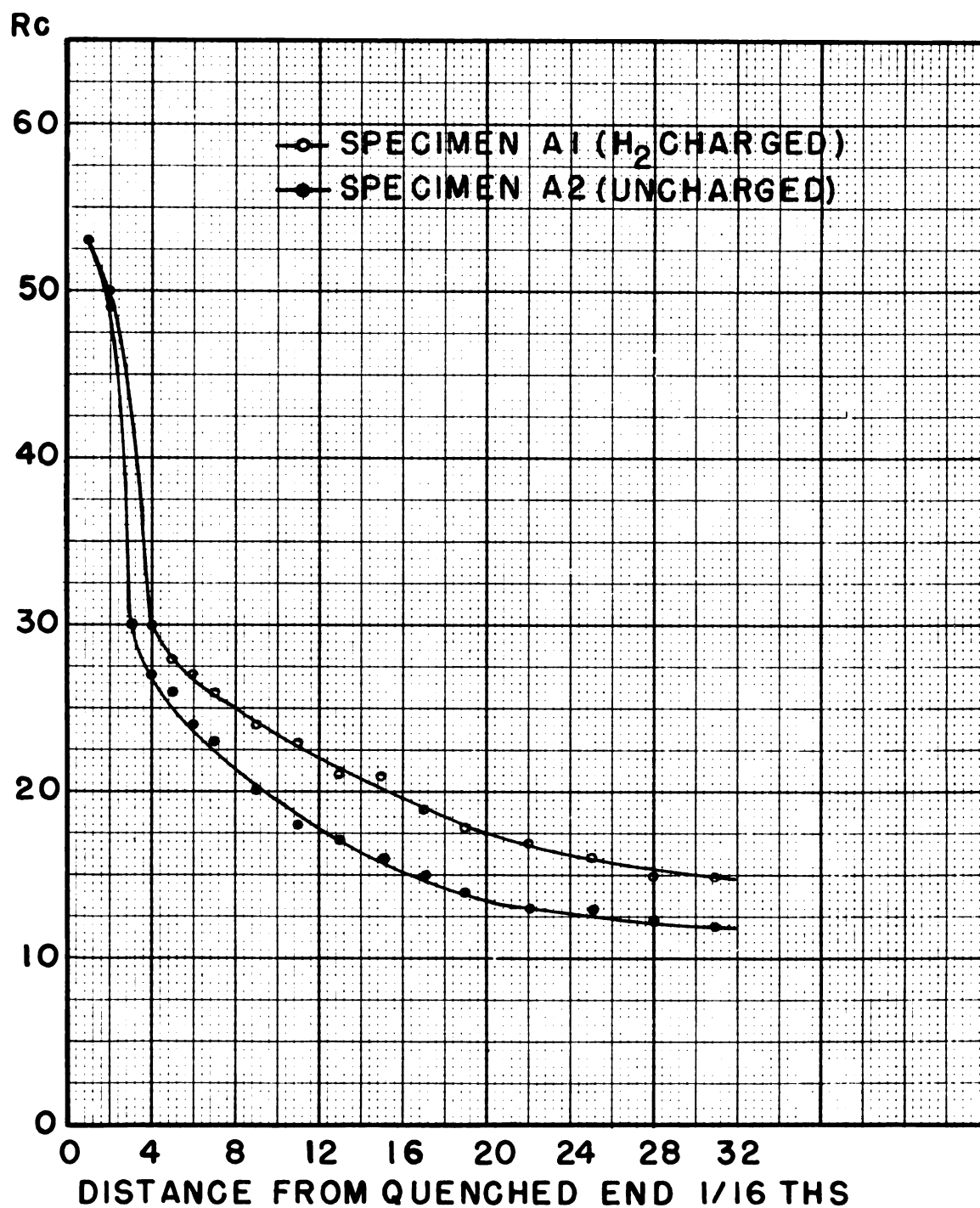
Figure 9.   End-quench curves.

It was decided to use "symmetrical U-curves" (57), produced from fully quenched specimens, as a measure of hardenability. In the case of symmetrical U-curves, the two halves are mirror images. Each half is produced by averaging hardness values taken along several radii. A typical specimen after hardness examination is shown in Figure 10.

All hardness tests were made with a Wilson "Tukon" machine using a 136° diamond with a 50 kilogram load. This machine was fitted with a stage and specially built indexing fixture. The positions for the hardness measurements were accurately located using this equipment.

Spray-quenching was used in order to obtain a reproducible quenching rate. The spray-quench fixture is shown in Figure 11. It consisted of a 4 inch pipe jacketed along a portion of its length with a 6 inch pipe. Water is forced at the specimen through 168 one-eighth inch holes arranged in eight rows. The holes are one-fourth inch apart in each row. When the 1 inch round by 4 inch long specimen is dropped down the 1 inch pipe, it is stopped and held in place by the microswitch actuating mechanism. The microswitch starts the 3 horsepower centrifugal pump, which sprays the specimen with 200 gallons of water per minute. The spray-quench equipment is shown, along with pressure furnace, in Figure 17.
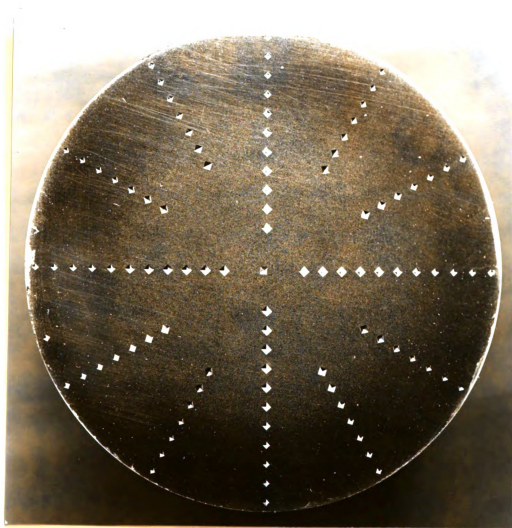
Figure 10.  Typical specimen after hardness examination, 5X.
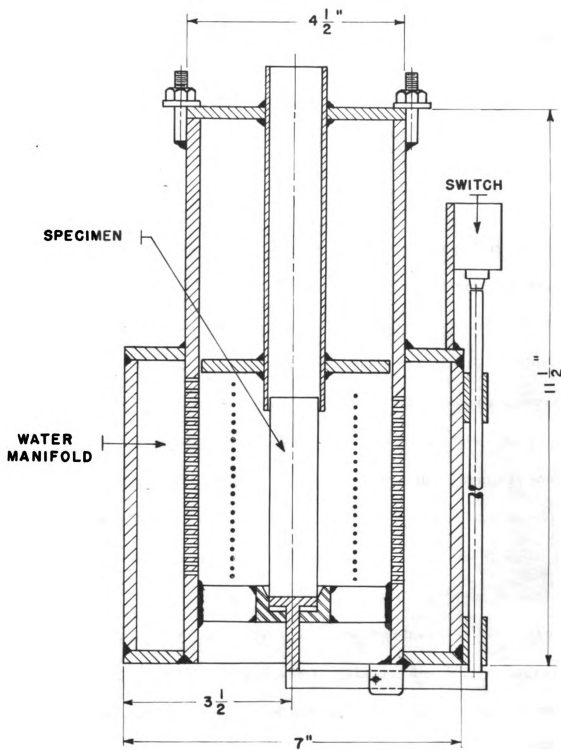
Figure 11. Spray-quench fixture.

The water was recirculated from the 100 gallon tank shown in the photograph. A 2 inch gate valve was used to control the water entering the quenching fixture.

The half U-curves prepared from specimens quenched with this equipment indicated that the quenching rate was very uniform from specimen to specimen.

A series of six specimens was quenched using this spray equipment. Specimens C-1, C-3, and C-5 were cathodically charged for twenty-four hours in 20 percent $H_2SO_4$ using a current of 3 amperes. Because of acid attack, the specimens were machined to the final 1 inch diameter after charging. All specimens were heated for 3.5 minutes in an agitated salt bath and then spray-quenched with water. The total time required for machining, heating, and quenching was less than fifteen minutes. This speed was thought necessary to prevent the loss of hydrogen. Specimens C-2, C-4, and C-6 were heated and quenched in a similar manner.

The specimens were sectioned and hardness values were taken on twelve equally spaced radii. The hardness tests were taken every millimeter starting 0.5 millimeter from the surface of the specimen. A typical specimen after hardness examination is shown in Figure 10. Averages of the twelve sets of hardness values were used to produce half U-curves. The tabulated results of these six

specimens are shown in Table III. Only the average values are given in this table. The two half U-curves shown in Figure 12 represent an average of the three charged specimens (C-1, C-3, C-5) and an average of the three uncharged specimens (C-2, C-4, C-6). Even though the charged specimens hardened to a greater depth, the difference is so small as to be almost negligible.

At this point it was concluded that the effect of cathodic hydrogen, if any, was very small. It was estimated, using data from another investigator (58), that the hydrogen content of the charged specimens was between 5 and 7 milliliters per 100 grams immediately after charging. Since the solubility of hydrogen in steel at 1550°F. is approximately 5 milliliters per 100 grams, and the heating time for the specimens was so short, it was thought that there was adequate hydrogen available to nearly saturate the austenite.

As a hydrogen content nearly equivalent to saturation at 1 atmosphere had a very small or no effect, it was decided to use high-pressure hydrogenation. Some of the advantages of this technique are: (1) increase in the hydrogen solubility, (2) longer austenization time, and (3) better temperature control.

TABLE III

HARDNESS (136° DIAMOND 50 KILOGRAM LOAD) OF C-1, C-3,
AND C-5, CATHODICALLY CHARGED; AND C-2, C-4,
AND C-6, UNCHARGED

| Depth (mm) | Specimen Number | | | Avg. | Specimen Number | | | Avg. |
|---|---|---|---|---|---|---|---|---|
| | C-1 | C-3 | C-5 | | C-2 | C-4 | C-6 | |
| 0.5 | 769 | 773 | 770 | 770 | 766 | 770 | 780 | 772 |
| 1.5 | 738 | 745 | 742 | 742 | 739 | 737 | 745 | 740 |
| 2.5 | 694 | 691 | 686 | 690 | 689 | 689 | 691 | 690 |
| 3.5 | 598 | 598 | 587 | 594 | 587 | 598 | 585 | 590 |
| 4.5 | 440 | 453 | 436 | 443 | 430 | 446 | 426 | 434 |
| 5.5 | 347 | 355 | 348 | 350 | 343 | 350 | 341 | 345 |
| 6.5 | 318 | 324 | 318 | 320 | 317 | 318 | 323 | 319 |
| 7.5 | 308 | 313 | 307 | 309 | 309 | 301 | 304 | 304 |
| 8.5 | 307 | 308 | 303 | 306 | 306 | 299 | 302 | 302 |
| 9.5 | 302 | 305 | 301 | 302 | 301 | 299 | 299 | 302 |
| 10.5 | 294 | 298 | 298 | 297 | 298 | 294 | 295 | 296 |
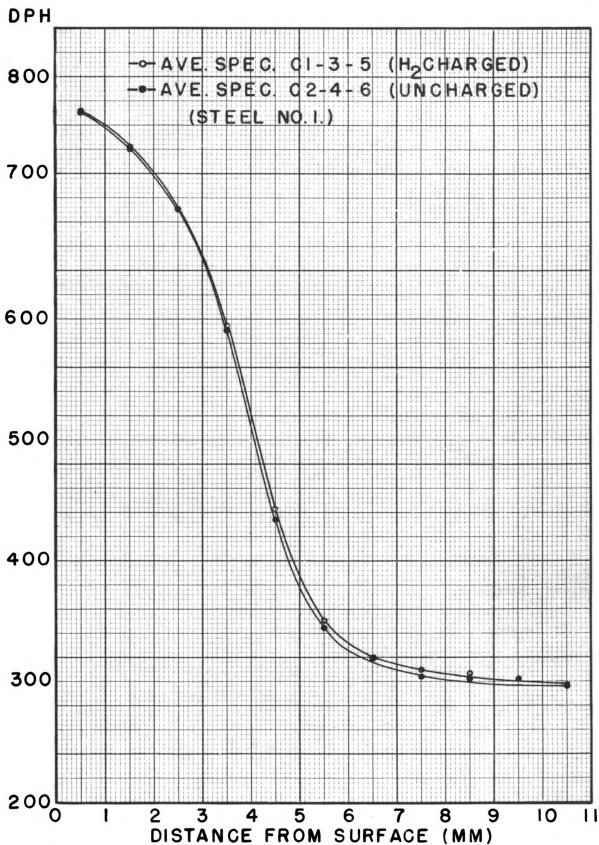
Figure 12.   Half U-curves.

## High-Pressure Hydrogenation

A sketch of the pressure-tight furnace is shown in Figure 13.
The furnace shell was made from a low carbon steel forging 8-1/2
inches in diameter and 11 inches long. The low carbon steel cover
flange was welded on. The furnace cavity was bored to a size of
8-1/2 inches deep by 5 inches in diameter, leaving a wall thickness
of 1-3/4 inches. The cover was held on by fifteen 1 inch studs and
nuts. A gasket was made from 1/16 inch thick copper. Five lands
1/8 inch wide were turned into the furnace gasket seat as shown in
Figure 14. A 2 inch thick by 11-1/2 inch diameter mild steel cover
was provided. A heating coil made from eighteen turns of 0.201 inch
cromel wire was used. Nickel leads were welded on as shown in
Figure 15. This coil had a cold resistance of 0.118 ohm. The coil
leads were made gas-tight through the furnace wall by a pile of mica
washers held in place by jam-nuts. Shorting was prevented on either
side of the mica pile by wrapping the coil leads with mica sheet.
Insulation for the furnace was cut from silica insulation bricks.
A 1-5/16 inch diameter zirconia refractory tube having a wall thick-
ness of 1/8 inch was placed inside the coil to prevent the specimens
from shorting the heating coil.

COIL LEADS

THERMOCOUPLE
LEADS

SPECIMEN

SEAL

▨ INSULATING BRICK

∎ MICA
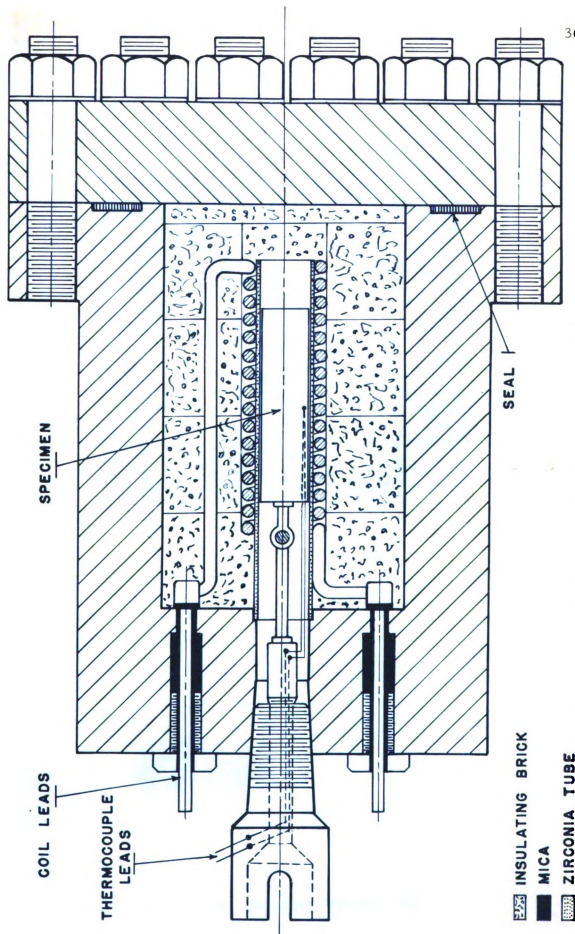
▥ ZIRCONIA TUBE

Figure 13. High-pressure furnace (scale, 1/2" = 1").
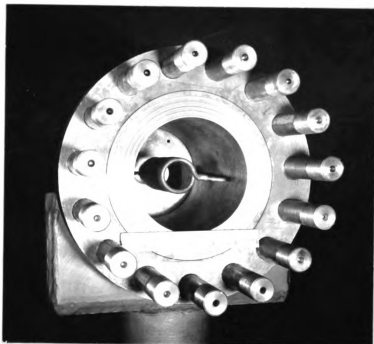
Figure 14.   Furnace shell with coil in place before introduction of
refractory insulation and zirconia tube.
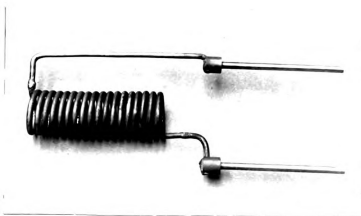


Figure 15.   Furnace heating coil.
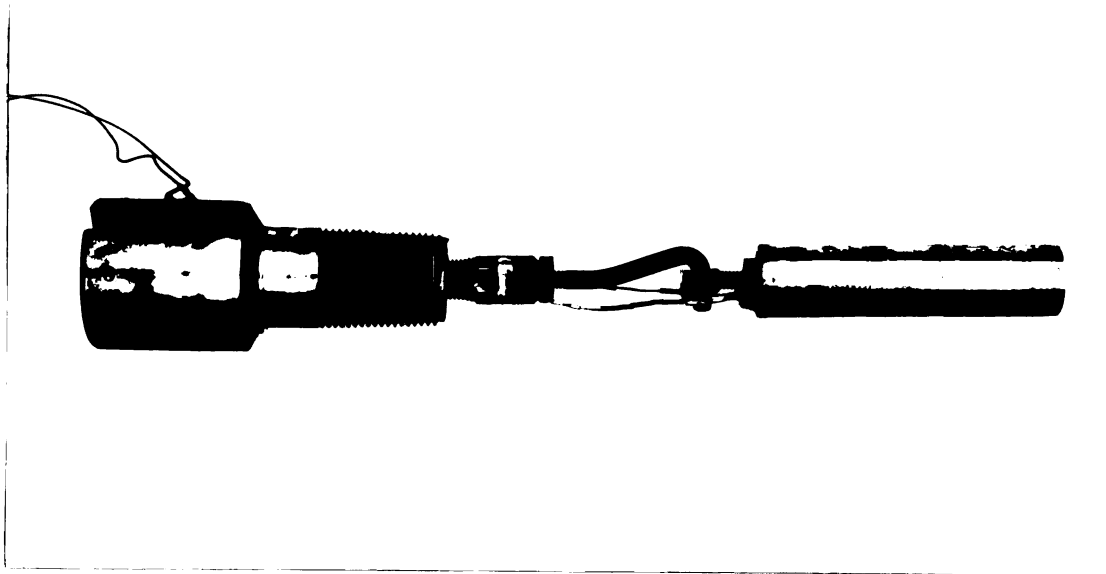
Figure 16. Assembly consisting of a 1 inch diameter by 4 inch long specimen with thermocouple in place, specimen holder, thermocouple seal tube, and furnace door.

After the insulating brick, heating coil, furnace thermocouple, and zirconia tube were in place, the cover was pulled down evenly with a torque wrench. It was calculated that a torque of 300 foot-pounds on each nut was necessary to seat the gasket.

As can be seen from Figure 17, the furnace was equipped with inlet and outlet valves. Standard oxygen cylinder valves were used.

The gas-tight furnace door is shown in Figure 16. This door was equipped with a standard 1 inch tapered pipe thread. Figure 16 also shows a 1 inch diameter by 4 inch specimen, a specimen hanger, the specimen thermocouple, and the thermocouple sealing tube attached to the furnace door. The specimen thermocouple was sealed into a small tube using a mixture of litharge and glycerine. When the furnace door is threaded into place, the specimen rotates with it.

After the furnace door is tight, the thermocouple is connected to the instrument shown in Figure 18. The centrifugal fan shown in Figure 17 was found necessary to keep the furnace shell cool. A hood which has been removed in Figure 17 was used to draw air away from around the furnace. The fan also rapidly removed any hydrogen that might have leaked from the furnace and thereby reduced the probability of an explosion.
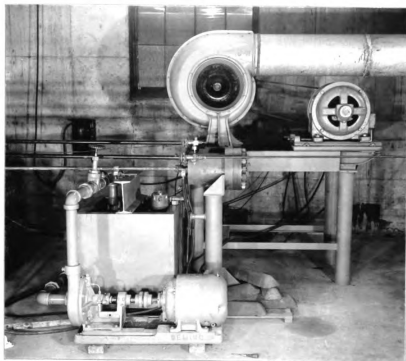
Figure 17.   View of high-pressure furnace and auxiliary equipment.
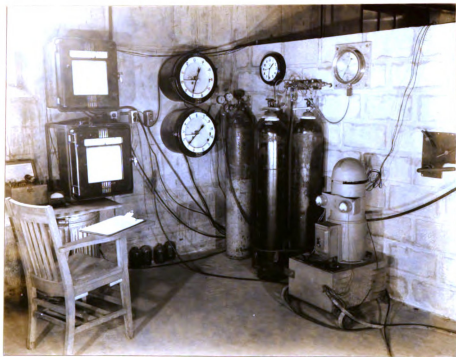
Figure 18. View of control equipment for high-pressure furnace.

The control equipment is shown in Figure 18. This equipment consisted of a portable potentiometer-type millivoltmeter, a 0-10 voltmeter, and two strip chart recording and controlling potentiometers. The millivoltmeter was used to measure the voltage drop across a shunt for accurately determining the current to the furnace heating coil. The 0-10 voltmeter was used to measure the voltage across the coil. The upper strip chart recorder was connected to the furnace thermocouple and was used to control the furnace temperature. The other strip chart recorder was used to record the temperature of the specimen in the furnace.

Nitrogen from the cylinder shown was used to purge the furnace of oxygen and also to provide an atmosphere for the control specimens. The three-cylinder manifold shown was used to furnish the hydrogen. The 0-3000 pound pressure gage indicated furnace pressure. The 200 ampere direct-current welder shown was used as a power supply for the furnace. Furnace valve controls are shown at the extreme right of the photograph.

## Furnace Operation

As representative of furnace operations, the heat-treatment of Specimen C-18 will be described. The specimen was assembled to the furnace door as shown in Figure 16. The specimen was then

placed in the furnace tube and the door was made secure. A commercial pipe sealer was used to prevent leakage around the door. After the thermocouple extension wires were attached to the thermocouple, the furnace was operated entirely from the control equipment shown in Figure 18. After purging the furnace with nitrogen several times, the nitrogen was purged out with hydrogen. The hydrogen pressure inside the furnace was then raised to 15 atmospheres (208 PSI gage). The power was turned on and held at 82 amperes throughout the run (approximately 800 watts). In one hour the specimen was at 1540°F. (835°C.). Hydrogen had to be released at various times during the run to keep the pressure at the desired level. After holding the specimen at temperature for thirty minutes, the hydrogen was released. The furnace door was then opened, the specimen removed, and placed in the quenching fixture and spray-quenched. The specimen was carefully sectioned with an abrasive cut-off wheel and made ready for hardness examination. The hardness values obtained from this particular specimen are given in Table XI.

## Effect of Pressure-Diffused Hydrogen

In this phase of the work, three steels were used. The compositions of these steels are given in Table II. Microstructures of

the three steels before heat-treating are shown in Figures 6, 7, and 8.

Ten specimens of steel number 1 were used. Specimens C-12, C-17, C-18, C-19, and C-20 were hydrogenized, during heat-treatment, using a pressure of 15 atmospheres. It was estimated that these specimens contained approximately 15 to 20 milliliters of hydrogen per 100 grams of steel at the time of quenching. Specimens C-10, C-13, C-14, C-15, and C-16 were heated in nitrogen at a pressure of 1 atmosphere. The results of the hardness examinations on these ten specimens are given in Tables IV through XIII.

Since the half U-curves for the specimens fell so closely into two groups, it was not possible to plot them all on a single graph. To represent all the data in the form of half U-curves the values of the hydrogenized specimen were averaged and the results plotted on the same graph with the average hardnesses of the control specimens. These curves are shown in Figure 19.

Two samples of steel number 2 were used. Specimen D-1, the control, was heat-treated in 1 atmosphere of nitrogen, and Specimen D-2 was hydrogenized using 15 atmospheres of hydrogen. The results of the hardness examinations are listed in Tables XIV and XV. The half U-curves for these specimens are shown in Figure 20.

Four samples of steel number 3 were treated. Specimens E-2 and E-4 were heated in 15 atmospheres of hydrogen, and the control specimens E-3 and E-5 were treated in 1 atmosphere of nitrogen. The results of the hardness tests are given in Tables XVI, XVII, XVIII, and XIX.

## Observations on Specimen Cracking

All specimens quenched from a hydrogen atmosphere cracked severely. Evidence of this cracking can be seen in Figures 22, 23, 24, 25, 26, and 27. The chip shown in Figure 24 spalled off from a specimen during quenching. No flakes were observed in the fracture surface of this chip. However, cracking that appeared to take place later exhibited flake containing fractures such as those shown in Figures 25 and 26. None of the specimens quenched from a nitrogen atmosphere showed any sign of cracking.

## Grain Size Determination

Since the small increase in hardenability displayed by the hydrogen-treated specimens might have been due to a difference in grain size, a thorough examination of this variable was made.

In most specimens the pearlite nucleating along the grain boundaries in the partially hardened area outlined the austenite grains.

Photomicrographs shown in Figures 28, 29, 30, and 31 are taken from Specimens C-10 and C-13 (control) and Specimens C-17 and C-20 (hydrogen-treated). Close examination of these photomicrographs revealed the grain size to be number 7 in all cases.

Photomicrographs of the partially hardened zone of specimens D-1 and D-2 are shown in Figures 32 and 33. These specimens both have a grain size of number 7. Samples taken from specimens E-3 and E-4 are shown in Figures 34 and 35. The grain size in both was number 7. The grain counts per square inch for all specimens examined are given in Table XX.

TABLE IV

SPECIMEN C-10 HARDNESS VALUES
(136° diamond 50 kilogram load)

| Depth (mm) | Row Number | | | | | | | | | | | | Avg. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | |
| 0.5 | 780 | 770 | 761 | 761 | 770 | 761 | 761 | 780 | 777 | 766 | 761 | 766 | 768 |
| 1.5 | 725 | 739 | 737 | 745 | 739 | 745 | 745 | 749 | 742 | 739 | 742 | 742 | 741 |
| 2.5 | 691 | 700 | 694 | 697 | 713 | 700 | 697 | 689 | 705 | 697 | 705 | 697 | 700 |
| 3.5 | 646 | 631 | 622 | 634 | 648 | 611 | 606 | 606 | 629 | 617 | 624 | 622 | 624 |
| 4.5 | 485 | 493 | 490 | 508 | 508 | 464 | 461 | 480 | 482 | 465 | a | 493 | 484 |
| 5.5 | 363 | 370 | 363 | 377 | 367 | 355 | 364 | 361 | 364 | 365 | 367 | 362 | 365 |
| 6.5 | 326 | 328 | 327 | 328 | 323 | 323 | 327 | 322 | 326 | 321 | 323 | 324 | 324 |
| 7.5 | 312 | | | 309 | | | 316 | | | 317 | | | 313 |
| 8.5 | 308 | | | 306 | | | 309 | | | 312 | | | 309 |
| 9.5 | 306 | | | 305 | | | 303 | | | 312 | | | 306 |
| 10.5 | 292 | | | 309 | | | 289 | | | 294 | | | 295 |

[a] Hardness in error due to machine fault.

TABLE V

SPECIMEN C-12 HARDNESS VALUES
(136° diamond 50 kilogram load)

| Depth (mm) | Row Number | | | | | | | | | | | | Avg. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | |
| 0.5 | 758 | 755 | 764 | 766 | a | b | b | b | b | b | b | 780 | 765 |
| 1.5 | a | 722 | a | a | a | b | b | b | b | b | b | a | 722 |
| 2.5 | 708 | 708 | 708 | 708 | 711 | 708 | a | 705 | a | a | a | 711 | 708 |
| 3.5 | 648 | 653 | 634 | 641 | 641 | 653 | 653 | 653 | 653 | 641 | 641 | 636 | 646 |
| 4.5 | 509 | 508 | 506 | 515 | 509 | 527 | 508 | 509 | 518 | 522 | 518 | 508 | 513 |
| 5.5 | 376 | 380 | 380 | 380 | 376 | 397 | 392 | 391 | 392 | 385 | 391 | 380 | 385 |
| 6.5 | 333 | 333 | 326 | 334 | 333 | 340 | 337 | 341 | 337 | 335 | 334 | 332 | 335 |
| 7.5 | 314 | | | 313 | | | 320 | | | 316 | | | 316 |
| 8.5 | 309 | | | 321 | | | 314 | | | 305 | | | 312 |
| 9.5 | 313 | | | 309 | | | 312 | | | 302 | | | 309 |
| 10.5 | 299 | | | 300 | | | 294 | | | 307 | | | 300 |

[a] Hardness value in error due to cracking.

[b] Hardness value lost due to chipped specimen.

TABLE VI

SPECIMEN C-13 HARDNESS VALUES
(136° diamond 50 kilogram load)

| Depth (mm) | Row Number | | | | | | | | | | | | Avg. |
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 0.5 | 777 | 770 | 770 | 777 | 777 | 773 | 773 | 780 | 780 | 773 | 780 | 786 | 776 |
| 1.5 | 737 | 742 | 745 | 749 | 739 | 749 | 742 | 737 | 742 | 739 | 745 | 745 | 743 |
| 2.5 | 691 | 686 | 689 | 697 | 694 | 684 | 700 | 689 | 678 | 691 | 689 | 694 | 690 |
| 3.5 | 604 | 609 | 611 | 622 | 600 | 593 | 615 | 606 | 579 | 598 | 598 | 611 | 604 |
| 4.5 | 462 | 458 | 461 | 483 | 468 | 469 | 441 | 447 | 459 | 462 | 465 | 469 | 462 |
| 5.5 | 358 | 368 | 357 | 369 | 367 | 359 | 361 | 348 | 353 | 365 | 372 | 362 | 362 |
| 6.5 | 328 | 326 | 324 | 322 | 326 | 335 | 326 | 323 | 318 | 323 | 326 | 322 | 325 |
| 7.5 | 318 | | | 318 | | | 323 | | | 313 | | | 318 |
| 8.5 | 310 | | | 311 | | | 315 | | | 309 | | | 311 |
| 9.5 | 312 | | | 314 | | | 312 | | | 309 | | | 312 |
| 10.5 | 300 | | | 295 | | | 299 | | | 314 | | | 302 |

TABLE VII

SPECIMEN C-14 HARDNESS VALUES
(136° diamond 50 kilogram load)

| Depth (mm) | Row Number | | | | | | | | | | | | Avg. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | |
| 0.5 | 755 | 770 | 766 | a | 773 | 783 | b | b | b | 764 | 780 | 777 | 771 |
| 1.5 | 734 | 737 | 739 | 716 | 739 | 739 | 734 | b | 734 | 745 | 745 | 745 | 737 |
| 2.5 | 681 | 684 | 678 | 694 | 700 | 694 | 689 | 705 | 684 | 697 | 708 | 697 | 693 |
| 3.5 | 602 | 611 | 604 | 602 | 609 | 600 | 615 | 624 | 609 | 627 | 606 | 609 | 610 |
| 4.5 | 483 | 486 | 467 | 465 | 456 | 488 | 486 | 511 | 472 | 480 | 488 | 476 | 480 |
| 5.5 | 374 | 376 | 370 | 358 | 372 | 371 | 369 | 376 | 377 | 377 | 367 | 374 | 372 |
| 6.5 | 329 | 330 | 326 | 330 | 330 | 330 | 334 | 334 | 333 | 330 | 330 | 330 | 331 |
| 7.5 | 315 | | | 317 | | | 320 | | | 320 | | | 318 |
| 8.5 | 312 | | | 312 | | | 311 | | | 315 | | | 313 |
| 9.5 | 307 | | | 305 | | | 311 | | | 301 | | | 306 |
| 10.5 | 309 | | | 306 | | | 296 | | | 294 | | | 301 |

[a] Reading in error due to machine fault.

[b] Hardness lost due to chipped specimen.

TABLE VIII

SPECIMEN C-15 HARDNESS VALUES
(136° diamond 50 kilogram load)

| Depth (mm) | Row Number | | | | | | | | | | | | Avg. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | |
| 0.5 | 764 | 734 | a | 766 | 770 | 786 | 766 | 773 | a | 766 | 773 | 773 | 767 |
| 1.5 | 719 | 734 | 686 | 734 | 742 | 742 | 737 | 739 | 739 | 737 | 734 | 739 | 732 |
| 2.5 | 658 | 678 | 670 | 678 | 697 | 691 | 684 | 689 | 684 | 689 | 694 | 678 | 683 |
| 3.5 | 569 | 604 | 596 | 600 | 620 | 609 | 602 | 604 | 604 | 606 | 617 | 587 | 602 |
| 4.5 | 468 | 474 | 465 | 464 | 483 | 477 | 465 | 480 | 462 | 488 | 483 | 472 | 465 |
| 5.5 | 376 | 366 | 380 | 363 | 357 | 367 | 368 | 362 | 377 | 372 | 370 | 384 | 370 |
| 6.5 | 335 | 329 | 334 | 328 | 326 | 328 | 329 | 328 | 333 | 328 | 326 | 330 | 330 |
| 7.5 | 318 | | | 316 | | | 309 | | | 317 | | | 315 |
| 8.5 | 313 | | | 314 | | | 306 | | | 312 | | | 311 |
| 9.5 | 299 | | | 307 | | | 304 | | | 306 | | | 304 |
| 10.5 | 291 | | | 301 | | | 301 | | | 295 | | | 297 |

a Reading in error due to operator fault.

TABLE IX

SPECIMEN C-16 HARDNESS VALUES
(136° diamond 50 kilogram load)

| Depth (mm) | Row Number | | | | | | | | | | | | Avg. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | |
| 0.5 | 766 | 758 | 761 | 755 | 770 | 783 | 766 | 766 | 761 | 766 | 764 | 773 | 766 |
| 1.5 | 742 | 737 | 734 | 742 | 742 | 737 | 737 | 739 | 745 | 734 | 734 | 731 | 738 |
| 2.5 | 700 | 678 | 678 | 691 | 697 | 691 | 689 | 691 | 697 | 691 | 686 | 684 | 689 |
| 3.5 | 609 | 593 | 598 | 622 | 617 | 620 | 611 | 598 | 620 | 598 | 606 | 596 | 606 |
| 4.5 | 491 | 485 | 477 | 488 | 505 | 506 | 488 | 471 | 495 | 477 | 477 | 490 | 488 |
| 5.5 | 373 | 386 | 370 | 389 | 383 | 387 | 376 | 381 | 380 | 377 | 376 | 397 | 381 |
| 6.5 | 333 | 399 | 325 | 331 | 324 | 330 | 334 | 329 | 322 | 330 | 330 | 329 | 335 |
| 7.5 | 318 | | | 307 | | | 315 | | | 310 | | | 313 |
| 8.5 | 310 | | | 305 | | | 309 | | | 308 | | | 308 |
| 9.5 | 303 | | | 303 | | | 305 | | | 305 | | | 304 |
| 10.5 | 300 | | | 302 | | | 305 | | | 295 | | | 301 |

TABLE X

SPECIMEN C-17 HARDNESS VALUES
(136° diamond 50 kilogram load)

| Depth (mm) | Row Number | | | | | | | | | | | | Avg. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | |
| 0.5 | 766 | 764 | 764 | 770 | 761 | 758 | b | b | 758 | 773 | 770 | 761 | 765 |
| 1.5 | a | a | 742 | a | 734 | a | a | a | 734 | 734 | 734 | 734 | 735 |
| 2.5 | a | 700 | 691 | a | 681 | a | 689 | 670 | a | a | a | 681 | 685 |
| 3.5 | 629 | 638 | a | a | a | 631 | 636 | a | a | 596 | 606 | a | 623 |
| 4.5 | 509 | 522 | 541 | 532 | 527 | 513 | 515 | 509 | 518 | 530 | 536 | 516 | 522 |
| 5.5 | 421 | 410 | 418 | 420 | 406 | 394 | 424 | 404 | 397 | 403 | 407 | 409 | 409 |
| 6.5 | 353 | 343 | 391 | 347 | 349 | 345 | 343 | 335 | 352 | 346 | 362 | 355 | 348 |
| 7.5 | 330 | | | 325 | | | 330 | | | 330 | | | 329 |
| 8.5 | 315 | | | 314 | | | 314 | | | 320 | | | 316 |
| 9.5 | 312 | | | 310 | | | 305 | | | 312 | | | 310 |
| 10.5 | 305 | | | 316 | | | 295 | | | 303 | | | 305 |

[a] Reading in error due to cracking.

[b] Hardness lost due to chipped specimen.

## TABLE XI

### SPECIMEN C-18 HARDNESS VALUES
(136° diamond 50 kilogram load)

| Depth (mm) | Row Number | | | | | | | | | | | | Avg. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | |
| 0.5 | 758 | a | a | 761 | 770 | b | b | b | a | 761 | 764 | a | 763 |
| 1.5 | a | a | a | a | a | 731 | a | a | 734 | a | a | a | 733 |
| 2.5 | a | a | a | a | a | a | a | a | a | 689 | 676 | a | 683 |
| 3.5 | 641 | 631 | 634 | 631 | 655 | 634 | 631 | 643 | a | 641 | 651 | 634 | 639 |
| 4.5 | 518 | 522 | 511 | 522 | 545 | 518 | 523 | 540 | 541 | 534 | 527 | 527 | 527 |
| 5.5 | 425 | 403 | 405 | 415 | 416 | c | 420 | 415 | 420 | 401 | 415 | 410 | 413 |
| 6.5 | 354 | 331 | 349 | 345 | 349 | 354 | 358 | 343 | 346 | 343 | 344 | 348 | 347 |
| 7.5 | 328 | | | 330 | | | 332 | | | 313 | | | 326 |
| 8.5 | 320 | | | 321 | | | 323 | | | 313 | | | 318 |
| 9.5 | 312 | | | 313 | | | 312 | | | 313 | | | 313 |
| 10.5 | 305 | | | 305 | | | 306 | | | 321 | | | 309 |

[a] Reading in error due to cracking.

[b] Hardness lost due to chipped specimen.

[c] Hardness lost due to machine failure.

TABLE XII

SPECIMEN C-19 HARDNESS VALUES
(136° diamond 50 kilogram load)

| Depth (mm) | Row Number | | | | | | | | | | | | Avg. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | |
| 0.5 | 764 | 766 | 764 | 761 | b | b | b | 766 | 780 | 764 | 766 | 766 | 766 |
| 1.5 | a | a | a | a | a | a | 728 | 728 | 734 | a | 734 | 728 | 730 |
| 2.5 | a | 702 | a | a | a | a | 700 | a | a | a | 689 | a | 697 |
| 3.5 | 643 | 646 | 641 | 653 | 636 | 624 | 641 | 631 | 641 | a | a | a | 640 |
| 4.5 | 518 | 553 | 540 | 541 | 532 | 530 | 525 | 509 | 530 | 549 | 538 | 509 | 531 |
| 5.5 | 407 | 412 | 425 | 416 | 410 | 416 | 406 | 398 | 426 | 420 | 420 | 434 | 416 |
| 6.5 | 344 | 343 | 349 | 353 | 345 | 357 | 355 | 348 | 351 | 369 | 360 | 316 | 349 |
| 7.5 | 325 | | | 324 | | | 330 | | | 333 | | | 328 |
| 8.5 | 325 | | | 318 | | | 326 | | | 326 | | | 324 |
| 9.5 | 313 | | | 310 | | | 315 | | | 315 | | | 313 |
| 10.5 | 309 | | | 307 | | | 304 | | | 305 | | | 306 |

[a] Reading in error due to cracking.

[b] Reading lost due to chipped specimen.

TABLE XIII

SPECIMEN C-20 HARDNESS VALUES
(136° diamond 50 kilogram load)

| Depth (mm) | Row Number | | | | | | | | | | | | Avg. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | |
| 0.5 | 766 | 758 | a | b | b | b | 773 | 764 | 770 | 752 | 764 | a | 764 |
| 1.5 | a | a | 711 | a | b | 722 | 728 | a | 722 | a | a | a | 721 |
| 2.5 | 702 | a | a | 686 | 708 | a | 697 | a | a | a | 713 | 691 | 700 |
| 3.5 | 648 | 648 | 636 | 636 | 646 | 651 | 643 | 634 | 641 | 643 | 648 | 634 | 642 |
| 4.5 | 637 | 536 | 532 | 530 | 518 | 538 | 551 | 527 | 509 | 522 | 547 | 534 | 540 |
| 5.5 | 409 | 409 | 425 | 399 | 410 | 424 | 420 | 406 | 421 | 409 | 404 | 403 | 412 |
| 6.5 | 353 | 349 | 356 | 349 | 353 | 353 | 361 | 359 | 354 | 348 | 343 | 344 | 352 |
| 7.5 | 328 | | | 330 | | | 336 | | | 334 | | | 331 |
| 8.5 | 319 | | | 323 | | | 323 | | | 329 | | | 324 |
| 9.5 | 312 | | | 312 | | | 315 | | | 318 | | | 314 |
| 10.5 | 313 | | | 306 | | | 305 | | | 311 | | | 309 |

[a] Reading in error due to cracking.

[b] Reading lost due to chipped specimen.

## TABLE XIV

### SPECIMEN D-1 HARDNESS VALUES
(136° diamond 50 kilogram load)

| Depth (mm) | Row Number | | | | | | | | | | | | Avg. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | |
| 0.5 | 691 | 689 | | 684 | 689 | | 686 | 684 | | 684 | 684 | | 686 |
| 1.5 | 660 | 660 | | 660 | 665 | | 663 | 660 | | 658 | 670 | | 662 |
| 2.5 | 653 | 651 | | 643 | 651 | | 653 | 643 | | 643 | 655 | | 649 |
| 3.5 | 627 | 615 | | 634 | 613 | | 641 | 624 | | 629 | 609 | | 624 |
| 4.5 | 587 | 577 | | 593 | 573 | | 589 | 579 | | 629 | 579 | | 588 |
| 5.5 | 559 | 555 | | 553 | 541 | | 553 | 545 | | 589 | 536 | | 554 |
| 6.5 | 522 | 522 | | 530 | 515 | | 520 | 522 | | 527 | 513 | | 521 |
| 7.5 | 493 | 495 | | 513 | 491 | | 493 | 503 | | 503 | 491 | | 498 |
| 8.5 | 472 | 469 | | 471 | 469 | | 483 | 482 | | 509 | 476 | | 479 |
| 9.5 | 453 | | | 453 | 446 | | 453 | | | 456 | | | 452 |
| 10.5 | 445 | | | 452 | | | 429 | | | 444 | | | 443 |

TABLE XV

## SPECIMEN D-2 HARDNESS VALUES
(136° diamond 50 kilogram load)

| Depth (mm) | Row Number | | | | | | | | | | | | Avg. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | |
| 0.5 | 689 | 689 | | 700 | b | | a | b | | 689 | a | | 692 |
| 1.5 | a | a | | a | a | | a | a | | a | a | | a |
| 2.5 | a | a | | a | a | | a | 658 | | 658 | a | | 658 |
| 3.5 | 651 | 648 | | 629 | 624 | | 641 | a | | 651 | 658 | | 643 |
| 4.5 | 609 | 615 | | 622 | 622 | | 606 | 602 | | 636 | 620 | | 617 |
| 5.5 | 562 | 575 | | 606 | 606 | | 564 | 564 | | 583 | 577 | | 580 |
| 6.5 | 541 | 541 | | 559 | 564 | | 540 | 536 | | 545 | 547 | | 547 |
| 7.5 | 520 | 509 | | 529 | 543 | | 520 | 515 | | 515 | 516 | | 521 |
| 8.5 | 483 | 485 | | 509 | 515 | | 498 | 490 | | 488 | 490 | | 495 |
| 9.5 | 465 | | | 498 | | | 477 | | | 461 | | | 475 |
| 10.5 | 447 | | | 476 | | | 458 | | | 955 | | | 459 |

[a] Reading in error due to cracking.

[b] Reading lost due to chipped specimen.

TABLE XVI

SPECIMEN E-2 HARDNESS VALUES
(136° diamond 50 kilogram load)

| Depth (mm) | Row Number | | | | | | | | Avg. |
|---|---|---|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | |
| 0.5 | 631 | 636 | a | a | 634 | a | 622 | 629 | 630 |
| 1.5 | a | a | 596 | 581 | a | a | 579 | 587 | 587 |
| 2.5 | a | a | a | 562 | 582 | a | a | a | 572 |
| 3.5 | 508 | 513 | 483 | 516 | 482 | 505 | 532 | 515 | 507 |
| 4.5 | 412 | 447 | 397 | 416 | 415 | 409 | 431 | 428 | 419 |
| 5.5 | 352 | 350 | 349 | 360 | 358 | 369 | 368 | 362 | 359 |
| 6.5 | 528 | 315 | 313 | 325 | 337 | 347 | 343 | 331 | 355 |
| 7.5 | 310 | | 290 | | 300 | | 317 | | 304 |
| 8.5 | 283 | | 277 | | 275 | | 296 | | 283 |
| 9.5 | 273 | | 271 | | 261 | | 288 | | 273 |
| 10.5 | 272 | | 272 | | 267 | | 277 | | 272 |

[a] Reading in error due to cracking.

TABLE XVII

## SPECIMEN E-3 HARDNESS VALUES
(136° diamond 50 kilogram load)

| Depth (mm) | Row Number | | | | | | | | Avg. |
|---|---|---|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | |
| 0.5 | 622 | 622 | 631 | 629 | 622 | 617 | 636 | 629 | 626 |
| 1.5 | 604 | 600 | 609 | 600 | 602 | 602 | 604 | 600 | 603 |
| 2.5 | 553 | 560 | 562 | 549 | 532 | 553 | 557 | 581 | 556 |
| 3.5 | 485 | 508 | 483 | 468 | 461 | 450 | 495 | 511 | 483 |
| 4.5 | 409 | 434 | 399 | 400 | 392 | 390 | 399 | 420 | 405 |
| 5.5 | 359 | 362 | 361 | 365 | 353 | 344 | 349 | 357 | 356 |
| 6.5 | 341 | 326 | 333 | 332 | 306 | 300 | 293 | 328 | 320 |
| 7.5 | 309 | | 313 | | 278 | | 295 | | 299 |
| 8.5 | 297 | | 294 | | 263 | | 274 | | 282 |
| 9.5 | 283 | | 277 | | 262 | | 269 | | 273 |
| 10.5 | 269 | | 271 | | 262 | | 268 | | 268 |

## TABLE XVIII

### SPECIMEN E-4 HARDNESS VALUES
(136° diamond 50 kilogram load)

| Depth (mm) | Row Number | | | | | | | | Avg. |
|---|---|---|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | |
| 0.5 | 631 | 624 | 631 | 638 | 629 | 638 | 627 | 631 | 631 |
| 1.5 | 596 | a | a | 585 | a | a | a | a | 591 |
| 2.5 | a | a | a | a | a | 564 | 585 | 591 | 581 |
| 3.5 | 530 | 508 | 509 | 490 | 529 | 501 | 536 | 516 | 515 |
| 4.5 | 434 | 430 | 436 | 437 | 409 | 401 | 462 | 434 | 430 |
| 5.5 | 392 | 374 | 380 | 376 | 369 | 354 | 397 | 380 | 378 |
| 6.5 | 333 | 337 | 352 | 330 | 324 | 326 | 343 | 347 | 337 |
| 7.5 | 315 | | 341 | | 301 | | 321 | | 320 |
| 8.5 | 303 | | 287 | | 276 | | 294 | | 290 |
| 9.5 | 277 | | 273 | | 273 | | 280 | | 276 |
| 10.5 | 276 | | 273 | | 280 | | 278 | | 277 |

[a] Reading lost due to cracking.

TABLE XIX

SPECIMEN E-5 HARDNESS VALUES
(136° diamond 50 kilogram load)

| Depth (mm) | Row Number | | | | | | | | Avg. |
|---|---|---|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | |
| 0.5 | 617 | 631 | 624 | 620 | 622 | 620 | 624 | 629 | 623 |
| 1.5 | 604 | 613 | 589 | 609 | 613 | 600 | 602 | 596 | 603 |
| 2.5 | 555 | 569 | 541 | 575 | 555 | 557 | 555 | 559 | 558 |
| 3.5 | 490 | 508 | 477 | 490 | 485 | 483 | 477 | 508 | 490 |
| 4.5 | 383 | 434 | 416 | 415 | 421 | 401 | 394 | 403 | 408 |
| 5.5 | 335 | 349 | 361 | 370 | 381 | 359 | 357 | 349 | 358 |
| 6.5 | 314 | 319 | 323 | 335 | 344 | 332 | 330 | 318 | 327 |
| 7.5 | 301 | | 292 | | 307 | | 296 | | 299 |
| 8.5 | 280 | | 282 | | 277 | | 273 | | 278 |
| 9.5 | 268 | | 263 | | 268 | | 260 | | 265 |
| 10.5 | 264 | | 274 | | 265 | | 261 | | 266 |

TABLE XX

GRAIN COUNT

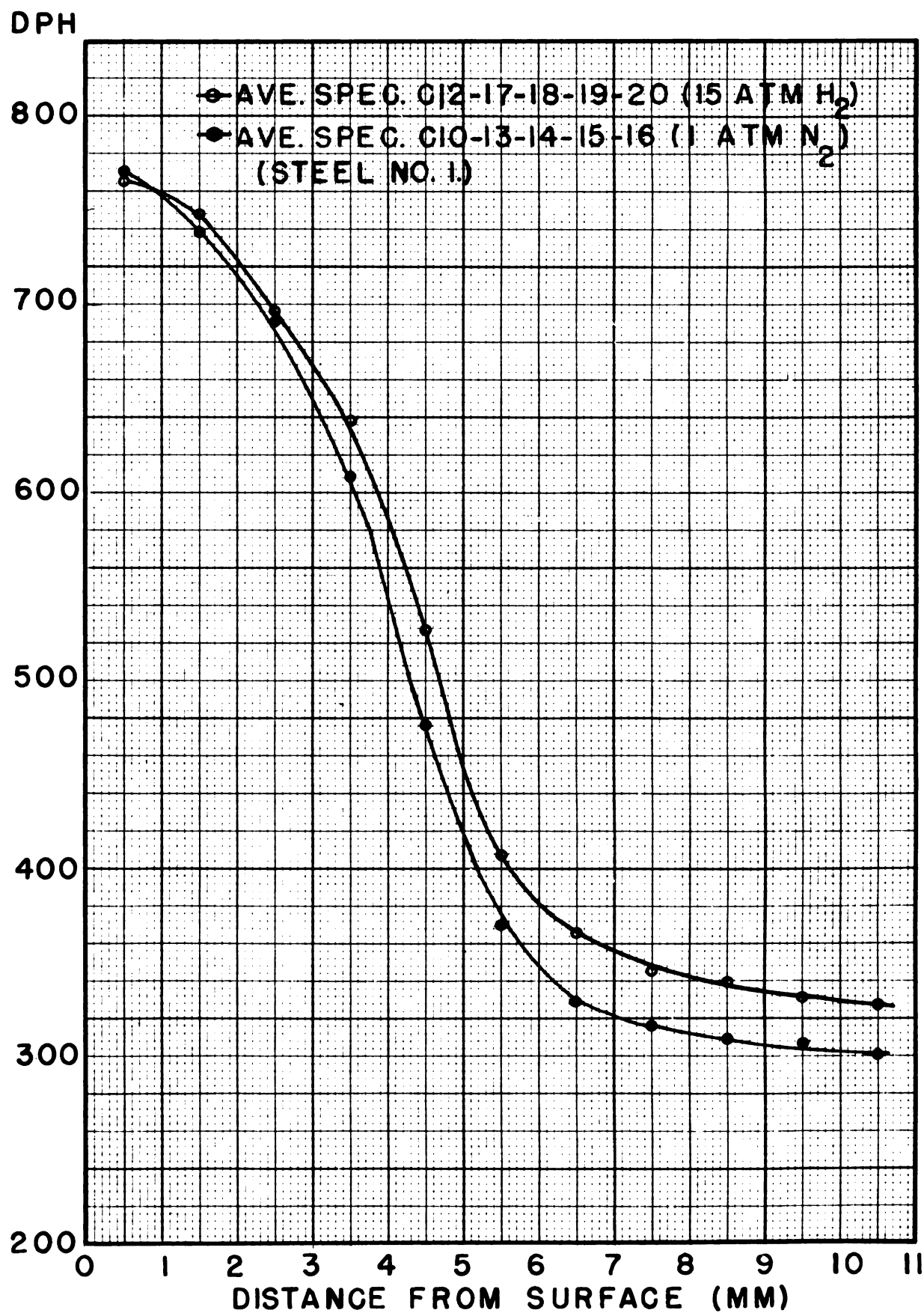| Specimen Number | Grains per Square Inch at 100X |
|---|---|
| C-10 | 70 |
| C-13 | 71 |
| C-17 | 69 |
| C-20 | 68 |
| D-1 | 69 |
| D-2 | 74 |
| E-3 | 69 |
| E-4 | 68 |

Figure 19.  Half U-curves.
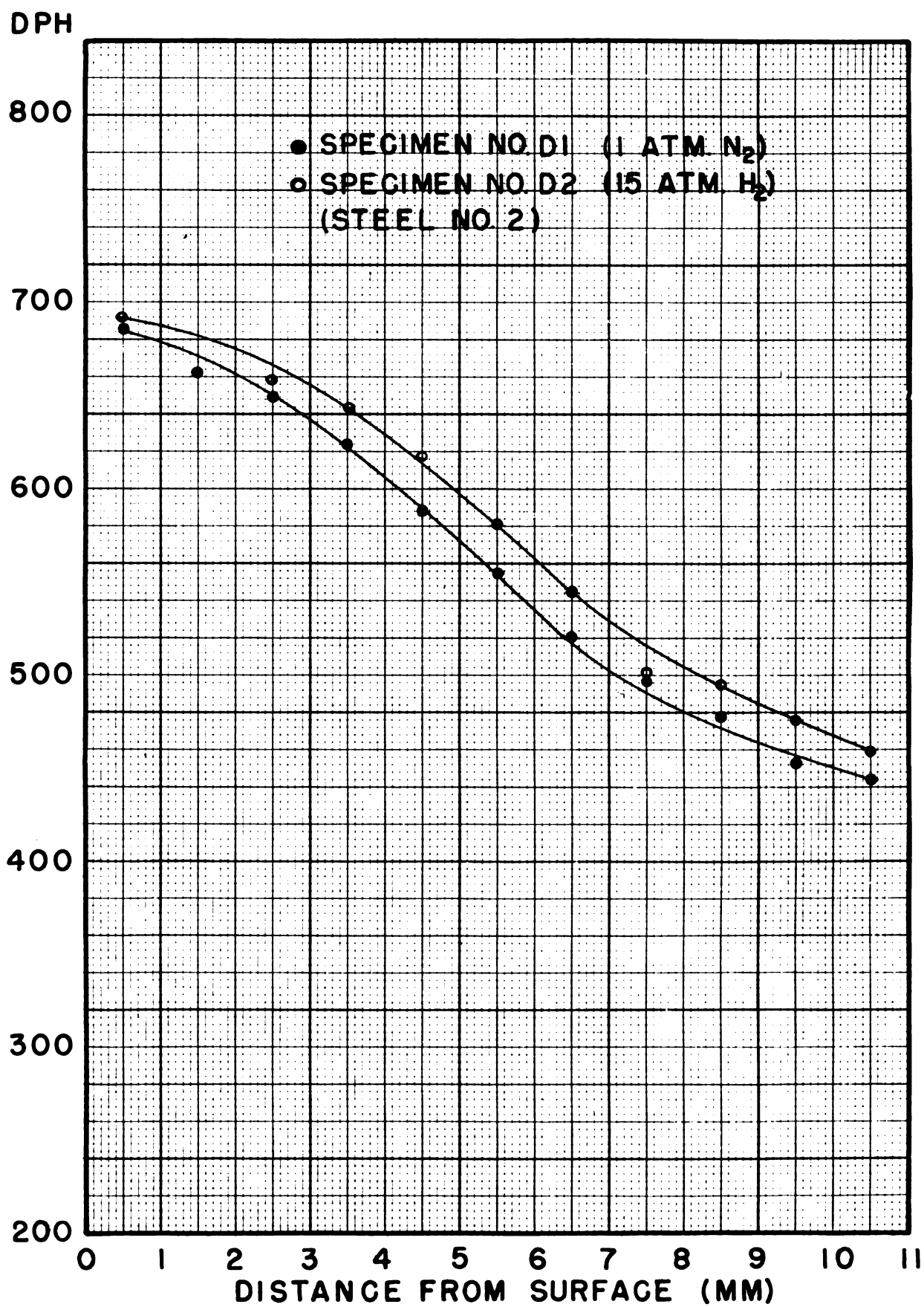
Figure 20. Half U-curves.
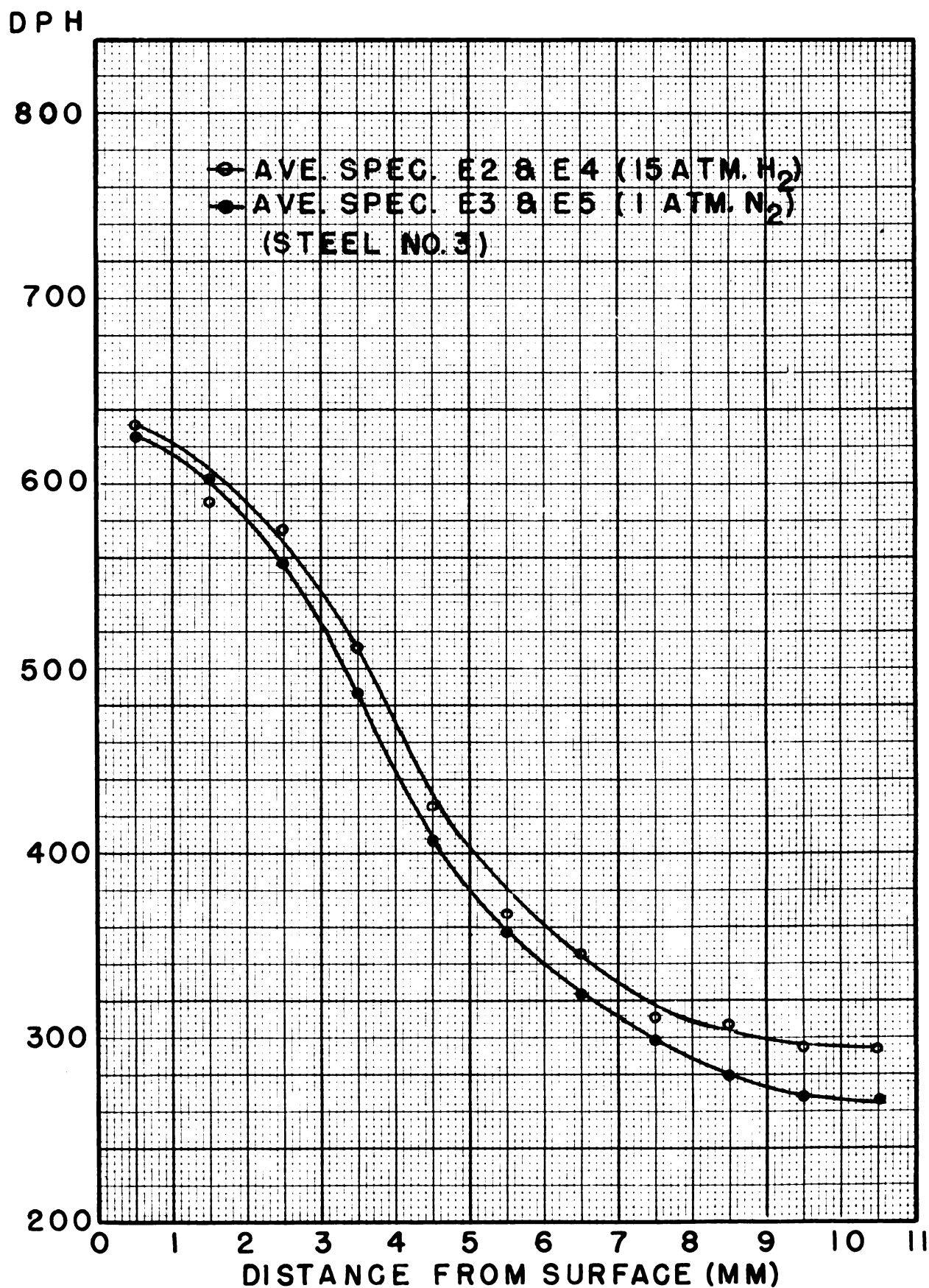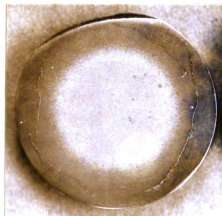
Figure 21. Half U-curves.

(a)                      (b)

Figure 22.   (a) Specimen C-10, 5 percent nital etchant, 2✕;
                  (b) Specimen C-20, 5 percent nital etchant, 2✕.



Figure 23.   Specimens C-19 and C-20, 2✕.

Figure 24.   Chip from Specimen C-19, 2X; thermocouple hole is
             visible.

Figure 25.  Specimen C-18 illustrating typical fracturing that oc-
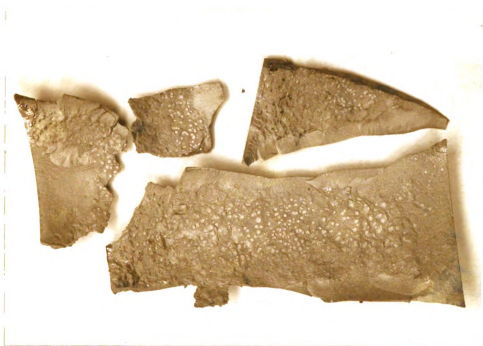curred in all hydrogen-treated specimens.

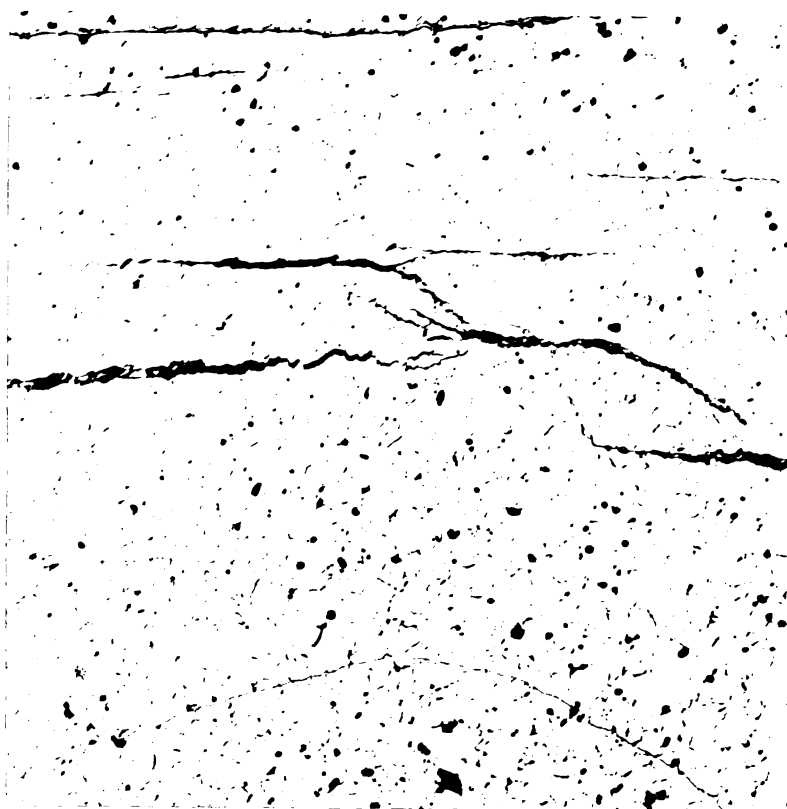Figure 26. Chips from Specimen C-18.

Figure 27.  View of microcracking in hydrogen-treated Specimen
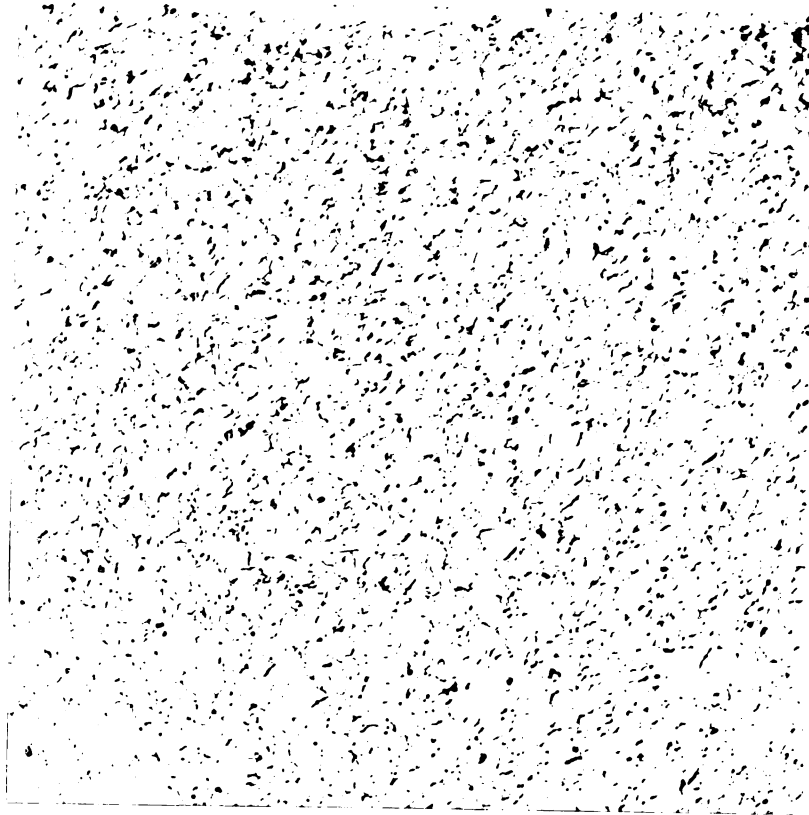E-4, picral etchant, 100X.

Figure 28.   Photomicrograph of Specimen C-10, picral etchant, 100X.
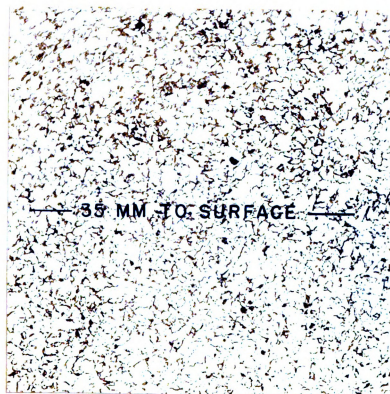
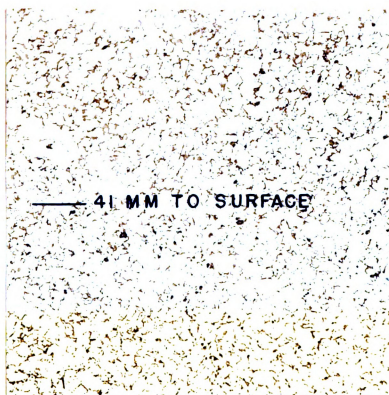Figure 29.  Specimen C-13, picral etchant, 100X.

Figure 30. Specimen C-17, picral etchant, 100X.

Figure 31. Specimen C-20, picral etchant, 100X.

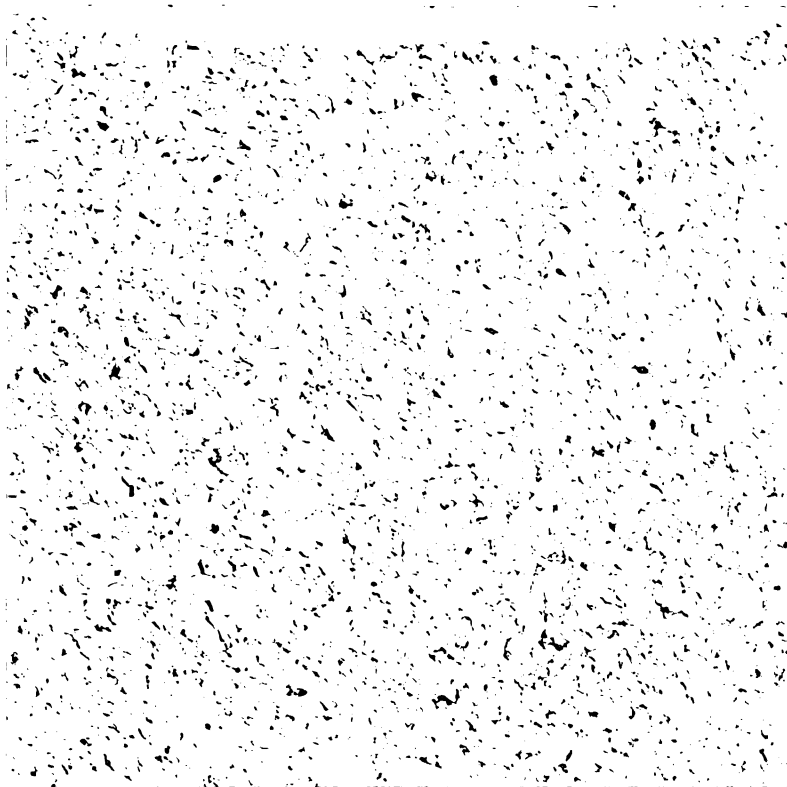Figure 32. Specimen D-1, picral etchant, 100X.

Figure 33.　Specimen D-2, picral etchant, 100X.

Figure 34.  Specimen E-3, picral etchant, 100X.

Figure 35. Specimen E-4, picral etchant, 100X.

## SUMMARY AND CONCLUSIONS

It can be clearly seen from the half U-curves shown in Figures 19, 20, and 21 that hydrogen has an effect on hardenability. However, the effect illustrated here appears to be much less than that found by Houdremont and Heller (59).

In this earlier work by Houdremont and Heller, nothing was said about specimen cracking. This indicates that the hydrogen content of the specimens was low. The specimens were heated in wet hydrogen gas held at 1 atmosphere. Thus, the greatest possible hydrogen content of the specimens would be on the order of 5 milliliters per 100 grams of steel. The results of similar hydrogen contents are shown in Figure 12 of this work. The difference is so small as to be inconclusive. Thus, the effect of a small amount of hydrogen found in this work does not agree with that found by Houdremont.

Houdremont illustrated the effect of hydrogen by fracturing the quenched specimens. His results are shown in Figure 5 of this report.

It was difficult to fracture the specimens examined in this work on account of cracking. However, the two specimens shown

in Figure 22 were polished and etched with 5 percent nital to show the extent of hardening. Even though these specimens exhibit a definite difference from hardness examinations (see Tables IV and XIII), this difference is not obvious from the etched specimens.

Upon examination of Figures 29 and 30, illustrating Specimens 13 (control) and C-17 (hydrogen-treated), it can be seen that it was necessary to go deeper into specimen C-17 to find sufficient pearlite to determine the grain size. This illustrates that the effect of hydrogen was to produce more martensite, not mere higher hardness.

The conclusions of this study are as follows:

1. Hydrogen in amounts on the order of 15 milliliters per 100 grams has a small but definite effect on the hardenability of steel.

2. The increase in hardenability, brought about by hydrogen content, is negligible in commercial heat-treating practice, as the hydrogen content of steel is ordinarily very low.

3. Cathodic charging will not furnish enough hydrogen to measurably affect hardenability.

4. The hardenability increase brought about by hydrogen appears not to change with carbon content (as in the case of boron).

5. Specimens containing hydrogen and martensite continue to crack for several hours after quenching.

6. Flakes, large enough to distinguish as such, require a period of time to form.

7. It appears that hydrogen has no effect on the austenitic grain size. At least this was the case in this work.

# LITERATURE CITED

1.  K. C. Barraclough, "The Significance of Hydrogen in Steel Man-ufacture," Murex Limited Review, vol. I, p. 320 (1954).

2.  Marion H. Armbruster, "The Solubility of Hydrogen at Low Pressure in Iron, Nickel and Certain Steels at 400 to 600 °C.," Journal, American Chemical Society, vol. 65, p. 1043 (1943).

3.  A. Sieverts, "Die Löslichkeit von Wasserstoff in Kupfer, Eisen und Nickel" (in German), Zietschrift Fuer Physikalische Chemie, vol. 77, pp. 598-606, Leipzig (1911).

4.  E. Martin, "The Occlusion of Hydrogen and Nitrogen by Pure Iron and Some Other Metals," Metals and Alloys, vol. I, pp. 831-835, New York (1930).

5.  G. A. Moore and D. P. Smith, "Occlusion and Evolution of Hydrogen by Pure Iron," Transactions, American Institute of Mining and Metallurgical Engineers, vol. 135, pp. 225-295, New York (1939).

6.  K. Iwase' and M. Fukusima, "Absorption of Hydrogen by Metals and Some Iron Alloys," Nippon Kinzoku Gakkai-Si, vol. I, p. 151 (1937).

7.  K. Iwase, "Occlusions of Gases by Metals in Solid and Liquid States," Science Reports, Tohoku Imperial University, vol. 15, p. 531 (1936).

8.  A. Sieverts, "Zur Kenntnis der Okklusion und Diffusion von Gasen durch Metalle," Zeitschrift Fur Physikalische Chemie (in German), vol. 60, pp. 129-201, Leipzig (1907).

9.  A. Sieverts und Hagenacker, "Uber die Absorption dis Was-serstuffs durch metallischer Nickel," Berichte Der Deutschen Chemischen Gesellschaft, vol. 42, pp. 338-347, Berlin (1909).

10. Carl A. Zapffe, "Iron Hydrogen," American Society for Metals Handbook, p. 1208, Cleveland, Ohio (1948).

11. R. C. Ray and R. B. N. Sahar, "Hydrides of Iron," Journal, Indian Chemical Society, vol. 23, p. 67 (1946).

12. J. H. Simons and W. R. Ham, "The Diffusion of Gases Through Metals from a Chemical Point of View," Journal of Chemical Physics, vol. 7, p. 899 (1939).

13. J. H. Andrew, A. K. Base, H. Lee, and A. G. Quanel, Journal of the Iron & Steel Institute, vol. 146, p. 181 (1942).

14. Donald P. Smith, Hydrogen in Metals, The University of Chicago Press, Chicago, Illinois, p. 32 (1948).

15. J. D. Hobsen and C. Sykes, "Effect of Hydrogen on the Properties of Low Alloy Steels," Journal of the Iron and Steel Institute, vol. 169, pp. 209-220 (1951).

16. G. Hagg, "Eigenschaften der Phasen von Ubergangselementen in binaren Systemen mit Bor, Kohlenstoff und Stickstoff," Zeitschrift fur Physikalische Chemie (in German), vol. 6B, pp. 221-232, Leipzig (1929).

17. F. Seitz, The Physics of Metals, p. 38, McGraw-Hill Book Co., New York (1943).

18. M. A. Grossman, Elements of Hardenability, American Society for Metals, Cleveland, Ohio (1952).

19. R. A. Grange and T. M Garvey, "Factors Affecting the Hardenability of Boron Treated Steels," Transactions, American Society for Metals, vol. 37, p. 136 (1946).

20. M. A. Grossman, Elements of Hardenability, American Society for Metals, Cleveland, Ohio, p. 138 (1952).

21. Ibid., p. 138.

22. W. Tofaute and H. Schottky, "Etsatz von Nickel in Austenitischen Chrom-Nickel-Stählen durch Stickstoff," Archive fur das Eisenhuettenwesen, vol. 14, p. 71 (1940).

23. M. A. Grossman, Elements of Hardenability, American Society for Metals, Cleveland, Ohio, p. 150 (1952).

24.   E. Houdremont and P. A. Heller, "Wasserstuff als Legierungs-
      element bei Stahl und Gusseisen," Stahl und Eisen, vol. 61, p.
      756 (1941).

25.   E. Houdremont, Handbuch der Sonderstahlkunde, Springer, Berlin
      (1943).

26.   C. L. M. Cottrell, "Effect of Hydrogen on the Continuous-Cooling
      Transformation Diagram for a Manganese-Molybdenum Steel,"
      Journal of the Iron and Steel Institute, vol. 176, pp. 273-282,
      London (1954).

27.   M. H. Armbruster, "The Solubility of Hydrogen at Low Pres-
      sure in Iron, Nickel and Certain Steels at 400 to 600°C.,"
      Journal, American Chemical Society, vol. 65, p. 1043 (1943).

28.   K. C. Barraclough, "The Significance of Hydrogen in Steel
      Manufacture," Murex Limited Review, vol. I, no. 13 (1954).

29.   D. J. Carney, J. Chipman, and Grant, "An Introduction to Gases
      in Steel," Electric Furnace Steel Proceedings, American Inst.
      of Mining & Met. Engrs., vol. 6, p. 34 (1948).

30.   M. W. Mallett, "The Water-Gas Reaction Applied to Welding-
      Arc Atmospheres," Welding Journal, Research Supplement, vol.
      25, pp. 396s-399s (1946).

31.   C. E. Sims, "Behavior of Gases in Solid Iron and Steel,"
      Gases in Metals, American Society for Metals, p. 148, Cleve-
      land, Ohio (1953).

32.   D. P. Smith, "Fundamental Metallurgical and Thermodynamic
      Principles of Gas-Metal Behavior," Gases in Metals, American
      Society for Metals, Cleveland, Ohio, p. 1 (1953).

33.   W. F. Giangue, "The Entropy of Hydrogen and the Third Law
      of Thermodynamics:   The Free Energy and Dissociation of
      Hydrogen," Journal, American Chemical Society, vol. 52, p.
      4816 (1930).

34.   R. M. Barrer, Diffusion in and Through Solids, Cambridge
      University Press, p. 224 (1951).

35. F. Seitz, The Physics of Metals, McGraw-Hill Book Co., Inc., New York, p. 200 (1943).

36. Donald P. Smith, Hydrogen in Metals, The University of Chicago Press, Chicago, Ill., pp. 57-58 (1948).

37. Ibid., p. 58.

38. W. Geller and T. Sun, "Einfluss von Legierungszusätzen auf die Wasserstoffdiffusion im Eisen und Beitragzum System Eisen Wasserstoff," Archive fur das Eisenhuttenwesen, vol. 21, p. 423 (1950).

39. P. L. Chang, and D. G. Bennett, "Diffusion of Hydrogen in Iron and Iron Alloys at Elevated Temperatures," Journal of the Iron & Steel Institute, vol. 170, pp. 205-213, London (1951).

40. J. B. Seabrook, N. J. Grant, and D. Carney, "Hydrogen Embrittlement of S.A.E. 1020 Steel," Transactions, American Institute of Mining & Met. Engrs., vol. 188, p. 1317.

41. W. A. Bell, "The Embrittlement of Steel by Hydrogen," Product Engineering, March, 1955, p. 192.

42. C. E. Sims, G. A. Moore, and D. W. Williams, "The Effect of Hydrogen on the Ductility of Cast Steels," Transactions, American Institute of Mining & Metallurgical Engineers, vol. 176, p. 306 (1948).

43. Ibid., p. 307.

44. J. D. Hobson and J. Hewitt, "The Effect of Hydrogen on the Tensile Properties of Steel," Journal of the Iron and Steel Institute, vol. 173, pp. 131-140, London (1953).

45. Ibid., p. 139.

46. S. A. Henes, "Arc Welding of Alloy Steels," The Welding Journal, vol. 23, p. 43, Research Supplement (1944).

47. C. B. Voldrich, "Cold Cracking in the Heat Affected Zone," The Welding Journal, vol. 26, Research Supplement (1947), pp. 153-169.

48. M. W. Mallett and Rieppel, "Arc Atmospheres and Underbead Cracking," The Welding Journal, Vol. 25, 1946, Research Supplement, p. 748.

49. C. Derge and E. E. Duncan, "Thermal Segregation: A Mechanism for the Segregation of Hydrogen in Steel," Journal of Metals, American Institute of Mining & Metallurgical Engineers, June, 1950, p. 884.

50. C. E. Sims, "Behavior of Gases in Solid Iron and Steels," Gases in Metals, American Society for Metals, Cleveland, Ohio (1953), p. 168.

51. D. J. Carney, J. Chipman, and N. J. Grant, "An Introduction to Gases in Steel," Electric Furnace Steel Proceedings, American Institute of Mining & Metallurgical Engineers, vol. 6, p. 34 (1948).

52. Sims, op. cit., p. 171.

53. L. M. Cottrell, "Effect of Hydrogen on the Continuous-Cooling Transformation Diagram for a Manganese-Molybdenum Steel," Journal of the Iron and Steel Institute, vol. 176, pp. 273-282 (1954).

54. Ibid., p. 282.

55. E. Houdremont and P. A. Heller, "Wasserstuff als Legierungselement bei Stahl und Gusseisen," Stahl und Eisen, vol. 61, p. 756 (1941).

56. E. Houdremont, Handbuch der Sondenstahlkunde, Springer, Berlin (1943).

57. M. A. Grossmann, Elements of Hardenability, American Society for Metals, Cleveland, Ohio, pp. 7-8 (1952).

58. J. D. Hobson and C. Sykes, "The Effect of Hydrogen on the Properties of Low Alloy Steel," Journal of the Iron & Steel Institute, vol. 169, p. 214 (1951).

59. E. Houdremont and P. A. Heller, "Wasserstuff als Leurungselement bei Stahl und Eisen," Stahl und Eisen, vol. 61, p. 756 (1941).

## Date Due

| | | | |
|---|---|---|---|
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |

Demco-293