THE TEMPERING OF PLAIN CARBON STEELS

By

STEWART GAILEY FLETCHER
B. S., Carnegie Institute of Technology
1938

Submitted in Partial Fulfillment of the
Requirements for the Degree of
DOCTOR OF SCIENCE
from the
Massachusetts Institute of Technology
1943

Signature Redacted
Signature Redacted
Signature Redacted

Department of Metallurgy
January 11, 1943
DISCLAIMER NOTICE

Due to the condition of the original material, there are unavoidable flaws in this reproduction. We have made every effort possible to provide you with the best copy available.

Thank you.

Despite pagination irregularities, this is the most complete copy available.

No page numbered 138
Metall.
Thesis
1943
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Chapter Number</th>
<th>Page Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>List of Illustrations</td>
<td>ii</td>
</tr>
<tr>
<td>Acknowledgments</td>
<td>vii</td>
</tr>
<tr>
<td>I. Introduction</td>
<td>1</td>
</tr>
<tr>
<td>II. Summary</td>
<td>3</td>
</tr>
<tr>
<td>III. Previous Work</td>
<td>6</td>
</tr>
<tr>
<td>Constituents</td>
<td></td>
</tr>
<tr>
<td>A. Martensite</td>
<td>6</td>
</tr>
<tr>
<td>B. Retained Austenite</td>
<td>9</td>
</tr>
<tr>
<td>C. Cementite</td>
<td>11</td>
</tr>
<tr>
<td>Changes in Properties on Tempering</td>
<td></td>
</tr>
<tr>
<td>A. Mechanical Properties</td>
<td>13</td>
</tr>
<tr>
<td>B. Solubility in Acids</td>
<td>18</td>
</tr>
<tr>
<td>C. Heat Effects</td>
<td>20</td>
</tr>
<tr>
<td>D. Electrical Resistivity</td>
<td>22</td>
</tr>
<tr>
<td>E. Magnetization</td>
<td>25</td>
</tr>
<tr>
<td>F. Volume Changes and Dilatation</td>
<td>29</td>
</tr>
<tr>
<td>G. X-ray Diffraction Studies</td>
<td>32</td>
</tr>
<tr>
<td>Summary</td>
<td>37</td>
</tr>
<tr>
<td>Chapter Number</td>
<td>Page Number</td>
</tr>
<tr>
<td>----------------</td>
<td>-------------</td>
</tr>
<tr>
<td>IV.</td>
<td>40</td>
</tr>
<tr>
<td>A. Production of High Purity Iron-Carbon Alloys</td>
<td>40</td>
</tr>
<tr>
<td>B. Commercial Alloys</td>
<td>49</td>
</tr>
<tr>
<td>C. Magnetic and Dilatometric Methods</td>
<td>49</td>
</tr>
<tr>
<td>D. X-ray Diffraction Methods</td>
<td>52</td>
</tr>
<tr>
<td>E. Direct Specific Volume Measurements</td>
<td>61</td>
</tr>
<tr>
<td>V. Plan of Experimental Work</td>
<td>65</td>
</tr>
<tr>
<td>VI. Experimental Results</td>
<td>66</td>
</tr>
<tr>
<td>Retained Austenite</td>
<td>66</td>
</tr>
<tr>
<td>Parameter Measurements</td>
<td>69</td>
</tr>
<tr>
<td>Tempering Results</td>
<td>72</td>
</tr>
<tr>
<td>A. Magnetic-Dilatometric Results</td>
<td>123</td>
</tr>
<tr>
<td>B. X-ray Work</td>
<td>125</td>
</tr>
<tr>
<td>C. Hardness Results</td>
<td>129</td>
</tr>
<tr>
<td>VII. Conclusions</td>
<td>131</td>
</tr>
<tr>
<td>VIII. Suggestions for Further Work</td>
<td>133</td>
</tr>
<tr>
<td>Bibliography</td>
<td>139</td>
</tr>
<tr>
<td>Appendix I - Calibration of Magnet</td>
<td>143</td>
</tr>
<tr>
<td>Appendix II - Calculation of Lattice Parameters</td>
<td>146</td>
</tr>
<tr>
<td>Appendix III - Errors in Parameter Determinations</td>
<td>148</td>
</tr>
<tr>
<td>Appendix IV - Errors in Retained Austenite</td>
<td>150</td>
</tr>
<tr>
<td>Appendix V - Miscellaneous Data on Alloys and Steels Used</td>
<td>151</td>
</tr>
<tr>
<td>Abstract</td>
<td>1-4</td>
</tr>
</tbody>
</table>
# LIST OF ILLUSTRATIONS

<table>
<thead>
<tr>
<th>Figure Number</th>
<th>Description</th>
<th>Page Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Effect of Carbon Content (Weight Per Cent) on Parameters of Austenite and Martensite</td>
<td>8</td>
</tr>
<tr>
<td>2</td>
<td>Effect of Tempering Temperatures from Esser and Cornelius</td>
<td>15</td>
</tr>
<tr>
<td>3</td>
<td>Effect of Tempering Temperatures from Luerssen and Greene</td>
<td>17</td>
</tr>
<tr>
<td>4</td>
<td>Solubility in Acids, Curves from Heyn and Bauer</td>
<td>19</td>
</tr>
<tr>
<td>5</td>
<td>Inverse-rate Heating Curves from Scott and Movius</td>
<td>21</td>
</tr>
<tr>
<td>6</td>
<td>Effect of Tempering Temperature at Temperature on Electrical Resistivity, Enlund</td>
<td>24</td>
</tr>
<tr>
<td>7</td>
<td>Effect of Tempering Temperature at Room Temperature on Electrical Resistivity, Enlund</td>
<td>24</td>
</tr>
<tr>
<td>8</td>
<td>Magnetization Curve from Sanford and Ellinger</td>
<td>27</td>
</tr>
<tr>
<td>9</td>
<td>Dilatation Curves Drawn by Maurer</td>
<td>30</td>
</tr>
<tr>
<td>10</td>
<td>Dilatation Curve from Hanemann and Traeger</td>
<td>30</td>
</tr>
<tr>
<td>11</td>
<td>Honda and Nishiyama's $\frac{\Delta a}{a}$ Curve for $\beta$-Martensite vs. Carbon Content</td>
<td>35</td>
</tr>
<tr>
<td>Figure Number</td>
<td>Description</td>
<td>Page Number</td>
</tr>
<tr>
<td>---------------</td>
<td>-----------------------------------------------------------------------------</td>
<td>-------------</td>
</tr>
<tr>
<td>12</td>
<td>Honda and Nishiyama's $\frac{\Delta a}{a}$ Curve for $\alpha$-Martensite</td>
<td>35</td>
</tr>
<tr>
<td></td>
<td>vs. Tempering Temperature</td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>Photograph of Induction Furnace</td>
<td>41</td>
</tr>
<tr>
<td>14</td>
<td>Drawing of Ingot Molds</td>
<td>45</td>
</tr>
<tr>
<td>15</td>
<td>Photograph of X-ray Specimen Holders</td>
<td>58</td>
</tr>
<tr>
<td>16</td>
<td>Effect of Carbon Content on Austenite and Martensite Parameters</td>
<td>71</td>
</tr>
<tr>
<td>17</td>
<td>Magnetization Curves for Steel D</td>
<td>74</td>
</tr>
<tr>
<td>18</td>
<td>Magnetization Curves for Steel C</td>
<td>76</td>
</tr>
<tr>
<td>19</td>
<td>Effect of Various Applied Fields on Magnetization-Time Curves for Tempering</td>
<td>77</td>
</tr>
<tr>
<td></td>
<td>of Steel C at 450° F.</td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>Standard Magneto-Dilatometer Tempering Curves for Steel B</td>
<td>79</td>
</tr>
<tr>
<td>21</td>
<td>Standard Magneto-Dilatometer Tempering Curves for Alloy 9</td>
<td>80</td>
</tr>
<tr>
<td>22</td>
<td>Heating Curves of Steel B at Various Applied Fields</td>
<td>81</td>
</tr>
<tr>
<td>23</td>
<td>Steel B, Heated to and Cooled from Various Temperatures</td>
<td>85</td>
</tr>
<tr>
<td>24</td>
<td>Magnetization and Dilatation Curves for Steel B, Heating Interrupted</td>
<td>87</td>
</tr>
<tr>
<td>25</td>
<td>Steel B, Effect of Time of Tempering at 200° F.</td>
<td>88</td>
</tr>
<tr>
<td>26</td>
<td>Steel B, Effect of Time of Tempering at 500° F.</td>
<td>90</td>
</tr>
<tr>
<td>Figure Number</td>
<td>Effect of Time of Tempering at 450°F, Steel B</td>
<td>Page Number</td>
</tr>
<tr>
<td>---------------</td>
<td>---------------------------------------------</td>
<td>-------------</td>
</tr>
<tr>
<td>27</td>
<td></td>
<td>91</td>
</tr>
</tbody>
</table>
| 28            | Effect of Time of Tempering at Room Tempera-
|               | ture, Steel C                              | 93          |
| 29            | Effect of Time of Tempering on Specific Vol-
|               | ume, Steel D                               | 94          |
| 30            | Effect of Time of Tempering at 212°F, Steel
|               | C                                         | 95          |
| 31            | Effect of Time of Tempering at 450°F on    |
|               | Steel C                                   | 103         |
| 32            | Effect of Time of Tempering at 500°F on    |
|               | Steel B                                   | 104         |
| 33            | Cooling Curves from 450°F, Steel B         | 109         |
| 34            | Effect of Time of Tempering at 650°F on    |
|               | Steel C                                   | 111a        |
| 35            | Effect of Time of Tempering at 500°F on    |
|               | Steel C                                   | 114         |
| 36            | Standard Magneto-Dilatometer Tempering Cur-
|               | ves, Alloy 4                               | 116         |
| 37            | Standard Magneto-Dilatometer Tempering Cur-
|               | ves, Steel C                              | 117         |
| 38            | Standard Magneto-Dilatometer Tempering Cur-
|               | ves, Steel D                              | 118         |
Figure 39
Standard Magneto-Dilatometer Tempering Curves, Alloy 4

Page Number 120

Figure 40
Standard Magneto-Dilatometer Tempering Curves, Alloy 9

Page Number 121

Figure 41
Standard Magneto-Dilatometer Tempering Curves, Steel B

Page Number 122

Figure 42
Microphotometer Traces of Steel C at 212° F.

Page Number 124

Figure 43
Microphotometer Traces of Steel D at 212° F.

Page Number 124

Figure 44
Microphotometer Traces of Steel C at 300° F.

Page Number 124

Figure 45
Effect of Tempering Time on Hardness of Steels C and D

Page Number 126

Table I
Typical Analysis of Electrolytic Iron

Page Number 45

Table II
Analysis of Cabot Spheron, Grade 6

Page Number 45

Table III
Summary of Experimental Heats and Analyses

Page Number 47

Table IV
Commercial Steels Used, Sources and Analyses

Page Number 50

Table V
Possible X-ray Lines

Page Number 55

Table VI
Results of Retained Austenite Determinations

Page Number 68

Table VII
Parameter Measurements

Page Number 70

Table VIII
First Stage Decomposition Calculations
ACKNOWLEDGMENTS

The writer wishes to express his appreciation to:

Professor Morris Cohen, under whose direction this research was carried out, for his continual interest, advice and helpful suggestions;

Professor J. T. Norton, for use of the X-ray equipment;

Professor John Chipman, for use of the Induction Furnace Laboratory;

Dr. A. W. Schneble, Jr., and Mr. T. B. Winkler, for their assistance in making the high purity iron-carbon alloys;

Mr. N. J. Grant, for forging the high purity ingots into bars;

Mr. Dara P. Antia, for his help in much of the X-ray work.
I. INTRODUCTION

One of the most important materials in the present industrial era, without which our mass production industries would never have developed, is the familiar group of alloys classified as tool steels. Of this large class of steels the most widely used are the plain carbon variety; that is, they contain no alloying elements other than those necessarily employed in steel manufacture except for 0.5 to 1.5 per cent carbon.

In the preparation of a tool made of this steel it is necessary to harden by a heat treatment. This results in the formation of an extremely hard constituent known as martensite. It is formed in plain carbon steels only on very rapid cooling (a water quench is required for any except very small pieces) from a temperature high enough that prior to quenching the steel consists principally of the face-centered cubic phase, known as austenite. Since martensite after quenching occupies more volume than the austenite from which it formed, and is not plastic enough to adjust itself uniformly to this condition, very great stresses are introduced into the steel. Unless prompt steps are taken after quenching to bring about the relief of these stresses, incipient cracks may form in the tool or die, and may readily culminate in premature failure. In order to relieve the quenching and transformation stresses and to make the brittle martensite tougher and more resistant to cracking, a quenched tool or die is always reheated to a
comparatively low temperature immediately after quenching. This re-
heating, called tempering, results in distinct changes (1) in the
condition of the martensite and (2) in the stresses resulting from the
quench and the hardening transformation.

The presence of some untransformed austenite, which in these steels
is not stable at room temperature, constitutes a second source of in-
stability in the tool. If even more toughness is required and maximum
hardness is not important, the quenched steel may be tempered at higher
temperatures, which bring about not only the changes in condition of
the martensite, but also causes the retained austenite to decompose.

A great amount of work has been carried out by many investigators
with the intention of determining the progress and mechanism of this
tempering process, and many of the resultant theories proposed are not
mutually consistent. Therefore, considerable controversy about the
mechanisms of tempering still exists.

This thesis research is undertaken in an attempt to clarify many
of the controversial aspects involved in the interpretation of the
tempering process as applied to plain carbon tool steels, and to pre-
sent a more complete picture of the details of the changes occurring
in such steels when tempered.
II. SUMMARY

The tempering of plain carbon steels was studied by means of magnetic and dilatometric measurements, using both isothermal and continuous heating and cooling methods, and by X-ray diffraction and specific volume determinations on specimens tempered at various times and temperatures.

These studies showed that:

(1) The changes on tempering commercial carbon steels were found to be almost identical with the changes in high purity iron carbon alloys, both with respect to temperature and to rate.

(2) Tempering of plain carbon steel may be divided into four steps. These steps were found to take place as follows:

(a) First Stage, 95 - 175° C (200 - 350° F); results in marked contraction, loss in tetragonality of martensite, a slight decrease in magnetization.

(b) Stress Relief, 150 - 230° C (300 - 450° F); produces only an increase in magnetization at low fields. Other properties insensitive.

(c) Second Stage, 230 - 290° C (450 - 550° F); results in expansion, a marked increase in magnetization, and disappearance of austenite lines.

(d) Third Stage, 260 - 370° C (500 - 700° F); causes a large contraction and a great decrease in magnetization.
(3) The First Stage of tempering is associated with the partial decomposition of martensite, the end product being an ill-defined "cubic" structure which has undergone only about one-fourth the total contraction required for complete decomposition of martensite, and therefore must contain much of the carbon still in solution. Zones of sub-precipitation of higher carbon content than average may account for the dark etching and poorly defined diffraction lines encountered.

(4) The Second Stage of tempering is merely a decomposition of the retained austenite. However, the decomposition product is not a ferrite-cementite aggregate, but a structure similar to that produced from the martensite during its initial decomposition in the first stage. Cementite as a discrete phase is not yet present, nor is there any evidence of a distinct compound containing less carbon.

(5) The Third Stage of tempering results in the development of cementite as a distinct phase by means of a gradual accumulation of carbon atoms in the originally poorly developed "precipitate". The "precipitate", which grows from the original martensite and austenite decomposition products, at first contains little carbon. Increasing time and temperature cause its enrichment in carbon and its ultimate development into cementite. This process can be followed by means of observing the progressive decrease in temperature and sharpening of the cementite Curie point.

(6) Above 370° C (700° F), ferrite and cementite are the two existing phases in tempered carbon steels.

(7) Evidence is obtained to indicate that the operation of the first stage of tempering produces an increase in hardness, while stress-relief has the reverse effect.
In order better to interpret the data obtained, it was necessary to know exactly the amount of austenite present. A positive technique of obtaining this figure by specific volume measurements was developed. This method is applicable only on steels consisting of the two phases austenite and martensite. The parameters of austenite and martensite are measured by means of X-ray diffraction, and the specific volumes of the two phases calculated from the parameters and atomic weights. These calculated figures, when compared with the actual measured specific volume, give the ratio of the phases, from which the per cent austenite may be produced.
III. PREVIOUS WORK

Before it is possible to study the changes in structure within a piece of hardened plain carbon tool steel when it is tempered, it is first necessary to determine the nature of the structure resulting from the quenching operation, i.e., the condition of the steel immediately prior to tempering.

The microconstituents of a fully hardened carbon steel at room temperature just after quenching are martensite, retained austenite, and in some cases some undissolved cementite.

Constituents

A. Martensite

Microscopically, martensite consists of a number of interlocking needles – an "acicular" structure – having definite directional relationships to the austenite lattice from which they were formed. Unless the steel has been tempered, these needles are very resistant to etching, so the untempered martensite has also come to be known as "white martensite".

Fink and Campbell, Kurdumoff and Kaminsky, Honda and Nishiyama, Ohman, and Hägg have shown conclusively that, structurally, martensite is a body-centered tetragonal solid solution of carbon in alpha iron. Since alpha iron (ferrite), under equilibrium conditions, can contain only 0.03 per cent carbon in solution at the eutectoid temperature, and less than 0.01 per cent carbon at room temper-
nature, it is evident that martensite represents a solid solution of an extreme degree of supersaturation. That this is the case is further indicated by the tetragonal rather than cubic nature of the crystal lattice of martensite, and its instability upon slight reheating.

Honda and Nishiyama, Ohman, and H"{a}gg found that not only was the crystal structure of martensite tetragonal, but the degree of tetragonality was a direct function of the carbon content, increasing with an increasing amount of carbon. Their values of lattice parameters of martensite and austenite have been plotted together, and are shown in Figure 1. Because of the good agreement between these investigators, it may well be concluded that the crystal structure of martensite has been definitely determined.

Though the crystal structure itself has been accurately reported, the exact location of the carbon atoms in relation to the iron atoms in the tetragonal lattice of martensite is still somewhat doubtful. There is little question that the carbon is present in interstitial rather than substitutional solid solution. Specific volume measurements, when correlated with the specific volumes for substitutional and interstitial solid solutions calculated from parameter measurements, compare very closely with the latter, showing that the type of solution is interstitial. Likewise, the increase of the size of the tetragonal unit cell with increasing carbon content indicates an interstitial solution, for a substitutional type would probably result in a decrease in parameter with carbon content because of the comparatively small radius of the carbon atom.
FIGURE 1. Effect of carbon content on dimensions of austenite and martensite unit cell.
The precise location of the carbon atom, however, is not so certain. The most probable position appears to be the center of the square faces of the body-centered tetragonal unit cell. This position, postulated by Seljakow, Kurdumoff, and Goodtaw7, and Honda and Nishiyama3, is the most reasonable one if the carbon is assumed to be located originally at the center of the face-centered cubes of austenite8, and the (110) plane and [111] direction of the martensite are parallel to the (111) plane and [110] direction of the austenite from which it formed9. This would place the carbon atom at the position (\(\frac{1}{2},\frac{1}{2},0\)) in the tetragonal martensite - the same as that mentioned above.

Ohman4 has pointed out that a more spacious location for the carbon atom would be that given by (\(\frac{1}{2},\frac{1}{2},0\)) in martensite. Honda and Nishiyama3 used this idea as the basis for their proposal of the existence of a body-centered cubic martensite after slight tempering of the tetragonal martensite. The observed contraction as a consequence of tempering at slightly elevated temperatures would then be attributed to the migration of carbon atoms from the position (\(\frac{1}{2},\frac{1}{2},0\)) to (\(\frac{1}{2},\frac{1}{2},0\)). This interpretation is still open to question.

B. Retained Austenite

Retained austenite - that still present in a steel after quenching - is identical with the austenite present above the Ac1 temperature, except that it is not an equilibrium constituent at room temperature, and therefore unstable.
Although it has been proved for some time that austenite is a face-centered cubic structure, it was only recently that the manner in which carbon was dissolved in austenite was definitely established. Petch\textsuperscript{47} has shown that the carbon atoms are held in solution interstitially, and are located at the centers of the austenite unit cells and at the mid-points of the edges. The positions correspond to the centers of the largest spaces between the iron atoms. This arrangement had been postulated earlier by Westgren and Phragmen\textsuperscript{3}.

The lattice parameter of austenite in quenched steels has been investigated by Westgren and Phragmen\textsuperscript{3,8}, Ohman\textsuperscript{4}, Honda and Nishiyama\textsuperscript{3}, and Hågg\textsuperscript{5}. The results of their independent investigations are in good agreement, and are plotted in Figure 1. It is seen that the parameter increases with carbon content (again an indication of interstitial solution of carbon in austenite), and is fixed for any given amount of carbon.

The isothermal transformation of austenite at temperatures below the $A_c_1$ has been studied carefully by Davenport and Bain\textsuperscript{10} in their classic work on the S-curve. More recent work by Greninger and Troiano\textsuperscript{11} has shown that the lower part of Bain's S-curve, in which austenite was represented as transforming isothermally to martensite, and which indicated that no retained austenite would be left after about three hours at $100^\circ$ C, was in error. While austenite may decompose isothermally at temperatures as low as this, the product was not martensite (martensite forming practically instantaneously on progressive cooling) and the time required was very great (over 10 days)
for a perceptible amount of transformation to take place*.

C. Cementite

In all of the work reported above, the steel had been treated in such a way that the cementite was all dissolved in austenite prior to quenching, so it was eliminated as an experimental variable. The effect, if any, of excess cementite on the character of the martensite and on the amount of the retained austenite has not yet been considered in research on carbon steels. In all probability its chief effect is that of effecting a lowering of the carbon content of the matrix, keeping carbon out of solution in the parent austenite, and thus causing the martensite and retained austenite to behave as though the steel as a whole contained less carbon.

Cementite itself has the chemical composition Fe₃C. Its crystal structure is of a complex orthorhombic type, the unit cell containing 12 iron and 4 carbon atoms and having the parameters a = 4.5144 Å, b = 5.0787 Å, and c = 6.7297 Å. It is ferromagnetic below the A₀ temperature (about 210° C [410° F]) and paramagnetic above that temperature.

As stated above, when a carbon steel is successfully quenched to room temperature for hardening, it is originally composed of a mixture of martensite, untransformed austenite, and perhaps some excess cementite (which, however, is assumed not to be present in steels discussed

---

* Ellinger and Sanford claimed that 1500 hours at 100° C (212° F) had no effect on the retained austenite.
in the following). Upon reheating the steel in order to "temper" it, the two constituents, martensite and austenite, undergo decomposition. In addition to structural changes the internal stresses which are set up by the quenching operation and by the formation of martensite are relieved. These two factors—structural alterations and stress relief—combine in varying degree to cause the distinct changes in mechanical properties and physical characteristics of steels when they are tempered.

After a piece of hardened carbon steel has been tempered at a temperature above 400°C (750°F) there is little doubt that the structure obtained consists of a very fine dispersion of cementite spheroids in a matrix of ferrite. This is easily proved both by microscopic examination and by X-ray diffraction pictures. Further heating below the Ac1 results only in an agglomeration of the cementite spheroids, accompanied by the expected softening effect. The processes by which tetragonal martensite and austenite decompose to produce this spheroidal structure, however, have not been so positively established, several different theories having been advanced by different investigators.

Many methods of attack have been employed in order to ascertain positively the mode of decomposition of martensite and the accompanying retained austenite. Among the properties studied have been the mechanical properties, thermal effects, solubility in acids, electrical resistivity, magnetization, and length and volume changes. Since the decomposition is obviously one which involves mainly a rearrangement of atoms rather than an extensive amount of diffusion, and the material
is crystalline, X-ray diffraction methods of study would be expected to give the most fundamental information for the establishment of a theory of the mechanism of tempering, but for reasons which will be taken up later, they are actually subjected to severe limitations by the very nature of the changes occurring. In spite of the difficulty of its application, however, X-ray diffraction has been widely used, and has shed a great deal of light on the mechanism of tempering.

Yet even though a great amount of data has been accumulated, much of which has been corroborated many times over, there has not been developed a clear-cut explanation of the actual physical process of tempering.

Changes in Properties on Tempering

A. Mechanical Properties

A tremendous volume of work has been done in the study of the effect of tempering the mechanical properties of plain carbon steels. Most of this work, however, has been carried out on low and medium carbon steels; i.e., those steels which are commonly used for structural and machine purposes, rather than the high carbon steels, which are used principally for cutting tools. We shall not concern ourselves here with the effect of tempering upon the low and medium carbon steels, except to say that in general, with increasing tempering temperatures after quenching, the steel becomes softer, has lower tensile and yield strengths, and higher elongation, reduction in area and impact properties.
Immediately after quenching, the hardness of a high carbon steel is somewhat lower than after the steel is permitted to "age" for a time at room temperature. Sykes and Jeffries\textsuperscript{38}, for example, found that a quenched 1.23 per cent carbon steel increased in hardness from 64.7 Rockwell C to 67.3 Rockwell C on "aging" 500 hours at room temperature. The same effect, taking place in a much shorter time and followed by a slight decrease in hardness, was encountered on tempering at 100° C (210° F). Steinberg and Subow\textsuperscript{39} reported similar results on an 0.98 per cent carbon steel. The fact that the steel is softer than would be expected as originally quenched must be assigned mainly to the retained austenite present; a hardening effect on long-time aging at room temperature is undoubtedly caused by the slow decomposition of the tetragonal martensite, for it is not likely that enough retained austenite would decompose at such low temperatures to affect the hardness materially.

The effect of temperature of tempering upon the hardness is shown very clearly in Figure 2\textsuperscript{40} for steels of various carbon contents. Some "secondary hardening" may be noticed, particularly in the higher carbon steels, at about 200 - 300° C (390 - 570° F). This effect is attributed to the decomposition of retained austenite into a harder product.

Time at temperature is generally considered to have but a secondary effect on the hardness at low tempering temperatures\textsuperscript{41}. Most of the change in hardness takes place in the first few minutes; thereafter the temperature of tempering is much more important than the time in the final value of hardness.
Abbildung 2. Härteänderungen beim Anlassen abgeschreckter Stähle.

FIGURE 2. The effect of tempering temperature on the Rockwell C hardness of a number of quenched plain carbon steels (Esser and Cornelius).
The other mechanical properties of high carbon steel tempered in the ranges in which structural changes have been observed have not been as adequately investigated as that of hardness. This is because the results of tensile tests and impact tests on steels tempered at low temperatures are apt to be very erratic because of the high internal stresses, the frequent presence of microcracks, the variation of austenitic grain size, and the inherent brittleness of martensitic structures. No reliable data have yet been reported on the tensile strength, yield strength, reduction in area and elongation for tempering at temperatures below 320° C (600° F). Tempering above that temperature results in a steady decrease in tensile strength and yield strength, and a corresponding increase in elongation and reduction in area\(^4\).\(^5\)

The impact strength of carbon tool steels has been studied with a view to determining the best tempering temperature for shock resistance. The principal impact tests employed have been the Charpy, using a V-notch; the Izod, using a keyhole notch; the unnotched Izod; and the torsion impact test. Figure 3 shows the results of three types of impact testing, as taken from work by Luerssen and Greene\(^44\) on a 1.06 per cent carbon tool steel, quenched from 790° C (1450° F). The torsion impact test showed a definite maximum corresponding to the tempering temperature of 150 - 200° C (300 - 390° F). This maximum was attributed to the relieval of stresses in the martensite accompanying the first stage of its decomposition, but prior to the decomposition of retained austenite. When the austenite decomposes a more brittle structure is obtained, at about 250° C (480° F), and the torsion impact
FIGURE 3. The effect of tempering temperature upon the impact properties of a quenched carbon tool steel (Luerssen and Greene).
value again is low. Further tempering at still higher temperatures cause the impact values to increase, as the carbides coalesce and the steel becomes more ductile. It is notable that neither the standard nor the unnotched Izod test shows the maximum in resistance to impact as indicated by the torsion impact test which corresponds to the first stage of martensite decomposition at 175°C (350°F).

B. **Solubility in Acids**

An interesting property of quenched and tempered steels that was investigated by the early researchers was the solubility in acids, particularly in dilute sulfuric acid solutions. Heyn and Bauer\textsuperscript{14} quenched a steel containing 0.95 per cent carbon, 0.35 per cent silicon and 0.17 per cent manganese, and investigated its rate of solution in 1 per cent sulfuric acid after tempering at various temperatures. Their curves, reproduced in Figure 4, show a maximum rate of solution corresponding to a tempering temperature of 400°C (750°F), culminating a gradually increasing rate of solution from tempering temperatures of 100°C (212°F) upward. Above 400°C (750°F) the rate of solution was found to decrease gradually, reaching its lowest point with a fully spheroidized steel.

Matsushita and Nagasawa\textsuperscript{21} also reported a very similar curve for the solubility of tempered 1.02 per cent carbon steel in 1 per cent sulfuric acid. A sharp maximum was found corresponding to 400°C (750°F) temper, confirming the work of Heyn and Bauer.
FIGURE 4. The rate of solution of a quenched carbon steel in 1 per cent sulfuric acid after tempering. Composition of steel: 0.95 per cent carbon, 0.35 per cent silicon, 0.17 per cent manganese. The times refer to time in solution (Heyn and Bauer^14).
It is doubtful if this data has aided markedly in interpretation of the tempering process, for the rates of solution do not seem to be directly related in any way with the actual structural changes that are known to take place. This view is supported by the fact that the temperature at which the maximum rate of solution is found does not appear as an inflection point for any of the other properties studied.

C. **Heat Effects**

The thermal changes which a hardened carbon steel undergoes during tempering were studied by Osmond as early as 1890\textsuperscript{12}, by Maurer\textsuperscript{13}, Heyn and Bauer\textsuperscript{14}, and Portevin\textsuperscript{15}. All of these early authors obtained indications of heat evolution on tempering hardened carbon steel, but in general the temperatures assigned by them to the maximum effect were somewhat higher than that which would now be expected. The curves given by them did not have prominent enough inflections, and the techniques used were not refined enough to permit very accurate observations on the tempering reactions. Scott and Movius\textsuperscript{16} produced much better inverse-rate heating curves for hardened carbon steel, and showed a pronounced evolution of heat in one containing 0.95 per cent carbon beginning at about 155° C (310° F), and reaching its maximum value at 250° F (480° F). These curves are reproduced in Figure 5. A higher carbon steel, containing a large amount of retained austenite, showed a two-stage heat effect on tempering, the first occurring at about 180° C (355° F) corresponding to the first evolution of heat noted above, and the second at 310° C (590° F). They attributed the first change in each of these cases to "simple carbide precipitation from martensite",
FIGURE 5. Inverse-rate heating curves for a hardened 0.95 per cent carbon steel. B represents the first break in the curve, M the maximum point of heat evolution, and E the end of the reaction (Scott and Movius."
and the second change in the higher carbon steel to the "completion of the change from austenite to martensite, which is more or less transformed into troostite". Similar results were obtained by Esser and Cornelius, who suggested a three-stage heat effect on tempering at progressively higher temperatures. The first represented the change from tetragonal to cubic martensite, the second corresponded to the decomposition of retained austenite into ferrite plus cementite, and the third to the change of Fe₃C from molecular to crystalline form.

All of the aforementioned experiments were concerned only with qualitative measurements. Quantitative measurements of the heat evolution on tempering have been made by Kawakami, Wever and Naeser, Stablein and Jaeger, and Esser and Bungardt. All these investigators found the heat evolved on tempering at various temperatures to vary practically linearly with carbon content, no effect being found in pure iron. The actual values reported varied considerably, but a fair average seems to be about 11 calories per gram for a eutectoid steel heated to 450°C (840°F). Perhaps the reason for the lack of better corroboration was that many of the measurements were made without considering the amount of retained austenite, which, of course, evolves considerable heat on decomposing.

D. Electrical Resistivity

The electrical resistivity of steels quenched and tempered has been used as a powerful tool in the study of tempering because of its structure sensitiveness.
Apparently the earliest work with resistance measurements was carried out by Campbell\textsuperscript{22}, but his measurements were made on specimens tempered at 100\textdegree{}C (180\textdegree{} F) intervals, and thus his curves did not indicate the various breaks later found by Enlund\textsuperscript{23}. Enlund conducted experiments on steels of varying carbon contents, and made his resistivity measurements both with continuously increasing temperatures, and at room temperature on samples tempered at progressively increasing temperatures. He showed quite clearly in both types of curves, which are reproduced in Figures 6 and 7, two principal breaks in the tempering process, both moving in the direction of decreased resistance. The first, at a temperature slightly above 100\textdegree{}C (210\textdegree{} F) he attributed to the precipitation of carbide from martensite; the second, at 260\textdegree{}C (500\textdegree{} F) to the decomposition of retained austenite. These temperatures were found to be independent of carbon content, although the magnitude of the effects were not, and both inflections were noted in steels of a carbon composition as low as 0.21 per cent.

Matsushita and Nagasawa\textsuperscript{21} produced similar curves for the resistivity of a steel containing 1.02 per cent carbon. The two distinct decreases in resistivity, however, were said by them to be caused by first, the precipitation of free carbon from martensite, and second, to the decomposition of beta-martensite. They entirely neglected the possibility of retained austenite, and their interpretations of both of these phenomena are therefore questionable.
FIGURE 6. Effect of tempering temperature upon electrical resistivity. These readings made at temperature on continuous heating. Temperature scale in degrees Centigrade. Carbon content and quenching temperature noted on each curve.

FIGURE 7. Effect of tempering temperature upon resistivity at room temperature. Specimens measured at room temperature after tempering as shown. Carbon content and tempering temperature noted on each curve (Enlund23).
E. **Magnetization**

Many magnetic studies have been carried out on tempered plain carbon steels. Barus and Strouhal in 1885 \(^{24}\) made measurements on a "quenched steel" tempered at several temperatures up to \(330^\circ\) C (625\(^{\circ}\) F). Their curve, containing only a few points, predicts a distinct maximum at a temperature somewhat above \(330^\circ\) C (625\(^{\circ}\) F). A more complete curve, again consisting of magnetization measurements made at room temperature of a steel (1.04 per cent carbon, 0.34 per cent manganese, 0.02 per cent silicon) tempered at various temperatures, is given by Scott and Movius\(^{16}\), who constructed it from the data of Burrows and Fahy\(^{25}\). It also shows a maximum at \(300 - 400^\circ\) C (570-750\(^{\circ}\) F), but again the data were too sparse and the method of measurement was apparently too insensitive to give a clear indication of the changes occurring, both of the first stage as detected by resistivity methods, and of the exact form of the rapid magnetic changes in the vicinity of the second stage (\(250 - 400^\circ\) C)(480 - 750\(^{\circ}\) F). The maximum in the magnetization curve was confirmed by Matsushita and Nagasawa\(^{21}\), who located it at \(300^\circ\) C (570\(^{\circ}\) F), and erroneously attributed this great increase to the decomposition of beta-martensite.

The work of Sanford and Ellinger\(^{26}\) at the National Bureau of Standards was carried out much more carefully, and the equipment used for measuring changes in magnetization was accordingly more sensitive than any of those used previously. In addition, it was found possible by use of their apparatus to make precise measurements of magnetization at temperature, and thus it became much easier to follow the course
of the transformations taking place. Working with a 0.75 per cent carbon, 0.52 per cent manganese, 0.12 per cent silicon steel, and using applied field strengths of 277 gilberts per centimeter (277 gauss) they found, as seen in Figure 8, (1) a pronounced increase in magnetization immediately upon beginning heating; this increase completed itself in $6\frac{1}{2}$ hours at 200° C (390° F). Continued heating resulted in a second increase in magnetization, at about 235° C (455° F). This increase was completed after only one hour's holding. At 300° C (570° F) a decrease in magnetization was obtained, again being complete within an hour. No decrease or increase in magnetization with time was observed at higher temperatures. These phenomena were interpreted by Sanford and Ellinger in this way: the first increase in magnetization (below 200° C [390° F]) was attributed to stress release in the highly stressed, freshly quenched martensite. It was conceivable, they held, that this stage was accompanied by precipitation of carbon from the solid solution, but because on cooling from this tempering treatment no $A_0$ transformation was noted, they concluded no carbide had been formed in quantities sufficient to be detected. The second increase in magnetization, at 235° C (455° F), was attributed to decomposition of the retained austenite, and was accompanied over the range of 200 to 300° C (390 - 570° F) by a progressive formation of carbide. After one hour at 300° C (570° F) they claim the formation of carbide was completed, suggesting however that it may likewise be completed at lower temperatures in a longer period of time.
Fig. 3—Typical Thermomagnetic Curve Showing Changes in Magnetization in Quenched Steel,
A—Maximum Temperature 200 Degrees Cent.
B—Maximum Temperature 235 Degrees Cent.
C—Maximum Temperature 300 Degrees Cent.

FIGURE 8. Magnetization curve obtained by Sanford and Ellinger\textsuperscript{26} at applied field of 277 gauss. Steel composition: 0.72 per cent carbon, 0.52 per cent manganese, 0.12 per cent silicon. Quenched and tempered as shown. Held $6\frac{1}{2}$ hours at 200\textdegree{} C (A), one hour at 235\textdegree{} C (B) and one hour at 300\textdegree{} C (C).
In a later work, Ellinger and Sanford investigated the effects of liquid air supercooling, aging (quenched specimens held at room temperature for two years), and tempering (quenched specimens tempered at 100°C for 1500 hours) on the magnetization-temperature curves of the same steel they used previously. They reported that the first increase in magnetization at 235°C (455°F) was appreciably affected by previous tempering, aging, and cooling in liquid air. Tempering and aging appeared to limit the first stage markedly, and cooling in liquid air also caused a less pronounced magnetization change, but was not as effective as the tempering and aging treatments. The reason given for the effect of tempering and aging was that precipitation of carbon during those treatments resulted in the presence of the more stable cubic form of martensite. No explanation was advanced for the decrease in effect caused by liquid air cooling; if such was a function of stresses in martensite, it would be expected that supercooling would cause an *increase* rather than decrease in the magnetization change.

The magnetization increase at 235°C (455°F) was markedly suppressed by aging, but was not affected by the tempering or liquid air treatments. This was attributed to the decomposition of some of the retained austenite during the prolonged aging; tempering for 1500 hours at 100°C (212°F) and cooling in liquid air were said to have no effect on the retained austenite. A progressive decrease in magnetization was observed in specimens held at 300°C (570°F); this decrease was changed appreciably both in magnitude and duration by previous aging. Little change was produced by tempering or supercooling. No explanation was advanced for this behavior.
F. Volume Changes and Dilatation

The first extensive research on volume and length changes when hardened steels are tempered was carried out by Maurer in 1908. He found that in quenched plain carbon steels of approximately eutectoid composition the specific volume (measured at 20°C) showed a decrease after tempering to temperatures up to 150°C (300°F), then an increase over the range of 150 - 250°C (300 - 570°F), and finally another decrease to about 450°C (840°F), after which it remained unchanged. In order to confirm these results, Maurer also conducted experiments with a dilatometer, making measurements of length at temperature, and on the same steel found an expansion to about 150°C (300°F), a contraction to about 200°C (390°F), a further expansion from 200 - 300°C (390 - 570°F), and another contraction from 300 - 450°C (570 - 840°F). Thereafter a uniform expansion was observed to the Ac critical point. This curve is reproduced in Figure 9.

Maurer, in attempting to interpret these curves, correctly attributed the expansion between 200 and 300°C (390 - 570°F) (increase in specific volume) to transformation of retained austenite, in 1908, and noted that it was more pronounced the higher the carbon content of the steel, and the higher the quenching temperature.

Many other researchers have noticed the same changes in specific volume. Among these may be mentioned Schulz, Heindhofer and Wright, Enlund, and Andrew and Honeyman.

The most complete and detailed dilatation study was carried out by Hanemann and Traeger. They divided the tempering-dilatation curve...
FIGURE 9. Dilatation curve drawn by Maurer in 1908\textsuperscript{13}, for a 1.2 per cent carbon steel quenched from 900° C. Temperature scale in degrees Centigrade.

FIGURE 10. Dilatation curve of a quenched 0.97 per cent carbon steel. During heating it was held 13 hours at 100° C, 7\frac{1}{2} hours at 235° C and 40 hours at 500° C (Hanemann and Traeger\textsuperscript{31}).
into three parts. The first part corresponded to the first contraction mentioned above. This contraction in a 0.97 per cent carbon steel rod 150 millimeters long and 10 millimeters in diameter, quenched from 780° C (1440° F), was effective over a range of about 95° C (200° F) to 190° C (375° F) on heating at a rate of 1° C (1.8° F) per minute. Figure 10 shows the curve they obtained for another specimen. This one was heated to 100° C (210° F) and held for 13 hours, in order for the reaction at that temperature to complete itself. It was then heated to 235° C (455° F), held for 7½ hours, heated on to 300° C (570° F), and held for 40 hours. The reactions involved were found practically to complete themselves during the times held at temperature. The first reaction (a contraction of 0.12 per cent in length at 100° C (210° F)) was attributed to the transformation of martensite to a phase called $\xi$ (zeta)-iron, dark etching, and in which elemental carbon is dissolved. The second reaction (producing a linear expansion of 0.035 per cent at 235° C (455° F)) was said to be caused by the transformation of retained austenite to zeta-iron. The third reaction, indicated by a linear contraction of 0.18 per cent in 40 hours at 300° C (570° F), was attributed to the breakdown of zeta-iron to ferrite plus cementite.

Matsushita and Nagasawa entirely missed the expansion effect during dilatation, and discussed only the contractions. In a 1.02 per cent carbon steel, they found the first contraction to occur between 100 and 170° C (210 and 340° F) and attributed it to the formation of $\beta$-martensite from $\alpha$-martensite. The second contraction (at 300 - 400° C [570 - 750° F]) was said to be caused by the formation
of cementite by the carbon atoms precipitated during the tempering of
\(\beta\)-martensite. This tempering of \(\beta\)-martensite, followed magnetically
by Matsushita and Nagasawa at 250° C (480° F), was erroneously inter-
preted; actually the increase in magnetization attributed by them to
decomposition of \(\beta\)-martensite was in reality caused by transformation
of the retained austenite. The \(\beta\)-martensite (or its equivalent) was
actually as yet unaffected.

G. X-ray Diffraction Studies

Prior to the discovery by Fink and Campbell\(^1\) in 1926 that freshly
quenched martensite was tetragonal in nature, it was believed that
martensite had a body-centered cubic structure like ferrite, but that
a high degree of lattice distortion caused the lines to be very broad.
Since Fink and Campbell's discovery, a great many investigators have
confirmed their results, and have established that the degree of tet-
ragonality of martensite (i.e., the axial ratio) increased directly
with the carbon content. These investigations were discussed earlier
in this section in more detail (pages 6 - 9).

The tempering of tetragonal martensite causes the X-ray doublet
to diffuse together and ultimately to become a single line which roughly
 corresponds to that of the ferrite equilibrium phase. However, the
exact manner in which these lines approach coincidence has never been
clearly established. Kurdjumow\(^2\) merely stated that his results on
a 1.44 per cent carbon steel quenched from 1100° C (2010° F) indicated
a rapid broadening of the martensite lines on tempering at 100° C (210° F),
resulting in a decreased axial ratio, even after only 80 minutes at 100°C (210°F). He stated that this was due to the precipitation of carbon from the lattice of the martensite; the mode and character of the precipitation were not speculated upon.

"Ohman also studied the tempering of martensite by means of X-ray photograms. He stated that his results supported those of Kurdjumow in that the decomposition of tetragonal martensite, designated by Ohman the \( \alpha' \)-phase, was a continuous progressive reaction, taking place much more rapidly at a temperature of 150°C (300°F) (15 minutes for almost complete decomposition of \( \alpha' \)) than at 105°C (220°F), where tempering for several days brought about only partial decomposition. In Ohman's words: "the decomposition of the \( \alpha' \)-phase on tempering is found to take place continuously, with a progressive decrease of the axial ratio".

It is well to emphasize here that as yet X-ray studies of the decomposition of martensite have not indicated any marked steps in the process, such as those so apparent in resistivity, dilatometric and magnetic measurements, and as evidenced by the inflection points encountered in these properties.

In an endeavor to support their theory that martensite, after completion of the first stage of tempering (about 150°C [300°F]), was now a body-centered cubic structure, with carbon still in solution (\( \alpha' \)-martensite), Honda and Nishiyama conducted some further X-ray experiments. After first establishing very good values for the variation of tetragonality of \( \alpha' \)-martensite with carbon content, they pro-
ceded to temper quenched steels of varying carbon content; then, by means of analysis of microphotometer traces of X-ray photograms of the tempered steels, they plotted a curve as shown in Figure 11. In this curve, $\Delta \frac{a}{a}$ of $\beta$-martensite, in per cent, is plotted against carbon content. According to the authors of this paper, the fact that the lattice constant $\Delta \frac{a}{a}$ increases linearly at first, then more slowly, is a proof that the body-centered cubic lattice is a solid solution of carbon in iron. It is difficult to imagine what the function $\Delta \frac{a}{a}$ measured, but it seems most likely to be the ratio of the parameter corresponding to the mean of the two martensite lines (110) and (101), or the broad line resulting therefrom after tempering, to that for pure iron.

Then, in order to account for the second stage of tempering, they tempered similar samples at higher temperatures, plotted $\Delta \frac{a}{a}$ vs. tempering temperature for each steel, and, since the curve produced (Figure 12) showed a uniform decrease in $\Delta \frac{a}{a}$ with increasing temperature, the gradual decomposition of $\beta$-martensite with increasing temperature was postulated.

In reviewing Honda's and Nishiyama's work on tempering, it is seen that they propose that tetragonal martensite (called $\kappa$-martensite by them), a true solid solution of carbon in iron, decomposes on heating at 150° C (300° F) to a cubic martensite (called $\beta$-martensite), likewise a true solid solution of carbon in iron. On tempering at temperatures upward of 150° C (300° F) the $\beta$-martensite in turn de-
FIGURE 11. Honda and Nishiyama's curve for $\Delta a/a$ of $\beta$-martensite vs. carbon content.

FIGURE 12. Honda and Nishiyama's curve for $\Delta a/a$ of $\beta$-martensite vs. tempering temperature, for a quenched 0.81 per cent carbon steel.
composes gradually to a ferrite plus carbide agglomerate. By this theory they attempted to reconcile the two-stage tempering of martensite as indicated by the resistivity, dilatation and magnetic measurements to the heretofore-thought-of one-stage process indicated by X-ray diffraction. A more critical discussion of Honda and Nishiyama's data will be presented in the section of this thesis on experimental results.

Refuting Honda's ideas as to the formation of $\beta$-martensite, and interpretation of X-ray diffraction measurements, Hagg proposed that all the phenomena could readily be explained by the assumption that cementite already is precipitated from martensite at the low tempering temperatures. He presents considerable parameter and specific volume measurement data in support of his hypotheses.

Hagg also studied the course of tempering with time at several temperatures by means of following parameter measurements of the martensite lines (101) and (110). The resultant curves indicated that tetragonal martensite is decomposed gradually; that is, carbon is given off and so the martensite gradually and uniformly becomes less tetragonal and approaches ferrite.

In all of these X-ray investigations the diffraction lines corresponding to retained austenite were also observed. However, neither the parameter of the austenite, nor the intensity of the lines, seems to change on short time heating until a tempering temperature of about 250° C (480° F) is reached, at which temperature the lines rapidly disappears. It is thus evident that until such a tempering temperature
is attained—at least within the short tempering times under which most of the investigations have been carried out (up to one hour)—no appreciable decomposition of retained austenite takes place.

**Summary**

A critical survey of the literature on the tempering of hardened plain carbon steels reveals, then, the existence of at least three irregularities in properties as the temperature of tempering is increased. These are:

1. About 1500°C (3000°F). The hardness drops very slightly, if at all, but the torsion impact values show a decided maximum. No definite break is observed in the rate of solubility in acid curve. A slight evolution of heat occurs, and the electrical resistivity decreases, while as yet no definite indication of a magnetic change is seen. The specific volume decreases, and there is a marked contraction. Microscopically the martensite becomes very dark etching compared to its character prior to heating; no change in appearance of austenite is noticed. X-ray diffraction lines of tetragonal martensite grow together and become very diffuse. All of the above-noted effects are more pronounced the higher the carbon content of the steel. It appears that this signalizes the breakdown of tetragonal martensite to some as yet indeterminate state.

2. About 2500°C (4800°F). The hardness of the hypoeutectoid steels continues to decrease somewhat, but that of the hypereutectoid steels seems to drop off at a considerably slower rate. The standard
Izod and unnotched Izod impact strengths are slightly higher, but on the other hand the torsion impact values have markedly fallen off from their maximum at 180° C (360° F). The rate of solution in acids is still increasing with temperature, no inflection points being observed. There is a distinct evolution of heat and a decrease in electrical resistivity. The magnetization curve reaches a sharp maximum, and a slight increase in specific volume and in length is observed. At this stage the austenite lines on an X-ray diffraction picture rapidly decrease in intensity with tempering time, so it is apparent that these effects are primarily the result of a decomposition of retained austenite.

(3) About 325° C (620° F). The principal changes reported here are the marked contraction and decrease in specific volume, and the rapid decrease in magnetization and electrical resistivity. These changes are accompanied by a steady lowering of hardness and of the tensile and yield strengths of the steel, and an increase in the ductility and all the impact properties. The metallographic appearance is that of a very fine dispersed structure, which etches almost uniformly dark, and in which distinct phases are extremely difficult if not impossible to distinguish. The exact character of this marked change is not known, but it is apparently connected with the completion of the decomposition of martensite and retained austenite into ferrite and cementite. Above this temperature the properties all change uniformly until the Ac₁ critical point is reached.
Thus we have discerned three stages of physical and structural changes during the tempering of a hardened carbon steel. The first stage, around 1500°C (3000°F) is associated with a change of the martensite; the second stage, at around 2500°C (4800°F) is associated with a decomposition of the retained austenite; and the third stage at about 3250°C (6200°F) with the formation of the equilibrium phases ferrite and cementite.

In addition to the structural changes observed and recorded above, the stresses known to be of great magnitude in the martensite must be relieved during some stage of the tempering. An increase in magnetization at an applied field of 277 gauss over the temperature range of 100 to 200°C (210 to 390°F) has been associated with such stress relief, though whether or not it is caused by a precipitation from martensite is as yet unknown.
IV. EXPERIMENTAL EQUIPMENT AND TECHNIQUES

A. Production of High Purity Iron-Carbon Alloys

Commercial carbon steels usually contain small but significant amounts of impurities and residual alloying elements which could influence the tempering characteristics after quenching. To evaluate the effect of this variable it was deemed desirable to produce some reasonably pure iron-carbon alloys. Alloys of this type of extremely high purity may be made by carburizing a carefully purified piece of iron in a mixture of pure hydrocarbon gases. Two such methods have been described recently by Mehl and Wells, and by Digges. It was not considered necessary for the purpose herein intended to obtain alloys of this extremely high purity, and after a consideration of alternative methods, it was decided to melt together commercially pure electrolytic iron and carbon in an induction furnace, using a reduced pressure in order to avoid the necessity for deoxidation prior to casting.

A suitable furnace was available in the Induction Furnace Laboratory at the Massachusetts Institute of Technology, and was used for the preparation of the high purity alloys. Figure 13 is a photograph of the furnace and accessory equipment, made with the detachable cover, containing a viewing window and arm for holding the ingot mold, removed. It will be seen that with this sort of an arrangement it was possible to melt and cast under a vacuum or under any desired atmosphere*. For

* Details of design and operation of this furnace are discussed elsewhere by A. W. Schneble, Jr. (50).
FIGURE 15: Photograph of induction furnace with dome removed. The vacuum line enters near the top left of the furnace.
the work in this thesis all heats were melted and poured under a vacuum amounting to between 2 and 10 millimeters of mercury.

Two separate series of heats were made in this furnace. The crucibles used for melting the first series of heats were made of alundum of especially high purity, and were supplied by the Lava Crucible Company. These crucibles are known by the trade name "Lavalox". Alundum was chosen because of its extremely good refractory characteristics at high temperatures, and because very little chemical action would be expected to take place between the molten metal and the crucible even at the reduced pressures used. This type of crucible was found to be quite satisfactory from a refractory and chemical point of view, but was structurally weak and was prone to crack badly, necessitating frequent replacement.

The second series of heats were melted in alundum crucibles from the Norton Company. Although these were reputed to be of a comparable degree of purity to those from the Lava Crucible Company, a considerably greater pickup of silicon (present in the crucible as silica for binding purposes, which was then reduced by carbon or carbon monoxide in the metal under the low pressures prevailing) was observed. They also appeared to be weaker mechanically, though the refractory characteristics were satisfactory.

The mold used for the first series of melts, shown in Figure 14, was more or less square in cross-section, with beveled corners. When completely full it held only 3.5 pounds of steel so, in order to increase capacity and to provide a zone for a shrinkage cavity to develop,
FIGURE 14. Cast iron molds used for making ingots of high purity alloys.
a hot top made of sillimanite was placed on top of the iron mold. Since it was found that very little shrinkage cavity was encountered, presumably because of the very rapid solidification (the arm of the furnace assembly holding the mold was water-cooled), practically all of the 5.5 pound ingot thus produced was usable.

For the second series of heats, in an attempt to get even greater capacity per heat, a round iron mold, also shown in Figure 14, was used with no hot top. It was subsequently discovered that this actually did not allow greater capacity, because the induction furnace itself was found to be incapable of melting successfully more than 6 pounds of metal without serious "bridging". However, it did do away with the necessity of a hot top, and since solidification took place very rapidly, little or no defects caused by shrinkage formed.

The electrolytic iron melting stock used was purchased from Plastic Metals, Inc., of Johnstown, Pennsylvania, and consisted of irregular pieces of cathode iron, as deposited, about \( \frac{1}{4} \) inch thick and an inch square. A typical analysis of this material, as supplied by the manufacturer, is given in Table I.

The carbon was charged with the electrolytic iron prior to applying power to the furnace. In the first series of heats it was introduced as a grade of carbon black known as Cabot Spheron, Grade 6, obtained from Godfrey L. Cabot, Inc. This carbon black, of an analysis as given in Table II, was in the form of minute spheres of carbon, and was "non-dusting". Unfortunately, under the influence of the high frequency field in the induction furnace, the particles became violently
### TABLE I

**Typical Analysis of Electrolytic Iron**

<table>
<thead>
<tr>
<th>Component</th>
<th>% by Weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total Carbon</td>
<td>.004</td>
</tr>
<tr>
<td>Sulfur - Sulfide</td>
<td>.002</td>
</tr>
<tr>
<td>Sulfate</td>
<td>.001</td>
</tr>
<tr>
<td>Manganese</td>
<td>.002</td>
</tr>
<tr>
<td>Phosphorus</td>
<td>.002</td>
</tr>
<tr>
<td>Silicon</td>
<td>.001</td>
</tr>
<tr>
<td>Nickel</td>
<td>.009</td>
</tr>
</tbody>
</table>

### TABLE II

**Analysis of Cabot Spheron, Grade 6**

<table>
<thead>
<tr>
<th>Component</th>
<th>Per Cent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Volatile Matter</td>
<td>5.</td>
</tr>
<tr>
<td>Ash</td>
<td>0.05</td>
</tr>
<tr>
<td>Carbon</td>
<td>95.</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>1.3</td>
</tr>
</tbody>
</table>
agitated, many of them being thrown out of the crucible entirely, resulting in an unavoidable loss in carbon in the molten metal. For this reason the carbon contents of the steels produced were considerably lower than they were expected to be.

In order to avoid this large loss in the second series of heats, Acheson graphite was employed as a source of carbon. Acheson graphite is not as pure as the Spheron No. 6 originally used, but because of the relatively small amount of carbon involved in the alloys it was felt that the difference in impurities introduced would be insignificant.

Unfortunately the extremely high temperatures of the lower part of the bath, resulting from attempts to melt the "bridging" of many of the second series of heats, caused an accumulation of impurities (mainly silicon) from the crucible in the metal. These impurities cannot be attributed to the inferior grade of carbon used, for they are in much greater quantity than could be obtained from that source.

A summary of the operating conditions and analyses of the metal obtained from these heats is included as Table III.

After cooling to room temperature these ingots were packed in cast iron chips to prevent decarburization and soaked at about 1800° F overnight to bring about thorough homogenization and relieve any cooling stresses. They were cooled in the furnace from the homogenizing temperature. They were then reheated and forged, partly to 3/4 inch rounds, and partly to 1/2 inch rounds. Ingots 14, 15, 17, 18, 19, 21, 22 and 23 were forged entirely to 1/2 inch squares.
TABLE III
Summary of Experimental Heats and Analysis

<table>
<thead>
<tr>
<th>Heat No.</th>
<th>Furnace Pressure</th>
<th>Time Min.</th>
<th>C</th>
<th>Mn</th>
<th>S</th>
<th>P</th>
<th>Si</th>
<th>Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td>4 *</td>
<td>2 - 5</td>
<td>12</td>
<td>0.63</td>
<td>none</td>
<td>0.06</td>
<td>0.03</td>
<td>0.04</td>
<td>none</td>
</tr>
<tr>
<td>7 *</td>
<td>4</td>
<td>23</td>
<td>0.34</td>
<td>none</td>
<td>0.03</td>
<td>0.05</td>
<td>0.23**</td>
<td>none</td>
</tr>
<tr>
<td>8 *</td>
<td>2 - 3</td>
<td>16</td>
<td>0.95</td>
<td>0.013</td>
<td>0.04</td>
<td>0.03</td>
<td>0.04</td>
<td>none</td>
</tr>
<tr>
<td>9 *</td>
<td>3</td>
<td>13</td>
<td>0.95</td>
<td>none</td>
<td>0.06</td>
<td>0.03</td>
<td>0.04</td>
<td>none</td>
</tr>
<tr>
<td>12 *</td>
<td>2 - 3</td>
<td>14</td>
<td>0.78</td>
<td>none</td>
<td>0.05</td>
<td>0.05</td>
<td>0.04</td>
<td>none</td>
</tr>
<tr>
<td>14 °</td>
<td>8 - 10</td>
<td>19</td>
<td>1.38</td>
<td>none</td>
<td>0.012</td>
<td>0.007</td>
<td>0.10</td>
<td>trace</td>
</tr>
<tr>
<td>15 °</td>
<td>3 - 12</td>
<td>21</td>
<td>1.44</td>
<td>none</td>
<td>0.037</td>
<td>0.005</td>
<td>0.06</td>
<td>trace</td>
</tr>
<tr>
<td>17 °</td>
<td>3 - 4</td>
<td>17</td>
<td>1.17</td>
<td>none</td>
<td>0.009</td>
<td>0.005</td>
<td>0.05</td>
<td>trace</td>
</tr>
<tr>
<td>18 °</td>
<td>4.5 - 5</td>
<td>24</td>
<td>0.70</td>
<td>none</td>
<td>0.012</td>
<td>0.004</td>
<td>0.10</td>
<td>trace</td>
</tr>
<tr>
<td>19 °</td>
<td>7 - 10</td>
<td>29</td>
<td>0.67</td>
<td>none</td>
<td>0.007</td>
<td>0.004</td>
<td>0.08</td>
<td>trace</td>
</tr>
<tr>
<td>21 °</td>
<td>8 - 10</td>
<td>45</td>
<td>0.92</td>
<td>none</td>
<td>0.006</td>
<td>0.006</td>
<td>0.05</td>
<td>trace</td>
</tr>
<tr>
<td>22 °</td>
<td>8 - 9</td>
<td>32</td>
<td>0.37</td>
<td>none</td>
<td>0.009</td>
<td>0.001</td>
<td>0.09</td>
<td>trace</td>
</tr>
<tr>
<td>23 °</td>
<td>7 - 8</td>
<td>35</td>
<td>0.79</td>
<td>none</td>
<td>0.004</td>
<td>0.003</td>
<td>0.01</td>
<td>trace</td>
</tr>
</tbody>
</table>

* Lava Crucible
° Norton Crucible

** The source of this large amount of silicon is unknown.
To eliminate any effect of pipe, every bar after forging was hot acid etched at each end. If cracks or pipe appeared the end was sawed off and another etch test made. In many of the ingots cast in the "square" mold, cracks appeared throughout the length of the bars, rendering them useless. These cracks must have been caused either by finishing at too low a temperature during forging, or by cracks carried through from the ingot stage, where they formed during the extremely rapid cooling. Steels low in manganese (and these contained none) are known to be rather difficult to work successfully; therefore, the former of the two causes mentioned above is considered to be the more plausible.

The half-inch rounds and squares were subsequently machined into round bars of 0.240 inches diameter and 4 1/2 inches long for magnetic and dilatometric uses, while the 3/4 inch rounds were turned down to a diameter of half an inch and were reserved for X-ray, specific volume and hardness measurements. The reason for leaving so much stock to be removed on machining was to avoid completely all effects of decarburization which may have taken place on heating prior to and during forging.

Samples for analysis were taken after forging by drilling a one-quarter inch hole one-inch deep in the center of cut ends of several bars taken from the same heat. Thus the chemical samples were truly representative of the test specimens.

In order further to insure complete homogeneity of specimens of these high purity steels, they were placed in an evacuated quartz tube, maintained at a vacuum by constant pumping, using a Cenco Hyvac pump. The tube was heated at 1800° F for 10 hours, furnace cooled to about
900° F, reheated to just above the Ac₃ₐ and cooled in air. After
this treatment, which consumed about 14 hours in each case, the sam-
pies were invariably bright and shiny, and no evidence of decarburi-
zation was discernible at the edges of a carefully polished metal-
lographic specimen cut from one of them.

B. Commercial Alloys

Four steels obtained from commercial sources were also included
for investigation. These steels, their section sizes and source are
given in Table IV.

As in the case of the high purity alloys, here also the sample
drillings for analysis were made by drilling a longitudinal quarter-
inch hole in the center of the ends of several bars.

These alloys were all turned down to a diameter of 0.240 inches
for use in the magnetic and dilatometric tests, and in addition were
employed in X-ray, specific volume and hardness investigations, as were
sections of the smaller diameter bars of steels A and B.

C. Magnetic and Dilatometric Methods

All the magnetic and dilatometric data were obtained by use of
the magneto-dilatometer constructed by Zmeskal. Briefly, it con-
sisted of a quartz dilatometer tube 3/8 inch in diameter and capable
of holding a specimen 0.240 inches diameter and 4 1/4 inches long, hori-
zontally placed within an alundum muffle, 1/2 inch in diameter. About
the muffle was a bifilar (nonmagnetizing) furnace winding. This was
surrounded by an air space, then by copper pipe, 2 inches in diameter,
on which was wound a coil of flattened copper tubing through which water
TABLE IV
Commercial Steels Used, Sources and Analyses

<table>
<thead>
<tr>
<th>Steel</th>
<th>Size</th>
<th>Source</th>
<th>C</th>
<th>Mn</th>
<th>S</th>
<th>P</th>
<th>Si</th>
<th>Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>3/4&quot; round</td>
<td>Heat Treatment</td>
<td>0.49</td>
<td>.53</td>
<td>.036</td>
<td>.063</td>
<td>.10</td>
<td>.12</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Lab. Stock</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>3/4&quot; round</td>
<td>Heat Treatment</td>
<td>0.94</td>
<td>.33</td>
<td>.015</td>
<td>.009</td>
<td>.13</td>
<td>none</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Lab. Stock</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>.257&quot; round</td>
<td>Wetherell Bros.</td>
<td>1.02</td>
<td>.35</td>
<td>.007</td>
<td>.018</td>
<td>.19</td>
<td>trace</td>
</tr>
<tr>
<td>D</td>
<td>13/32&quot; round</td>
<td>Wetherell Bros.</td>
<td>1.26</td>
<td>.34</td>
<td>.023</td>
<td>.024</td>
<td>.17</td>
<td>.16</td>
</tr>
</tbody>
</table>

was passed to protect the copper magnet winding, just outside of it, from the furnace heat. The magnet winding was made up of 65 pounds of No. 14 copper magnet wire, and was capable of producing a field of upwards of 1500 gauss when connected directly to a 220-volt, direct current line.

Any changes in length of the specimen during the time it was in test were transmitted to an Ames dial gage by means of a quartz rod. The dial gage was calibrated so that each division represented 0.0001 inches. It was easy to estimate length changes to ± 0.00002 inches, which corresponds to about five millionths of an inch per inch length of the specimen.

The magnetization of the specimen within the dilatometer rod was measured by observing the deflections of a ballistic galvanometer produced by a reversal of the magnetic field. The galvanometer current
was generated by a secondary coil 2 inches long and .432 inches average diameter, consisting of 114 turns of 30 gage constantan wire, wound on the quartz dilatometer rod at a point near the middle of the specimen location. The galvanometer scale (a mirror galvanometer was used so the scale consisted of a graduated ground glass plate at some distance from the galvanometer itself, on which an image of a pointer was reflected by the galvanometer mirror) was divided into 240 divisions, but the most magnetic specimen used created a deflection of only 210 divisions. By careful observation of large deflections it was possible to estimate to ±0.2 divisions, making the full-scale accuracy better than 0.2 per cent. For smaller deflections it was possible to estimate to ±0.1 divisions, thus maintaining approximately the same degree of accuracy. It was found that the deflection as measured on the galvanometer scale was linear with respect to the current developed in the secondary circuit over the entire range. Since this current is directly proportional to the change in flux produced, the galvanometer deflection is therefore a direct, linear function of the intensity of magnetization*.

The temperature of the specimen was measured by means of a noble metal thermocouple (chosen because no magnetic materials could be permitted, and because of its non-oxidation), the hot junction of which was inserted alongside the specimen inside the quartz dilatometer tube. The cold junction was in a vacuum bottle at 32° F. For accurate mea-

* For a discussion of the calibration of the magnet, see Appendix I.
surements a Type K Leeds and Northrup potentiometer was used; the
temperature at the hot junction could be read to ± 0.1° F, but was
usually reported to the nearest half degree. The couple used was
carefully standardized against the melting points of Bureau of Standards samples of tin, zinc and aluminum.

The heating, holding and cooling of the furnace was controlled
by a copper-constantan thermocouple connected through a Brown po-
tentiometer controller equipped with constant temperature, heating
rate, holding time and cooling rate controls.

During the course of a heating or cooling run, dilatation readings
and galvanometer deflection measurements were made at 12.5° F inter-
vals. Ordinarily, two different applied fields, 265 gauss and 1000
gauss, were used for the magnetic measurements and were alternated for
each reading. Measurements during continued holding at any tempera-
ture were made at definite intervals of time at temperature.

D. X-ray Diffraction Methods

The X-ray diffraction patterns produced during the course of this
work were divided into two classes:

(1) Photograms of treated steel, with lines from an aluminum
filter acting as a standard of reference; determination of amount of
austenite;

(2) Photograms of treated steel, with lines from platinum powder
as the standard of reference; determination of lattice parameters.
(1) Use of Aluminum Filter. In an attempt to employ X-ray diffraction photograms to determine the amount of a phase present in any multiphase crystalline system, the first method that would come to mind would be a study of the comparative line densities of the phases involved. It is well known that the more of a phase present to reflect the X-ray radiation, the more intense the reflection, and thus the more dense the diffraction lines produced. If then, in hardened steel consisting solely of austenite and martensite, the intensities of the reflections from those respective constituents could be compared and referred to each other, the proportions of the two phases could be determined. A practical study of this case would soon indicate, however, that the method would be dependent to a critical extent on the amount of breaking down the martensite would have undergone before examination, either by spontaneous decomposition at room temperature, or by a tempering during the last stages of quenching or during the surface preparation for X-ray examination. For this reason a more reliable comparison must be chosen.

The method used by Gardner, employing a precalibrated aluminum standard made of filter paper coated with aluminum paint and placed in the X-ray beam in front of the specimen, was adopted. This procedure resulted in the recording of an aluminum standard line, the density of which on the film could be measured with a densitometer and compared to the density of the austenite line. Gardner found that the ratio of these line densities (using the aluminum \((200)_c\) and austenite \((200)_a\) lines) was, except perhaps at the very extremes, a linear function of
the austenite content of the solid steel sample. He was able to report values of per cent austenite accurate to within \( \pm 1 \) per cent, using this method.

The actual technique necessary for obtaining satisfactory results is explained in full in the reference mentioned (33). Briefly, one surface of the specimen was very carefully ground to a radius about that of the camera to be used, with special precautions being taken to prevent overheating during grinding which conceivably might cause some austenite to decompose. In order to remove the cold working effects of grinding, this surface was then electrolytically attacked by a solution of 5 per cent HCl and 5 per cent H\(_2\)SO\(_4\) in water, the specimen being the anode and a current density of 6 amperes per square inch (9.3 milliamperes per square millimeter) being used. After about 6 minutes a layer of 0.003 inches was dissolved away, and under proper conditions the new surface was smooth and still curved. The specimen was then ready to be photogrammed.

Two X-ray cameras were employed, both of them being of the focussing type, the Phragmen No. 2 and No. 2A of the Massachusetts Institute of Technology Metallurgy Department standard equipment. These cameras recorded lines corresponding to the range of \( \sin^2 \theta \) from 0.2321 to 0.7014. Each of the cameras was supplied with its own standard aluminum reference, which had been constructed and calibrated previously.

Chromium radiation from a gas-type X-ray tube operating at about 45 - 50 kilovolts was employed. This radiation would cause the lines listed in Table V to be discernible on the film over the actual range
TABLE V

Lines Obtained on X-ray Films Over Useful Range
Phragmen No. 2 Camera, Chromium Radiation
Sin² θ = 0.235 to 0.435
(Calculated for a 1.00% Carbon Steel)

<table>
<thead>
<tr>
<th>Phase</th>
<th>Line</th>
<th>Sin² θ</th>
<th>Sin θ</th>
<th>θ</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Austenite</td>
<td>(111)α</td>
<td>.250</td>
<td>.500</td>
<td>.526</td>
<td></td>
</tr>
<tr>
<td>Martensite</td>
<td>(101)α</td>
<td>.254</td>
<td>.504</td>
<td>.529</td>
<td></td>
</tr>
<tr>
<td>Platinum</td>
<td>(111)α</td>
<td>.255</td>
<td>.505</td>
<td>.530</td>
<td></td>
</tr>
<tr>
<td>Cementite</td>
<td>(200)α</td>
<td>.256</td>
<td>.506</td>
<td>.531</td>
<td>weak</td>
</tr>
<tr>
<td>Martensite</td>
<td>(110)α</td>
<td>.266</td>
<td>.516</td>
<td>.542</td>
<td></td>
</tr>
<tr>
<td>Ferrite</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cementite</td>
<td>(120)α</td>
<td>.267</td>
<td>.517</td>
<td>.542</td>
<td>weak</td>
</tr>
<tr>
<td>Aluminum</td>
<td>(111)α</td>
<td>.276</td>
<td>.525</td>
<td>.552</td>
<td>(3)</td>
</tr>
<tr>
<td>Platinum</td>
<td>(200)α</td>
<td>.282</td>
<td>.531</td>
<td>.560</td>
<td></td>
</tr>
<tr>
<td>Cementite</td>
<td>(121)α</td>
<td>.296</td>
<td>.544</td>
<td>.575</td>
<td></td>
</tr>
<tr>
<td>Aluminum</td>
<td>(200)α</td>
<td>.299</td>
<td>.547</td>
<td>.579</td>
<td>(3)</td>
</tr>
<tr>
<td>Austenite</td>
<td>(111)α</td>
<td>.303</td>
<td>.550</td>
<td>.583</td>
<td></td>
</tr>
<tr>
<td>Martensite</td>
<td>(101)α</td>
<td>.305</td>
<td>.552</td>
<td>.584</td>
<td>(1)</td>
</tr>
<tr>
<td>Cementite</td>
<td>(210)α</td>
<td>.308</td>
<td>.555</td>
<td>.589</td>
<td></td>
</tr>
<tr>
<td>Cementite</td>
<td>(022)α</td>
<td>.317</td>
<td>.563</td>
<td>.597</td>
<td></td>
</tr>
<tr>
<td>Martensite</td>
<td>(110)α</td>
<td>.320</td>
<td>.566</td>
<td>.601</td>
<td>(1)</td>
</tr>
<tr>
<td>Ferrite</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cementite</td>
<td>(103)α</td>
<td>.323</td>
<td>.568</td>
<td>.605</td>
<td></td>
</tr>
<tr>
<td>Austenite</td>
<td>(200)α</td>
<td>.334</td>
<td>.578</td>
<td>.616</td>
<td></td>
</tr>
<tr>
<td>Cementite</td>
<td>(211)α</td>
<td>.336</td>
<td>.580</td>
<td>.618</td>
<td></td>
</tr>
<tr>
<td>Platinum</td>
<td>(200)α</td>
<td>.340</td>
<td>.583</td>
<td>.623</td>
<td>(1)</td>
</tr>
<tr>
<td>Aluminum</td>
<td>(200)α</td>
<td>.352</td>
<td>.593</td>
<td>.635</td>
<td>(2),(3)</td>
</tr>
<tr>
<td>Cementite</td>
<td>(202)α</td>
<td>.370</td>
<td>.608</td>
<td>.654</td>
<td></td>
</tr>
<tr>
<td>Cementite</td>
<td>(113)α</td>
<td>.373</td>
<td>.611</td>
<td>.657</td>
<td></td>
</tr>
<tr>
<td>Cementite</td>
<td>(122)α</td>
<td>.382</td>
<td>.618</td>
<td>.666</td>
<td></td>
</tr>
<tr>
<td>Austenite</td>
<td>(200)α</td>
<td>.403</td>
<td>.635</td>
<td>.688</td>
<td>(1),(2)</td>
</tr>
<tr>
<td>Cementite</td>
<td>(212)α</td>
<td>.423</td>
<td>.650</td>
<td>.708</td>
<td>weak</td>
</tr>
<tr>
<td>Platinum</td>
<td>(220)α</td>
<td>.681</td>
<td>.826</td>
<td>.971</td>
<td>(4)</td>
</tr>
</tbody>
</table>

Notes: (1) Used for parameter measurements. (2) Used for line density measurements. (3) Aluminum foil displaced from periphery of camera. (4) Used for determination of film shrinkage and other systematic errors.
of angles used \((\sin^2 \theta = 0.235 \text{ to } 0.435)\). This data is given for the location of lines from a steel having a carbon content of about one per cent.

The density of the lines was recorded on a microphotometer which was the property of the Physics Department. By appropriate measurements of the peaks of the aluminum \((200)_A\) line and the austenite \((200)_T\) line on the resultant trace, the ratio of their densities on the film could be established, and the amount of retained austenite determined therefrom.

(2) Use of Platinum Powder. Another method for computing the amount of retained austenite is based on the accurate determination of the lattice parameters of the constituent phases.

Ordinarily lattice parameters may be calculated to a fair degree of accuracy from films taken on either the Phragmen No. 2 or 2A camera by measuring the distance of the lines from one end of the darkened part of the film, and comparing with a standard calibration chart. The exposed portion of the film was limited by knife edges built into the camera, the images of which provided the limits from which lines were measured.

It was found, however, that slight variations in the position of the specimen on the periphery of the camera, which was very difficult to control with a high degree of accuracy for a small solid piece, resulted in shifting of the lines with respect to the reference points, and therefore caused the parameters to vary slightly. To overcome this difficulty it was found that a small amount of platinum powder...
applied to the surface of the specimen would produce excellent reference lines, one near each end of the film. One of these lines, the (200)$_{\alpha}$ line, was located about halfway between the martensite (101)$_{\alpha}$ and the austenite (200)$_{\gamma}$, and was thus in an excellent position for use as a reference line. The other platinum line used, the (220)$_{\alpha}$, was at a considerable distance, and could be used to correct for the film shrinkage and other systematic errors in technique. Table V gives the angles corresponding to the platinum lines observed.

Another distinct advantage of this method of attack is that the exact angle of the platinum standard lines can be computed very accurately, because its lattice parameter is known very exactly. Since the radius of the camera is known to be close to 50 millimeters, the angles of the martensite and austenite lines of interest can be readily calculated from the distance of their separation from the standard platinum line. In this way any small error in the camera radius or in the location of the specimen on the periphery becomes a second order effect, and is negligible in comparison to the normal error in line measurement.

Although it was originally planned to use a specimen for X-ray work large enough to be supported by the sides of the camera, it later became expedient to use the ends of some of the quarter-inch rounds. Since these were too small to be self-supporting on the camera, two separate jigs were built to hold them in place. These are illustrated in Figure 15 along with a block machined to a 50 millimeter radius (simulating the periphery of the camera) for accurately setting the po-
FIGURE 15. Photograph of accessories for holding small specimens in position on the X-ray camera. The left-hand jig is for use with specimens which do not have to be rotated, while the center jig enables the specimen to be rotated in a plane perpendicular to the X-ray beam. The block on the right is for positioning the specimens in the jig; it simulates the curvature of the camera.
sition of the specimen. One of these jigs holds the specimen stationary during the exposure, while the other is designed so that the specimen may be continuously rotated about its principal axis with the aid of a flexible shaft. This rotating jig was found to be required in order that smooth lines could be produced on the photograms of the large-grained steels.

The position of the lines on the films were measured on a viewing box with a measuring hairline arrangement reading to 0.02 millimeter divisions on the vernier scale. It is felt that most of the line measurements were accurate to ± 0.02 millimeters for the martensite lines (101) and (110), which usually were relatively broad, and ± 0.01 millimeters for the more sharply defined platinum (200) and austenite (200) lines.

The method of calculation of the lattice parameters of martensite and austenite from these measurements are explained in Appendix II, and the standard errors inherent in the calculations in Appendix III.

The specific volumes of martensite and austenite may be readily computed from their lattice parameters. According to Jette and Foote\textsuperscript{55} and, independently, Stockdale\textsuperscript{36}, the density of a crystalline substance may be expressed by

\[ \rho = K \frac{nW}{V} \]

where \( \rho \) is the density, \( K \) a factor determined analytically from Avogadro's number and the ratio of the absolute wave length scale\textsuperscript{*} to the Ångstrom unit scale, and equal to 1.65023 ± 0.00015 according to Jette.

\* This differs from the Ångstrom scale but little, the ratio of the two being determined by the relation of the parameter of calcite by Siegbahn\textsuperscript{51} in setting up the standards of X-ray wave lengths, and the corrected value for this parameter, recently determined more precisely.
and Foote\textsuperscript{35}, and 1.65029, according to Stockdale; \( n \) is the number of atoms per unit cell, \( W \) is the average atomic weight per lattice point, and \( V \) is the volume of the unit cell in cubic Ångstrom units as calculated from the X-ray data.

This equation was more useful in this work in reciprocal form, giving the specific volume

\[
\frac{V}{nW} = \frac{V}{V_{K}W}
\]

and was used in this way to calculate the specific volumes of the martensite and austenite in a piece of quenched steel.

After obtaining these calculated specific volumes and knowing the overall specific volume of the specimen, it became possible to compute the amount of retained austenite, assuming no third phase was present. This was done by use of the formula

\[
\text{Weight per cent austenite} = \frac{V_{X} - V_{s}}{V_{X} - V_{Y}} \times 100
\]

where \( V_{X} \) and \( V_{Y} \) are the calculated specific volumes of martensite and austenite respectively, and \( V_{s} \) is the overall specific volume of the sample, obtained directly from a density measurement.

With the technique used in this experimental work, it was possible to calculate the amount of retained austenite in a quenched steel, providing no other phases than martensite and austenite were present, with a possible error of \( \pm 3 \) per cent of austenite. This undoubtedly represents the maximum error since all of the individual variations were assumed to reinforce one another, whereas in actual practice it is more probable that some would tend to be offset by others. Details of the error calculations are given in Appendix IV.
E. **Direct Specific Volume Measurements**

The determination of the amount of retained austenite by the X-ray specific volume method requires, as seen in the equation above, a knowledge of the overall specific volume of the specimen. The most accurate and direct method for the determination of this value is to weigh the specimen in air, and then in water. The specific volume of the specimen may be found by substituting the proper values in the equation:

\[ V_s = V_w \times \left(1 - \frac{W_W}{W_A}\right) \]

where \( V_s \) is the overall specific volume of the sample, \( V_w \) is the specific volume of the water at the temperature of test, and \( W_W \) and \( W_A \) are respectively the weights of the specimen in water and in air.

These measurements were made according to the technique of Koh. Briefly, the procedure was to make the specimen clean and smooth, and to wash it carefully in benzene, ether and alcohol, and finally to dry it with a blast of warm air. It was then weighed in a laboratory balance to an accuracy of 0.0001 grams. The specimen was then laid in a wire frame made of copper wire, especially designed for the purpose, and suspended from the stirrup of the balance by a very fine platinum wire. This unit was then suspended in a beaker containing distilled water, with 0.004 per cent of sorbitol laureate added as a wetting agent. It was weighed in this condition and, the weight of the support and wire being determined, the weight in water of the specimen could be deduced. A precision thermometer was used to measure the temperature to within \( \pm 0.1^\circ \text{C} \) immediately after each reading, and the corresponding specific volume of water taken from a chemical handbook.
This method of weighing, using specimens of about 7 or 8 grams, gives an accuracy of at least 1 part in 80,000 in the actual weight, and of about 2\(\frac{1}{2}\) parts per 10,000 in the apparent specific volume.

The true specific volume of the steel, or rather of the constituents martensite plus austenite, can be estimated from this value of the apparent specific volume, if the amount and specific volume of inclusions are known even approximately. If the only inclusions were manganese sulphide, and all the sulfur were so tied up, the specific volume correction for a steel containing 0.03 per cent sulfur would be \(-0.00040\).

The overall specific volume used in calculations in this thesis is that corresponding to the specific volume corrected for the sulfur present.
V. PLAN OF EXPERIMENTAL WORK

In the study of tempering mechanisms it is first important to establish conclusively the structural constitution of the steel immediately prior to the tempering treatment. Since it has been well established that a small piece of plain carbon steel drastically quenched from a temperature high enough to bring about complete austenizing contains only martensite and austenite, this problem reduces itself to an accurate determination of the relative amounts of the two phases, and the dependency of that ratio on the carbon content, quenching temperature and quenching medium.

To attack this phase of the problem successfully it was decided to employ X-ray diffraction methods for determination of lattice parameters of the martensite and austenite. A new way of calculating the ratio of those constituents was worked out, utilizing the specific volumes as computed from the measured parameters and the measured specific volume of the sample. This new method has certain advantages over the Gardner technique\(^3\) in that a standard precalibrated filter is not required, and the value of per cent retained austenite finally determined from the specific volume data is an average of the entire test sample, rather than of the infinitesimal volume covered by the X-ray beam.

These accurate parameter measurements provide also a check on the variation of parameter with carbon content for both austenite and martensite, as reported by Honda and Nishiyama\(^3\), Ohman\(^4\), and Hågg\(^5\).
Impurities and residual elements present in commercial carbon steels, principally in solid solution, may have a pronounced effect on the rates of reaction, both during cooling (quenching) and reheating (tempering). They may also cause the lattice parameters to become distorted from those naturally developed when iron and carbon alone were present. Therefore it was considered desirable to carry out comparative studies on high purity iron-carbon alloys as well as on commercial steels. For this purpose several heats of high purity iron-carbon alloys were melted in the Induction Furnace Laboratory, forged, and used for many of the measurements in this thesis. Other materials used, the commercial steels, were obtained through commercial channels, and were considered to be representative.

Once the structural constitution was well defined, the process of tempering plain carbon steels was followed in several ways, using, in the main, techniques already developed and in general use at the Massachusetts Institute of Technology. The properties to be measured in order to obtain a survey of the tempering process were (1) the intensity of magnetization (under various applied fields), (2) dilatation (measured simultaneously with the intensity of magnetization), (3) specific volume, and (4) hardness. In addition, X-ray diffraction photograms were made at various stages in the tempering process in order to determine its effects on lattice changes.

The magnetic and dilatometric data were procured while the specimens were being heated, cooled, or held at temperature, or while any desired time-temperature variation was produced. These simultaneous
measurements were carried out in the apparatus built specifically for that purpose by Zmeskal. 34

All the other data, as well as some additional intensity of magnetization values, were secured at room temperature on specimens tempered various times at the tempering temperatures under consideration.

By proper correlation of the results obtained from all these experiments, it is hoped that the process and mechanism of tempering plain carbon tool steel could be described more completely, and with greater intrinsic accuracy than heretofore.
VI. EXPERIMENTAL RESULTS

Retained Austenite

The first problem to be undertaken in a systematic study of tempering changes is the definite establishment of the amount of retained austenite in the as-quenched steel. Since it has been well known that retained austenite as well as martensite decomposes during tempering with an appreciable effect on nearly all the properties of the steel, correct interpretation of changes in these properties requires a knowledge of the amounts of the constituents contributing to them.

A method was devised to give this information easily and quickly, and at the same time to supply other information as to the nature of the structure. This method of determining the amount of retained austenite was described fully in Chapter IV. It assumed the presence of only two constituents, austenite and martensite, and made use of the difference in their specific volumes for calculating the quantities of each constituent present.

The results of applying this method of determination of amount of retained austenite are outlined in Table VI. Included also are results for some of the same specimens obtained by (1) The Gardner technique\textsuperscript{33}, and (2) a point-counting technique*. The very good

\textsuperscript{*} Made by tempering the steel so as to darken martensite but not to change austenite when polished and etched. A photomicrograph then would show dark martensite and light martensite, the relative amounts of which would be determined statistically.
agreement of these three systems speaks well for the applicability of any of them to a problem of this type.

The method proposed here, i.e., that of utilizing calculated and observed specific volumes, has the advantage over the Gardner method in two ways, (1) the amount of austenite obtained is representative of the whole volume of the sample, and not of a very thin layer which contributes to the X-ray diffraction lines, and (2) no empirically established precalibration is required, such as is necessary in the case of the aluminum filter. With relation to the point-counting procedure, the specific volume method does not require laborious preparation of a number of high quality photomicrographs, and the even more laborious statistical analysis of those photomicrographs. In addition, once the parameters of a particular steel composition have been accurately determined, they should be constant for all pieces of the same steel quenched under similar conditions; and thus, a measurement of the overall specific volume is all that should be required for each austenite determination.

On the other hand, the specific volume method is limited to samples consisting solely of martensite and austenite in which no inadvertent cracking or tempering has taken place, and in which the composition is uniform throughout, i.e., no carburization or decarburization has resulted during heat treatment. If inclusions of known amount, composition and density are present, the method is still applicable, for the measured specific volume of the steel can be corrected accordingly. (See Appendix IV). These conditions, especially in the case of alloy
TABLE VI

Amount of Austenite Retained After Quenching

<table>
<thead>
<tr>
<th>Carbon Content</th>
<th>Quenching Temp. °F</th>
<th>Quenching Medium</th>
<th>Per Cent Retained Austenite by Volume</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Specific Method</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Volume Method</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Density Method</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Counting Method</td>
</tr>
<tr>
<td>Alloy 23</td>
<td>0.79</td>
<td>1500</td>
<td>water</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>13.1</td>
</tr>
<tr>
<td>Alloy 14</td>
<td>1.38</td>
<td>1880</td>
<td>oil*</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>41.8</td>
</tr>
<tr>
<td>Steel B</td>
<td>0.94</td>
<td>1500</td>
<td>oil*</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>17.6</td>
</tr>
<tr>
<td>Steel C</td>
<td>1.02</td>
<td>1575</td>
<td>oil*</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>18.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>17.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>17.2</td>
</tr>
<tr>
<td>Steel D-1</td>
<td>1.26</td>
<td>1800</td>
<td>oil*</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>43.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>44.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>39.0</td>
</tr>
<tr>
<td>Steel D-2</td>
<td>1.26</td>
<td>1800</td>
<td>oil*</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>42.3</td>
</tr>
</tbody>
</table>

* Special high-speed quenching oil
steels, are often impossible to meet, so they represent a very serious limitation. In the case of the plain carbon steels and high purity iron-carbon alloys used throughout this thesis work, the method is ideal.

Parameter Measurements

In making the parameter measurements on austenite and martensite as required in the specific volume technique for retained austenite determination, an opportunity to compare the present results with those obtained by other investigators presented itself.

Table VII gives the results of the parameter determinations made on the alloys and steels used in this work. These values, together with those reported by other investigators are plotted in Figure 16 in terms of the number of carbon atoms present per lattice point. In this graph the solid line in each case is the average straight line drawn through all the points, while the broken line represents only the results of the determinations as reported in Table VII. The lines for martensite parameter coincide in the two cases, but the austenite and martensite determined in this work are both higher on the average than the previously reported results. The reason for this behavior is not apparent, though it is felt that the results reported in Table VII are accurate to $\pm 0.001\text{Å}$ for the parameter of austenite and martensite, and $\pm 0.001\text{Å}$ for $a_o$ of martensite (see Appendix III).

Previously the parameters of these constituents had been plotted in terms of weight per cent carbon (see page 8) and straight lines were said to represent the variations of parameter with carbon content.
TABLE VII

Results of Austenite and Martensite Parameter Measurements

<table>
<thead>
<tr>
<th>Carbon Content Wt. %</th>
<th>Carbon Atoms per Lattice Point</th>
<th>Parameter (Angstrom)</th>
<th>Parameter (Angstrom)</th>
<th>Parameter (Angstrom)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Austenite a₀</td>
<td>Martensite a₀</td>
<td>Martensite c₀</td>
</tr>
<tr>
<td>Alloy 23</td>
<td>0.79</td>
<td>3.585</td>
<td>2.854</td>
<td>2.958</td>
</tr>
<tr>
<td>Alloy 21</td>
<td>0.92</td>
<td>3.591</td>
<td>2.855</td>
<td>2.969</td>
</tr>
<tr>
<td>Steel B</td>
<td>0.94</td>
<td>3.592</td>
<td>2.854</td>
<td>2.973</td>
</tr>
<tr>
<td>Alloy 9</td>
<td>0.95</td>
<td>3.592</td>
<td>2.849</td>
<td>2.971</td>
</tr>
<tr>
<td>Steel C</td>
<td>1.02</td>
<td>3.597</td>
<td>2.852</td>
<td>2.975</td>
</tr>
<tr>
<td>Steel D</td>
<td>1.26</td>
<td>3.606</td>
<td>2.849</td>
<td>3.010</td>
</tr>
<tr>
<td>Alloy 14</td>
<td>1.38</td>
<td>3.614</td>
<td>2.851</td>
<td>3.014</td>
</tr>
</tbody>
</table>
FIGURE 16. Effect of number of carbon atoms per lattice point on parameters of austenite and martensite. The broken lines indicate experimental results obtained in this thesis, while the solid lines are the average of all reported results.
However, this is a misleading practice for the lattices would be expected to expand linearly not with an increase in weight per cent carbon, nor even with an increase in atomic per cent carbon (as would be the case if the solid solution were a substitutional type) but with the number of carbon atoms per lattice point. This is the logical type of plot if the carbon atoms are dissolved interstitially, which is believed to be the case.

It will be noted that the values obtained in the course of this investigation agreed fairly well with those previously published, and with the exception previously mentioned of the higher $a_0$ values for both austenite and martensite. This discrepancy, however, is not serious, even though the reason for it is not apparent.

**Tempering Results**

A. **Magnetic-Dilatometric Results**

The magnetic and dilatometric work carried out may be divided into three classifications, depending on the conditions under which the measurements were made. These are: (1) the continuous type of experiment in which magnetic and dilatometric measurements were made during the slow, continuous heating or cooling of the specimen in the apparatus; (2) the isothermal type of experiment in which magnetic and dilatometric measurements were made as the specimen was held at a given tempering temperature, having been brought to that temperature
rapidly by insertion directly into the hot magnetometer; and (3) the room temperature type of experiment in which only magnetic measurements were made at room temperature on specimens tempered for various lengths of time at elevated temperatures in ordinary tempering furnaces and baths.

No attempt will be made in the following discussions to treat these different types of experiments separately, because of the close interrelation between the results obtained. They will be discussed more on the basis of the phenomena observed than on the mode of observing them.

(1) **Effect of Various Applied Magnetic Fields.** The magnetometer used in this experimental work had a maximum applied field of about 1600 gauss, but any lower field could be applied at will. Various values of field strength have been chosen for magnetization work of this sort by different experimenters, usually because they were conveniently obtained with the equipment used. In order to determine what values of applied field would be most likely to yield the most information of property changes, the magnetization curves for a steel containing 1.26 per cent carbon were obtained for both the annealed state and the as-quenched condition. These curves are reproduced in Figure 17. The effective field, $H_{\text{eff.}}$, produced by an applied field of 1500 gauss amounts to about 1380 gauss for the annealed steel, and 1400 gauss for the quenched piece. The difference from the applied field is caused by the demagnetization effect of the specimen. The demagnetizing factor, $\gamma$, which has been used in all the calculations
FIGURE 17. Magnetization curves for Steel D, 1.26 per cent carbon, annealed and quenched.
of this thesis is 0.0815 for a length-diameter ratio of 17.7 to 1 (length = 4.25 inches, diameter = 0.24 inches).

An inspection of Figure 17 will reveal that the two applied fields most generally used for this work, 1000 and 265 gauss, were located in different parts of the magnetization curves. The higher applied field, 1000 gauss, is such that the saturation value is not too remote; it is in the relatively flat part of each curve approaching saturation, and the magnetization obtained there should respond well to structural changes that will tend to produce a change in the saturation value, and be less sensitive to the internal changes which tend to alter the shape of the curve.

To include the latter condition, an intermediate value of applied field was employed, amounting to 265 gauss. This field brings the steel to a position on the curve where the slope is rapidly changing; the magnetization as measured at that applied field should be more sensitive magnetically to minor internal conditions such as stress, grain size and the like.

Figure 18, depicting the magnetization curves of Steel C (1.02 per cent carbon) during tempering at 230° C (450° F), also indicates that the applied fields used would be expected to yield the most information.

Final proof that applied fields of 1000 and 265 gauss would suffice to give the changes sought is indicated in Figure 19, in which the change in magnetization during the tempering run reported above is plotted for various field strengths. The curves of 265 and 1000 gauss are seen to give representative indications of all changing magnetic conditions during tempering.
MAGNETIZATION CURVES
STEEL C
QUENCHED FROM 1575° F
TEMPERED AT 450° F

FIGURE 18. Magnetization curves for Steel C (1.02 per cent carbon) after tempering various times at 450° F. The applied field of 265 gauss corresponds to an effective field of about 150-200 gauss, the applied field of 1000 gauss to an effective field of 890-920 gauss. (Measurements made at room temperature.)
FIGURE 19. Tempering curves at 450° F for Steel C (1.02 per cent carbon) for various applied fields. (Measurements made at room temperature.)
Accordingly, the two fields 1000 and 265 gauss were employed for magnetic measurements throughout the bulk of the work.

(2) **Effect of Impurities in Steel.** It was originally believed that the minor impurities in plain carbon steels, such as manganese, silicon, phosphorus and the like, were of some importance in determining the course of tempering. Therefore, two samples of almost identical carbon content, one being made of a commercial steel (Steel B)* and the other of a high purity iron-carbon alloy (Alloy 9)*, were quenched identically in water from 815°F (1500°F) and standard magnetization-dilatation runs made. These runs were carried out by heating at 3°C (5.4°F) per minute to 540°C (1000°F) and subsequent cooling at the same rate, making observations en route. The curves produced, given in Figures 20 and 21, were almost identical. Therefore, it was decided that the minor impurities had no appreciable effect on the course of tempering, and, since the quantity of high purity alloy was limited, the major portion of the work could be concentrated on the commercial steels without loss of any important information.

(3) **Critical Inspection of Typical Magnetization-Dilatation Tempering Curves.** From Figures 20 and 21 many important inferences may be drawn as to the changes taking place in a piece of quenched carbon steel as it is tempered. To facilitate the following discussion, however, a composite magnetization-dilatation curve, Figure 22, was constructed, showing the magnetization curves at four different

* See compositions on pages 47 and 50.
FIGURE 20. Standard magneto-dilatometer tempering curves; Steel B, 0.94 per cent carbon.
FIGURE 21. Standard magneto-dilatometer tempering curves for Alloy 9, 0.95 per cent carbon.
FIGURE 22. Heating curves of Steel B (0.94 per cent carbon) for magnetization at various applied fields and for dilatation, showing the stages of tempering.
applied fields, and the dilatation curve obtained on reheating a specimen of Steel B (0.94 per cent carbon) after quenching from 815° C (1500° F).

The first striking feature observed on examining Figure 22 is the general similarity of the magnetic tempering curves made at the three highest applied fields, and the marked dissimilarity of the curve obtained at low field (265 gauss). This dissimilarity serves as a confirmation of the ideas expressed above that when approaching saturation the magnetization is mainly subject to major structural changes, while at low fields many other factors may be impressed upon the magnetization and its dependency upon temperature profoundly altered.

The next most obvious feature is that when all the curves are taken under consideration, including the dilatation curve, it is apparent that they may be divided into stages with respect to temperature, each step resulting in a pronounced change in one or other of the characteristics plotted. These steps correspond to the stages of tempering previously reported (see Chapter III), and are marked off on Figure 22.

In all of the following discussion the temperatures used to designate the various steps in tempering are not to be considered as definite limits. They represent only the range of maximum change for each stage at a heating rate of 3° C (5.4° F) per minute. At a faster rate of heating they would in all probability be shifted to higher temperatures, and at slower rates to lower temperatures.
The term *stage* as applied to the tempering phenomena related in the following implies a region in which a discrete structural change is taking place in the decomposition of austenite and martensite.

The first stage, between about 100°C and 160°C (210°F and 320°F), is characterized by a decrease in specific volume (a contraction in the dilatation curve), and by a slight decrease in magnetization. This decrease in magnetization is readily apparent at high fields, but at an applied field of 265 gauss it appears not as a real decrease but as a retarded rate of increase – the slope of the curve becomes less positive.

The second stage, between 230°C and 310°C (450°F and 590°F), is marked by a sudden great increase in magnetization, and a nearly simultaneous increase in specific volume (expansion). The magnetic effect is nearly the same at all applied fields used, perhaps being slightly more pronounced at the low field (265 gauss).

The third stage, which overlaps the second stage, lies between 265°C and 360°C (510°F and 675°F). The magnetization at all fields decreases sharply, as does the specific volume (contraction). This effect tapers off as the upper temperature limit is approached, and above 360°C (675°F) all the tempering curves become very regular.

Prior to the second stage of tempering the magnetization at low field (265 gauss) is observed to increase with temperature, while at higher fields it decreases. This effect is particularly pronounced in the temperature range immediately before the second stage sets in. This phenomenon is attributable to stress relief, and will be discussed later along with the various stages of tempering.
(4) General Discussion. Thus far only the standard form of magnetization-dilatation curve has been considered. They have confirmed the presence of at least three distinct stages of decomposition in the tempering process which are characterized by well defined aberrations in these curves. In order to establish more firmly the nature of structural changes taking place in each of these stages, some special magnetization-dilatation experiments were undertaken, and data obtained for isothermal tempering at several temperatures.

A specimen of Steel B (0.94 per cent carbon), quenched from 815° C (1500° F), was heated at the standard rate to 150° C (300° F), 205° C (400° F), 260° C (500° F), 315° C (600° F) and 540° C (1000° F), with controlled cooling to room temperature between each heating cycle. The results of this set of experiments are given in Figure 23.

These curves contain a great deal of information with respect to the reactions taking place, for the cooling curves from each of the intermediate temperatures reveal characteristics which are not obtainable in the ordinary tempering experiment.

It will be observed that if a continuous heating curve is constructed from this set it will correspond almost exactly to the standard type of tempering curve for this steel as given in Figure 20. This in itself is indicative of the fact that no structural transformations take place during the cooling from any tempering temperature for this type of steel. In other words, transformations and other changes may take place on heating to (and holding at) the tempering temperature, but not also on cooling after tempering as so often is the case in the various alloy steels. The general concurrence of the
FIGURE 23. Magnetization and dilatation curves of Steel B (0.94 per cent carbon) heated to and cooled from 300°F, 400°F, 500°F, 600°F and 1000°F successively.
intermediate cooling and subsequent heating curves also bear out this conclusion.

On the other hand, cooling curves from the tempering temperature can indicate to a large degree the nature and progress of the tempering reactions which have taken place on heating (and holding). For example, the presence of a marked increase in magnetization on cooling in the region of $175^\circ$ C ($350^\circ$ F) to $230^\circ$ C ($450^\circ$ F) would be indicative of the presence of cementite in the steel, for the Curie point of cementite (above which it is paramagnetic, below which it is ferromagnetic) lies within that range of temperatures. When tempering is carried out on a quenched steel containing no cementite (as is the case in all the work reported here), the presence of cementite as a product of tempering is detectable in this way. Zmeskal$^{34}$ has reported that using the same apparatus the Curie point of cementite could be distinctly observed in an annealed steel of as low a carbon content as 0.15 per cent.

A second type of survey curve was produced in order to obtain an idea of the kinetics of the various tempering reactions. This work, also carried out on Steel B (0.94 per cent carbon) quenched from $815^\circ$ C ($1500^\circ$ F), resulted in the curves of Figure 24. The specimen was heated at the standard rate of $3^\circ$ C ($5.4^\circ$ F) per minute to a temperature of $95^\circ$ C ($200^\circ$ F) and held there for 27 hours. This resulted in the marked contraction observed in Figure 24, a slight increase in magnetization at low field, and a decrease at high field. The kinetics of this first stage tempering are plotted in Figure 25, the features of which will be discussed later.
STEEL B
0.94 C
QUENCHED FROM 1500°F
27 HRS. AT 200°F
17 HRS. AT 300°F
33.5 HRS. AT 450°F

FIGURE 24. Magnetization and dilatation curves for Steel B (0.94 per cent carbon). The heating was interrupted at 200°F for 27 hours, at 300°F for 17 hours and at 450°F for 33.5 hours.
Figure 25. Effect of time of tempering at 200°F on magnetization and length of Steel B (0.94 per cent carbon) (measured at 200°F).
Following the hold at 95° C (200° F) the specimen was heated to 150° C (300° F) and held there for 17 hours, during which time the magnetization showed a significant increase, particularly at low field, and there was a further slight contraction. The kinetics of the tempering at this temperature are shown in the log time plot of Figure 26.

The specimen was then heated further to 230° C (450° F) and held there for 33.5 hours, the reaction-rate curves being given in Figure 27. This tempering temperature caused a great increase in magnetization followed by a decrease for both high and low field. The maximum was reached after a tempering time of 1.5 hours. The length of the specimen was found to increase slightly for the first 0.4 hour, then to decrease continuously until the full 33.5 hours had expired. The final value of magnetization was considerably higher than the original, while the final length was less than the original.

After the specimen had completed 33.5 hours at 230° C (450° F) heating was continued to 540° C (1000° F), and then cooling to room temperature at the standard rate of 3° C (5.4° F) per minute was carried out without any remarkable differences from the standard type of curve (Figure 20) being observed.

As a result of this experimental work it was confirmed that tempering of quenched carbon tool steels was primarily a three-stage process, as has been often mentioned before.

(a) Room Temperature Tempering. In order to determine the effect of aging at room temperature on magnetization and volume, pieces of Steel C (1.02 per cent carbon) were quenched and the magnetization and specific volume measured at various
FIGURE 26. Effect of time of tempering at 300° F on magnetization and length of Steel B, 0.94 per cent carbon (measured at 300° F).
FIGURE 27. Effect of time of tempering at 450°F on magnetization and length of Steel B, 0.94 per cent carbon (measured at 450°F).
intervals up to 167 hours. The results are plotted in Figure 28. The magnetization at high field did not show much change, but that at low field was slightly increased with time. This may have been due to a small amount of stress relief, which will be discussed later. The volume at first increased, then showed a gradual decrease. A slight tempering of the martensite might cause the decrease, as in the first stage of tempering, but reasons for the cause of the initial increase are unknown.

The specific volume of Steel D (1.26 per cent carbon), plotted in Figure 29, showed a similar but less pronounced effect on aging at room temperature.

(b) The First Stage of Tempering. It has already been shown that in carbon steels the first stage of tempering takes place between 100°C (210°F) and 160°C (320°F). It results in a marked contraction and a slight decrease in magnetization. Although the contraction often has been observed before, as for example by Hanemann and Traeger31 (see page 29), the actual progress of the length changes has not been completely followed. This was done, however, for Steel B (0.94 per cent carbon), and Figure 25 shows both the contraction observed and the magnetic changes which take place during holding at this stage, readings being made on the specimen while it was at temperature. A similar reaction curve is given in Figure 30 for Steel C (1.02 per cent carbon) tempered
FIGURE 28. Effect of time of tempering at room temperature on magnetization and specific volume of Steel C, 1.02 per cent carbon (measured at room temperature).
FIGURE 29. Effect of time of tempering on specific volume; Steel D, 1.26 per cent carbon (measured at room temperature).
FIGURE 30. Effect of time of tempering at 212° F on magnetization and specific volume of Steel C, 1.02 per cent carbon (measured at room temperature).
at 100° C (210° F) for various intervals then cooled to room temperature before measuring. The curves thus represent the reaction as reflected in the properties at room temperature. The same general trends are to be noticed in each case for the magnetization curves, but the contraction is indicated much more clearly in Figure 25, where the many readings were to an accuracy in length of one part in 200,000 (thus in volume of one part in 70,000) while the specific volume accuracy of Figure 30 could be only one part in 10,000 at best. The same sort of contraction during tempering at 100° C (210° F) was observed on Steel D (1.26 per cent carbon) as shown in Figure 29.

The first stage of tempering has been attributed to the decomposition of tetragonal martensite to cubic martensite⁵ and to a ferrite-cementite aggregate. Hanemann and Traeger⁶ have considered the product of this low temperature tempering to be a distinct phase, different from martensite, and from a ferrite-cementite aggregate, and which was designated by them as the zeta-phase.

There is no doubt that the contraction is caused by some sort of change in the martensite, while austenite is unaffected. This may easily be shown by photomicrographs, in which it is seen that martensite is altered by tempering so that it becomes dark on etching, while austenite remains white, and is not decomposed. Incidentally, further proof of the stability
of retained austenite in this range of temperatures may be
gained from the fact that no pronounced increase in magneti-
zation is observed such as would take place upon its decom-
position. That part of the tempering process is reserved
for higher temperatures.
Although martensite does undergo changes which result in its
darkening and contraction, the amount of contraction observed
is not nearly that which would take place had it decomposed
completely into ferrite and cementite. Table VIII, calculated
from the data obtained from this work, shows that only about
one-quarter of the expected overall contraction from marten-
site into a ferrite-cementite aggregate has taken place in
the first stage.
Another argument against the complete breakdown from marten-
site to ferrite and cementite is based on the fact that ac-
tually the presence of cementite is not detected until late
in the third stage of tempering, at about 340° C (650° F).
This will be discussed in more detail in a later section.
The theory advanced by the Japanese to account for this pre-
liminary decomposition of martensite is that the carbon atom
moves its position slightly, allowing a collapse of the tet-
ragonal structure into a body-centered cubic martensite. They
believed that cubic martensite was a true solution and pre-
sented the curves given in Figures 11 and 12 (page 35) as
proof of their contentions. The validity of those curves has
# TABLE VIII

**Fraction of Total Martensite Contraction Occurring**

in First Stage of Tempering

<table>
<thead>
<tr>
<th>Carbon Content</th>
<th>Amount of Austenite</th>
<th>Measured Contraction</th>
<th>Volume Change</th>
<th>Calculated Volume Change for Complete Decomposition of Martensite</th>
<th>Fraction of Total Martensite Contraction Occurring in First Stage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Weight Per Cent</td>
<td>Volume Per Cent</td>
<td>Inches/Inch</td>
<td>Measured Martensite</td>
<td>Corrected to 100% of Martensite</td>
<td></td>
</tr>
<tr>
<td>Steel B</td>
<td>0.94</td>
<td>17.6</td>
<td>0.00114</td>
<td>-0.54</td>
<td>-0.42</td>
</tr>
<tr>
<td>Steel C</td>
<td>1.02</td>
<td>18.4</td>
<td>0.00135</td>
<td>-0.40</td>
<td>-0.49</td>
</tr>
<tr>
<td>Steel D</td>
<td>1.26</td>
<td>45.0</td>
<td>0.00110</td>
<td>-0.33</td>
<td>-0.58</td>
</tr>
</tbody>
</table>
been discussed in Chapter III and that discussion need not be repeated here, except to state that it is felt that they do not prove the existence of a true solid solution.

In addition to the doubt cast on the Japanese argument by a critical inspection of their data, there are two other factors which are in evidence against their beliefs. The first is the rapid etching character of the first stage decomposition product, which indicates perhaps more than any other phenomenon the presence of a fine precipitate, or at least of some sort of heterogeneity. Secondly, the very pronounced diffuseness of X-ray diffraction patterns of this product is evidence against a separate and distinct phase retaining the carbon in solution, but appears rather to be an indication of a partially decomposed phase with considerable indefiniteness as to its own true crystal structure. This reasoning may be applied in a like manner against the conception of Hanemann and Traeger\(^{31}\) that a new phase is formed.

The evidence obtained in this present work, the slight decrease in magnetization and the partial contraction during the first stage, when correlated with X-ray diffraction work, seems to indicate that tetragonal martensite undergoes a partial decomposition. This results in the formation of a sub-precipitate of higher carbon content, removing some carbon from the tetragonal solid solution and allowing an incomplete and inhomogeneous collapse of the martensite to ferrite.
It would be expected that such a transition precipitate would cause a decrease in magnetization, not only by virtue of the step toward the formation of cementite but by the disregistry thereby introduced. Such disregistries would tend to increase the effect of demagnetization, resulting in lower measured values of magnetization.

This sub-precipitate, which probably develops from regions in the martensite having statistically high concentrations of carbon, does not contain as much carbon as cementite, and is likely produced without much diffusion, for it persists until the third stage of tempering sets in. A new phase in the true sense of the word is not generated, but rather a poorly developed structure part-way along the path to the true equilibrium condition, and still having a high degree of registry with the matrix. The fact that this structure remains over a considerable temperature range does not mean that it is necessarily a thermodynamically stable phase.

(c) The Second Stage of Tempering. This step in the general decomposition caused by reheating a martensite-austenite aggregate obtained by a successful quench is assigned to the changes produced as a result of the decomposition of austenite. There appears to be no pronounced controversy over this issue, for the changes are large and distinctive, and the disappearance of austenite may be easily followed by many means.

One of the properties most sensitive to the decomposition of austenite into a ferritic aggregate is the magnetization. Aus-
tenite is paramagnetic, and ferrite is ferromagnetic. Decomposition of even a slight amount of austenite, therefore, would result in pronounced magnetic changes. That this is true is indicated very clearly in the tempering curves of Figures 20, 21, 36, 37 and 38. In all of these cases there is a pronounced increase in magnetization starting at about 230°C (450°F) and culminating in a peak value at between 260 and 290°C (500 and 550°F). After cooling to room temperature the magnetization is found to have attained a value very much higher than the original as-quenched value.

In addition to the increase in magnetization there is also an increase in length, an expansion. In many cases this expansion is somewhat masked by the large contraction brought about by the overlapping third stage. However, if much austenite is present, the expansion may be easily observed.

Figure 24 (page 87) reveals that on isothermal tempering at 230°C (450°F) the magnetization reaches a maximum then decreases. This is true at both high and low field. In a like manner, the dilatation curve shows a maximum, and thereafter a contraction. The downward course of these curves, however, is a result of the third stage of tempering, and will be considered in the next section.

The kinetics of the second stage of tempering are shown in Figures 27 and 31, for Steels B (0.94 per cent carbon) and C (1.02 per cent carbon) respectively for a temperature of
230° C (450° F), and in Figure 32 for a temperature of 260° C (500° F), using Steel B (0.94 per cent carbon).

The magnetization curves in each case appear as normal reaction curves, having the same general shape as the isothermal austenite decomposition reactions at sub-critical quenching temperatures. For Steel B at 250° C (450° F), in which case the readings were made continuously at temperature, the maximum in magnetization is reached in about 1.5 hours; at 260° C (500° F) the reaction was much more rapid, reaching a maximum in only 0.25 hours. For Steel C, whose results were obtained at room temperature on a specimen tempered for different times at 230° C (450° F), the maximum was reached only after 10 hours at temperature. The reason for this wide discrepancy is that near the peak of the magnetization-temperature curve it is found that the magnetization at room temperature is not nearly so sensitive as the magnetization at temperature to subsequent changes. The position of the magnetization curves on cooling to room temperature after heating to 260° C (500° F) and 315° C (600° F) as shown in Figure 23 (page 85) bear out this assumption. It is noted there that, while there is a considerable decrease in magnetization at temperature, the change produced at room temperature is very slight; in fact, at low field the magnetization is even higher after heating on to 315° C (600° F).

The maximum point in the time-magnetization curves does not indicate the finish of austenite decomposition, though it is granted that the greater portion of the austenite has disap-
FIGURE 31. Effect of time of tempering at 450°F on magnetization of Steel C, 1.02 per cent carbon (measured at room temperature).
FIGURE 32. Effect of time of tempering at 500° F on magnetization and length of Steel B, 0.94 per cent carbon (measured at 500° F).
peared. By that time the decrease caused by the third stage has set in and has gained the ascendancy. This occurs even earlier in the case of the dilatation curve, for its peak is reached after only 0.4 hours in the case of Steel B (0.94 per cent carbon) at 230°C (450°F) and 0.05 hours at 260°C (500°F). The tendency to contract produced by the third stage of tempering is considerably greater than the tendency toward decreased magnetization; it is also true that the decomposition of austenite has a less pronounced effect on expansion (indeed, in many cases no expansion is observed unless considerable amounts of austenite are present) than on the magnetization. Therefore, the presence of peaks at different times is compatible with the changes assumed to be taking place. No mention is made here of the type of product that austenite generates on its decomposition during tempering, for that discussion is reserved for the section on the third stage of tempering. Suffice it to say that it is a ferritic type of product, much like the product of the first stage of martensite tempering. The specific volume of Steel D (1.26 per cent carbon) showed a general increase on tempering at 230°C (450°F) for times up to 17 hours. The original decrease as indicated in Figure 29, page 94, was caused by the first stage contraction. Apparently the third stage has not yet set in for this steel in 17 hours at 230°C (450°F).

(d) The Third Stage of Tempering. At the end of the second stage of tempering there would be present in the steel (1) the decomposition product of martensite formed during the first
stage, and (2) the decomposition product of austenite formed during the second stage - provided no other reactions had set in. As it is indicated by Figure 32 especially, however, the third stage of tempering, characterized by a decrease in magnetization and by a pronounced contraction, enters the picture before the second stage is complete.

The final product obtained after the third stage of tempering is completed is definitely a spheroidal-type ferrite-cementite aggregate. Assuming, then, that the reactions of the third stage follow those of the second stage (as they do except for a minor amount which takes place concurrently), the product of martensite decomposition in the first stage and the product of austenite decomposition in the second stage must together decompose further to ferrite and cementite.

It has been shown that martensite initially breaks down into an ill-defined ferritic structure, still containing some of the carbon in solution, and in which has developed a sub-precipitate of higher carbon content. This structure remains stable until the temperature of 265° C (510° F) is reached on a standard heating rate curve. (At constant temperature it may undergo further decomposition at a lower temperature if enough time is allowed.)

In all probability the austenite decomposition product has the same general character. This is to be expected because of the uniform manner in which the simultaneous further decomposition takes place in the third stage. Austenite can-
not be considered as having transformed first to martensite, which then was immediately tempered, for martensite of the carbon content under consideration here is formed at low temperature only. It is also impossible for austenite to decompose directly into a ferrite-cementite aggregate, or the presence of cementite in the structure would be detected on cooling from the point of maximum magnetization by reason of the presence of its Curie point. This is not observed, as will be shown later. It is much more likely that a product similar to that formed from martensite is produced, ferritic in nature, but having a poorly defined transition precipitate concentrating the carbon somewhat.

The third stage of tempering then becomes nothing more than the genesis and growth of cementite. The progress of this development has been studied by means of critical observations of the presence and nature of the Curie point attributable to cementite.

Normally, cementite regains its ferromagnetism on cooling rather sharply at about 190 - 210°C (375 - 410°F). This phenomenon may be readily observed in any of the cooling curves after heating to 540°C (1000°F).

Several specimens of Steel B (0.94 per cent carbon) were quenched and rapidly heated in the magnetic apparatus to 230°C (450°F). After varying times at temperature the specimens were started to cool at a rate of 3°C (5.4°F) per minute, and the cooling curves of magnetization obtained.
The cooling curves drawn for magnetization at an applied field of 1000 gauss are given in Figure 33. After eleven minutes at 230° C (450° F) the magnetization was still increasing because of the continuing decomposition of austenite, and on cooling no evidence of a Curie point indicative of the presence of cementite was observed. As the length of time at temperature was increased, however, the shape of the cooling curve approached more and more closely to that of the equilibrium cooling. This indicates the gradual approach to a cementite precipitate. Since it has been proved that cementite is not present as such below 230° C (450° F), but only a sub-precipitate relatively low in carbon is present, the continuous change in shape of these curves toward that of equilibrium indicates that the sub-precipitate is gradually growing in size, and gradually assuming a higher percentage of carbon through diffusion.

Such a cementite-like sub-precipitate, removing some iron atoms from positions where they could contribute to the magnetic characteristics, would be expected to have a higher and much more ill-defined Curie point than cementite itself; this seems to be the case here.

It is worthy of note in this connection that the initial product of the austenite and martensite decompositions is more magnetic than the equilibrium structure of ferrite and cementite at room temperature. It is known that if some of the iron is tied up with carbon in the form of cementite the total magnetization is decreased. In this case tempering
FIGURE 33. Effect of time of tempering at 450°C on magnetization curves during subsequent cooling. Steel B, 0.94 per cent carbon.
to a temperature of 260° C (500° F) has not brought about the expected decrease at room temperature; at 1000 gauss applied field the magnetization is almost 4 per cent greater than the ferrite-cementite aggregate, as shown in Figure 23. This points to the conclusion that at 260° C (500° F) cementite has not yet formed.

After even 67 hours at 250° C (450° F) the actual composition Fe₃C has not been reached, nor is it present after heating to 260° C (500° F). (Note the cooling curve from 260° C (500° F) in Figure 23, page 85.) As a matter of fact, heating even to 315° C (600° F) does not give true cementite, as also shown in the cooling curves of Figure 23.

The ill-defined and misplaced Curie point mentioned earlier could not be produced by the cementite particles being too small to have a great influence, for Sanford and Ellinger have shown that the smaller the cementite particle size the more distinct the Curie point, to a certain limit, below which the magnetization again drops off.

It is interesting to note that the reaction at the third stage of tempering was found to take place extremely rapidly at 345° C (650° F), as measured at room temperature on specimens of Steel C (1.02 per cent carbon) after tempering for various intervals. The data is plotted in Figure 34, and shows that after only one minute (0.017 hours) at temperature there is practically no further magnetic change. The
austenite has all been decomposed for there is a great increase in magnetization during the first minute.

The third stage of tempering accounts for three-fourths of the contraction caused by the decomposition of martensite into ferrite and cementite, while the contraction to the ill-defined cubic structure during the first stage takes care of the remainder.

From a consideration of all this information, it must be concluded that (1) cementite as such is not present prior to the third stage of tempering, (2) cementite is only the final form of the precipitate which has its genesis and growth during the third stage of tempering, and (3) this precipitate has its genesis in the poorly formed sub-precipitate established during the first and second stages of tempering.

Recently the author's attention has been directed to a paper by Arbusow and Kurdjumow[^52], in which it was stated that the first decomposition of martensite was found to be accompanied by the precipitation of a new carbide phase, which is highly dispersed and has a different structure than Fe₃C. With an increasing tempering temperature to just over 300°C (570°F) the structure slowly changes to that of Fe₃C, and rapidly between 350 and 380°C (660 and 715°F). This work was carried out on single crystals of martensite studied by X-ray diffraction. It appears that the changes taking place and
FIGURE 34. Effect of time of tempering at 650° F on magnetization of Steel C, 1.02 per cent carbon (measured at room temperature).
reported by Arbusow and Kurdjumow are identical with those discussed above. This tends to confirm the hypothesis presented here for the nature of structure changes during tempering.

(e) Stress Relief. As yet no mention has been made of the unusual behavior of the magnetization curve at low fields in the temperature range between the first and second stages of tempering (between 160 and 250° C (320 and 450° F)). The normal temperature coefficient of magnetization is negative, and indeed at high fields that appears to be the case in quenched as well as annealed steels. But at an applied field of only 265 gauss, the magnetization is seen to increase throughout this range of temperatures rather than decrease. This is well illustrated in Figure 22, page 81, but may be observed in all of the other standard heating curves. This affect has been attributed to stress relief, mostly for want of a more definite assignation. Nothing has been encountered in this work which would tend to refute this hypothesis. Indeed, some evidence may be presented in support of it.

As more stresses are present, the thermal coefficient of magnetization would be expected to become more and more positive if a positive slope were at all indicative of their presence. Figure 23, page 85, shows that after cooling from 150° C (300° F) and 195° C (400° F) the slope of the curve
on heating becomes less and less positive. This would indicate that whatever was causing the positive slope was gradually being eliminated. Since such behavior would be expected if stresses were the cause and since no structural changes were observed in this temperature range, the relief of those stresses are manifested.

Isothermal reaction curves at 1500°C (3000°F) are given in Figures 26, page 90, and 35. Figure 26 shows the curves obtained from measurements made at temperature as a part of the run shown in Figure 24, page 87. Both of these curves show that the magnetization gradually increases with time, while there is a slight decrease in the volume. Figure 35, obtained for Steel C after tempering for various times and cooling to room temperature before measuring, was carried out to 500 hours, as compared to but 18 for Steel B. This long period of time was apparently enough to cause some austenite to decompose, and to produce an increase in specific volume as well as in magnetization.

The increased magnetization shown for Steel B (0.94 percent carbon) in Figure 26 does not reflect decomposition of austenite, for no corresponding increase in volume was noted, nor was there any such indication of austenite decomposition when the specimen was heated to higher temperatures (see Figure 24). No austenite decomposed until a temperature of about 220°C (425°F) was reached.
FIGURE 35. Effect of time of tempering at 300° F on magnetization and specific volume of Steel C, 1.02 per cent carbon (measured at room temperature).
(5) **Effect of Carbon Content.** The effect of carbon content on the changes in magnetization and in volume during tempering is shown in Figures 36, 21, 20, 57 and 58. These curves are for Alloy 4 (0.63 per cent carbon), Alloy 9 (0.95 per cent carbon), Steel B (0.94 per cent carbon), Steel C (1.02 per cent carbon) and Steel D (1.26 per cent carbon) respectively.

It is easily seen, by comparing these curves, that the increasing carbon content causes an increased contraction during the first stage of tempering until 1.02 per cent carbon is reached, after which the contraction tends to decrease. This effect lends itself to ready explanation, for while the unit contraction of martensite increases rapidly with carbon content (see Table VIII), the large amount of retained austenite present in the higher carbon content steels, which does not contribute to the reactions, tends to decrease the effect of martensite contraction. Increasing carbon content also results in a more pronounced maximum in magnetization during the second stage in tempering because of the larger amount of austenite retained. On the whole, however, the amount of carbon present over the range studied (0.63 to 1.26 per cent) does not seem to have a profound effect on the character or temperature of the changes found to take place, but only on their magnitude.

(6) **Effect of Supercooling.** Three specimens were quenched in water from the austenitizing temperature and then immediately supercooled by immersion in liquid nitrogen at a temperature of \(-196^\circ C\) (\(-321^\circ F\)), and holding there for 10 minutes after the specimen had come to temperature. The standard magnetization-dilatation curves
FIGURE 36. Standard magneto-dilatometer tempering curves; Alloy 4, 0.63 per cent carbon.
FIGURE 37. Standard magneto-dilatometer tempering curves for Steel C, 1.02 per cent carbon.
FIGURE 38. Standard magneto-dilatometer tempering curves, Steel D (1.26 per cent carbon).
made after this treatment on Alloys 4 (0.63 per cent carbon) and 9
(0.95 per cent carbon) and Steel B (0.94 per cent carbon) are shown
in Figures 39 to 41 respectively.

Comparing these curves with those for the same alloys not super-
cooled, as shown in Figures 36, 21 and 20, it is observed that except
in the case of Alloy 4 (0.63 per cent carbon) the peak in magnetization
of the second stage of tempering is markedly decreased in prominence
and is displaced to a slightly lower temperature, and the values of
magnetization at room temperature prior to tempering are considerably
higher. In addition, the contraction observed in the first stage is
more pronounced, and the slight expansion characteristic of the second
stage is entirely eliminated.

Alloy 4 (0.63 per cent carbon) did not seem to be appreciably
affected by the supercooling; only slight deviations from the standard
curves obtained after quenching to room temperature only are observable.

These effects are caused by a decrease in the amount of retained
austenite brought about by the supercooling. The effect of austenite
upon the peak in the magnetization curve is smaller, the less austenite
present. The increased first stage contraction can, according to the
same reasoning, be attributed to an increase in the amount of marten-
site contributing to the reaction. In the case of Alloy 4 (0.63 per
cent carbon) the amount of austenite retained at ordinary temperatures
was so small that further cooling did not seem to cause an appreciable
decrease of its amount.
FIGURE 39. Standard magneto-dilatometer tempering curves; Alloy 4 (0.63 per cent carbon) supercooled.
FIGURE 40. Standard magneto-dilatometer tempering curves; Alloy 9 (0.95 per cent carbon) supercooled.
FIGURE 41. Standard magneto-dilatometer tempering curves; Steel B (0.94 per cent carbon) supercooled.
B. **X-ray Work**

In addition to the X-ray diffraction photograms made at room temperature in order to establish the amount of austenite present, a series of photograms were made of specimens of Steels C (1.02 per cent carbon) and D (1.26 per cent carbon) quenched and tempered for various times at 100° C (210° F). These photograms were made with platinum powder on the surface of the steel sample as a reference material.

Microphotometer traces of the photograms thus obtained are reproduced in Figures 42, 43, 44. The height of the platinum (200)\(_x\) line should not be taken as an indication of any sort, but only its position should be considered, for the amount of powder sprinkled on the surface of the steel controls its intensity.

Figure 42 represents the traces obtained from films made on Steel C (1.02 per cent carbon) tempered at 100° C (210° F). The distinct tetragonality of martensite is clearly seen in the as-quenched curve. After 10 minutes at 100° C (212° F), however, the tetragonality has begun to decrease slightly, and by the time 1.7 hours have elapsed the two martensite (101)\(_x\) and (110)\(_x\) lines have grown together into one very broad line, indicative of the decomposition product. The position of this single (110)\(_x\) line shifts slowly to higher angles, representing a slightly decreasing parameter, and the line becomes somewhat less broad as time is increased. After 167 hours, however, the line is still very broad and represents a higher value of the parameter than the ferrite line of annealed steel.
FIGURE 42
Steel C (1.02 C)
Tempered at 212° F

Photographs of microphotometer traces showing shift in martensite lines during tempering.
A very similar type of coalescence and shifting of the martensite doublet on tempering at 100° C (210° F) is observed for Steel D (1.26 per cent carbon), as shown in Figure 45. In this case it appears that a somewhat longer time is required for complete loss of tetragonality, because a slight indication of the presence of tetragonality is still observable after 1.7 hours' tempering, whereas complete coalescence of the doublet was observed for Steel C (1.02 per cent carbon) in the same time. It would be expected that a higher carbon content would require a longer time for complete decomposition to the product of the first stage of tempering, particularly if carbon diffusion out of the matrix into the higher concentration transition precipitate takes place.

At 150° C (300° F) the decomposition of tetragonal martensite, the first-stage product, takes place much more rapidly, as is shown in Figure 44 for Steel C (1.02 per cent carbon). In this case after only 10 minutes the tetragonality has disappeared and the single broad "cubic" line appears.

These results are conversant with the magnetic and dilatometric data obtained on the same steel, and support the explanation of the mechanism of the first stage of tempering based thereon.

C. Hardness Results

(1) Room Temperature. The hardnesses obtained on aging specimens of Steels C (1.02 per cent carbon) and D (1.26 per cent carbon) at room temperature for 167 hours are plotted in Figure 45a. These curves indicate clearly that a maximum in hardness is reached after about one day at room temperature, after which the hardness decreases. The reason
FIGURE 45. Effect of time of tempering on hardness of Steels C (1.02 per cent carbon) and D (1.26 per cent carbon). (Measurements made at room temperature.)
for this maximum is not apparent, for in the same period of time very little change was observed either in magnetization or in specific volume (see Figures 29 and 30), which implies that no definite structural change has taken place.

The lower hardness recorded for Steel D (1.26 per cent carbon) is attributed to the relatively large amount of austenite retained. Austenite is very soft compared to martensite, and therefore causes the initial hardness to fall below 60 Rockwell C.

In a way the hardness value of 59 Rockwell C recorded for a specimen containing as much as 43 per cent austenite is very remarkable because of the low inherent hardness of the austenite.

(2) Hardness After Tempering at 150° C (300° F). Tempering Steel C (1.02 per cent carbon) at 150° C (300° F), as shown in Figure 45b, causes an initial increase in hardness. However, as the tempering time is increased, the relief of stresses causes the hardness to fall off noticeably.

This is evidence that the decomposition of tetragonal martensite, as has taken place in the first stage of tempering, has brought about a definite increase in hardness. As shown in Figure 35, the first stage is completed at least by the end of 0.17 hours, which corresponds to the maximum in the hardness curve. After that time operating factor is stress relief. Therefore, it appears that stress relief in this range causes a decrease in hardness. This phase of the tempering problem, being contrary to previous ideas as to the operation of these phenomena on hardness should be investigated much more thoroughly and critically.
(3) Hardness After Tempering at 260° C (450° F). At 260° C (450° F) the hardness-time curves for Steels C (1.02 per cent carbon) and D (1.26 per cent carbon) are not at all similar. The curve for Steel C (1.02 per cent carbon), as shown in Figure 45c, indicates a marked decrease in hardness in the first 10 minutes of tempering, and thereafter a less rapid decrease. This is apparently caused by the rapid relieval of quenching and transformation stresses on first heating, and thereafter by the gradual formation of cementite that takes place in the third stage of tempering.

On the other hand, Steel D (1.26 per cent carbon) shows an initial increase in hardness, which does not reach a maximum until after 5 or 4 hours. This increase in hardness, caused by the decomposition of austenite in the second stage of tempering, is enough to bring the hardness of Steel D (1.26 per cent carbon) above that of Steel C (1.02 per cent carbon), which should be expected from consideration of the carbon contents of the specimens.
VII. CONCLUSIONS

The data presented in the preceding chapter lead to the following conclusions.

(1) Commercial plain carbon steels behave during tempering after quenching in much the same way as steels of a relatively high degree of purity; the common elements present in commercial plain carbon steels cause no important distinctive tempering peculiarities.

(2) The amount of austenite retained in quenched plain carbon steels is dependent more upon the carbon content of the austenite than upon the presence of small amounts of other elements.

(3) Tempering plain carbon steels may be divided into three stages based upon structural changes.

(4) The first stage of tempering, between 90 and 160° C (195 and 320° F), is characterized by a contraction, a slightly decreased magnetization, a slightly increased hardness, and the loss of tetragonality of martensite. The cause of these changes is the formation of a relatively stable sub-precipitate, having a higher carbon concentration than the martensite, and probably the result of a very limited amount of diffusion.

(5) The second stage of tempering, between 230 and 310° C (450 and 590° F), is characterized by an expansion, a marked increase in magnetization, an increased hardness in steels containing much retained
austenite, and the disappearance of austenite. These phenomena are caused by the transformation of retained austenite into a ferritic product not unlike the first martensite decomposition product.

(6) The third stage of tempering, between 265 and 360° C (510 and 675° F), overlaps the second stage somewhat, and is caused by the genesis and development of cementite. It is characterized by a decrease in volume, a decrease in magnetization as the precipitate becomes more and more like cementite and loses its ferromagnetism and a decrease in hardness. True cementite does not actually exist until a temperature of about 360° C (675° F) is attained.

(7) All these phenomena will occur at somewhat lower temperatures than those ascribed to them if given enough time. This fact indicates they are all dependent upon diffusion for their operation.

(8) Between 160 and 250° C (195 and 450° F) and in all probability to some extent below and above these temperatures a certain amount of stress relief takes place, resulting in an increased magnetization, particularly at low fields, and a slight decrease in hardness.

(9) The precipitation taking place during the first stage of martensite decomposition results in an increased hardness in the steel, while stress relief at slightly higher temperatures causes a softening without an appreciable structural change.
VIII. SUGGESTIONS FOR FURTHER WORK

Among the many interesting and more specialized subjects that should be investigated carefully to throw more light on the mechanism of tempering in plain carbon steels are:

(1) Calculations, based on the known radii of the iron and carbon atoms and the crystal structures involved, to determine the physical possibilities of the various transformations proposed. For example, the shift of the carbon atom producing cubic martensite, and the ease with which the cementite lattice may be generated from the martensite lattice are subjects of great interest and theoretical importance.

(2) X-ray diffraction studies of the austenite line. Does its sharpness change during the first and second stages of tempering, indicating stress relief? Does its position change during tempering at any stage, indicating the loss or pickup of carbon? May the decomposition of austenite during the second stage of tempering be followed by observing the austenite line intensity, and in what way would this correlate with the magnetic and dilatometric data?

(3) X-ray diffraction studies of the martensite lines; how the doublet closes during the first stage of tempering should be carefully worked out, and also the observation of change in sharpness and position of the single line after the doublet has disappeared as tempering proceeds to higher temperatures is important.
(4) More extensive hardness measurements as tempering proceeds. While a great many hardness-tempering curves have been constructed, there is still need of careful correlation of hardness changes with the stages of the tempering process. Both hot hardness and ordinary hardness measurements would supply valuable information.

(5) Development of a more sensitive technique for determining the amount of austenite present by the specific volume method. The major source of error is the measurement of the martensite lines. If those lines can be made sharper, or if higher indices lines could be used, the method would be rendered much more accurate.
BIBLIOGRAPHY


DISCLAIMER NOTICE

MISSING PAGE(S)

138
Appendix I

CALIBRATION OF MAGNET

A. Standardizing the Ballistic Galvanometer

For a ballistic galvanometer such as is used in the magneto-dilatometer constructed by Zmeskal\textsuperscript{34}, the throw is proportional to the quantity of current discharged in the secondary circuit, or

\[ Q = Gd \]  \hspace{1cm} (1)

If a mutual inductance is used for standardizing the galvanometer, the equation

\[ G = \frac{M}{r} \left( \frac{i}{d} \right) \]  \hspace{1cm} (2)

applies, where \( G \) is the galvanometer constant, \( M \) the mutual inductance in millihenries, \( r \) the resistance of the secondary circuit and galvanometer, \( i \) the current applied to mutual inductance, and \( d \) the observed deflection.

Using a 50 millihenry mutual inductance, the data given in Table IX were obtained.

The two values of \( G \) obtained, \( 1.117 \times 10^{-8} \) and \( 1.121 \times 10^{-8} \), enable the value \( 1.12 \times 10^{-8} \) to be used as the galvanometer constant without any element of doubt.

B. Calibration of the Magnet

To calibrate the magnet, using current reversal and air as the only core material, from equation 8 in Zmeskal's thesis\textsuperscript{34}, it is seen that the applied field, \( H \), is given by

\[ H = \left( \frac{Gr}{2AS} \right) D \times 10^8 \]  \hspace{1cm} (3)
TABLE IX
Standardization of Ballistic Galvanometer

A. With Pickup Coil in Circuit

\[ r = 6490 \text{ ohms, } M = 50 \times 10^{-3} \text{ henries, } \frac{M}{r} = 7.70 \times 10^{-6}; \]
\[ r = 6450 \text{ ohms, } M = 50 \times 10^{-3} \text{ henries, } \frac{M}{r} = 7.75 \times 10^{-6} \]

<table>
<thead>
<tr>
<th>Current Amps.</th>
<th>Observed Deflection</th>
<th>i/d</th>
</tr>
</thead>
<tbody>
<tr>
<td>19.85 \times 10^{-3}</td>
<td>13.6</td>
<td>14.60 \times 10^{-2}</td>
</tr>
<tr>
<td>20.70</td>
<td>14.4</td>
<td>14.38</td>
</tr>
<tr>
<td>23.06</td>
<td>16.0</td>
<td>14.42</td>
</tr>
<tr>
<td>62.24</td>
<td>43.0</td>
<td>14.47</td>
</tr>
<tr>
<td>102.23</td>
<td>70.3</td>
<td>14.56</td>
</tr>
<tr>
<td>124.04</td>
<td>85.4</td>
<td>14.52</td>
</tr>
<tr>
<td>149.35</td>
<td>102.3</td>
<td>14.60</td>
</tr>
<tr>
<td>220.78</td>
<td>152.1</td>
<td>14.52</td>
</tr>
<tr>
<td>299.76</td>
<td>208.0</td>
<td>14.41</td>
</tr>
</tbody>
</table>

Average: \( \frac{i}{d} = 14.50 \times 10^{-2} \); \( G = 1.117 \times 10^{-8} \)

B. Without Pickup Coil in Circuit

<table>
<thead>
<tr>
<th>Current Amps.</th>
<th>Observed Deflection</th>
</tr>
</thead>
<tbody>
<tr>
<td>62.42 \times 10^{-3}</td>
<td>43.5</td>
</tr>
<tr>
<td>102.47</td>
<td>71.0</td>
</tr>
<tr>
<td>124.50</td>
<td>85.9</td>
</tr>
<tr>
<td>143.54</td>
<td>99.0</td>
</tr>
<tr>
<td>203.88</td>
<td>141.1</td>
</tr>
<tr>
<td>285.15</td>
<td>197.4</td>
</tr>
</tbody>
</table>

Average: \( \frac{i}{d} = 14.45 \times 10^{-2} \); \( G = 1.121 \times 10^{-8} \)
From the above redetermination of $G$, we have $Gr = 7.225 \times 10^{-5}$.

$A$ is the cross-sectional area of the coil, measured to be 0.945 square centimeters, and $S$ is the number of turns in the secondary, 114. $D$, of course, is the measured galvanometer deflection.

We thus determine that

$$H = 33.5 \ D \quad (4)$$

Experimentally, it is found that with air alone as a core material a current of 7.81 amperes through the primary produces a deflection of 29.8. This current, then, corresponds to an applied field of $H = 1000$ gauss, and serves as a calibration standard.

Table IX has shown that the deflection of the galvanometer is linear with respect to the current in primary in mutual inductance; this current in turn is directly proportional to the applied field, air being the core material. It is seen, therefore, that Table X can be constructed, giving the applied field in terms of gauss for any current introduced into the primary winding.

This calibration differs but slightly from Zmeskal's, but has been used throughout most of the work reported in this thesis.
TABLE X

Calibration of Magnet

<table>
<thead>
<tr>
<th>Applied Field (Gauss)</th>
<th>Primary Current (Amps.)</th>
<th>Milli- volts*</th>
<th>Applied Field (Gauss)</th>
<th>Primary Current (Amps.)</th>
<th>Milli- volts*</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>0.39</td>
<td>1.30</td>
<td>800</td>
<td>6.25</td>
<td>20.83</td>
</tr>
<tr>
<td>100</td>
<td>0.78</td>
<td>2.60</td>
<td>900</td>
<td>7.03</td>
<td>23.43</td>
</tr>
<tr>
<td>200</td>
<td>1.56</td>
<td>5.21</td>
<td>1000</td>
<td>7.81</td>
<td>26.03</td>
</tr>
<tr>
<td>265</td>
<td>2.07</td>
<td>6.90</td>
<td>1100</td>
<td>8.59</td>
<td>28.63</td>
</tr>
<tr>
<td>300</td>
<td>2.34</td>
<td>7.81</td>
<td>1200</td>
<td>9.37</td>
<td>31.24</td>
</tr>
<tr>
<td>400</td>
<td>3.12</td>
<td>10.41</td>
<td>1300</td>
<td>10.15</td>
<td>33.84</td>
</tr>
<tr>
<td>500</td>
<td>3.91</td>
<td>13.02</td>
<td>1400</td>
<td>10.93</td>
<td>36.44</td>
</tr>
<tr>
<td>600</td>
<td>4.69</td>
<td>15.62</td>
<td>1500</td>
<td>11.71</td>
<td>39.05</td>
</tr>
<tr>
<td>700</td>
<td>5.47</td>
<td>18.22</td>
<td>1600</td>
<td>12.50</td>
<td>41.65</td>
</tr>
</tbody>
</table>

* Using an external shunt so that 3 amperes is equivalent to 10 millivolts on the measuring potentiometer.
Appendix II

CALCULATION OF LATTICE PARAMETERS

The lattice parameters of austenite and martensite which were obtained in this thesis were calculated from measurements taken on an X-ray film exposed in either the Phragmen No. 2 or No. 2A camera, both of which have ranges of \( \sin^2 \theta \) from 0.2321 to 0.7014.

A pair of platinum lines, the \((200)\alpha\) and \((220)\alpha\), obtained on the same film at the same time as the austenite and martensite lines, were made from platinum powder sprinkled on the surface of the steel exposed to X-rays, and were used as the standard reference points from which the austenite and martensite line positions were measured. Table V (page 55) in the text gives the relative position of these lines on the films.

A. Preparation of Platinum Powder

The platinum powder was carefully prepared for use, and its contamination scrupulously avoided. The platinum was originally obtained as 1/8 inch wire from the Chemical Stock Room. Filings were made with a fine, sharp file. These filings were screened into four groups, 400 mesh, 500 mesh, 200 mesh and the remainder coarser than 200 mesh. It was later found, however, that only the 400 and 500-mesh powders were satisfactory.

The screened powder was annealed for 30 minutes at 540° C (1000° F) to bring about a fine grained recrystallization. Its parameter was carefully measured on a back reflection camera and found to be 3.9145 Å.
B. Calculation of Platinum Lines

Chromium radiation was employed, the value of the $K_\alpha$ radiation being $\lambda = 2.28503$ Å.

Using the formula
\[ \lambda = \frac{2a \sin \theta}{\sqrt{k^2 + k^2 + l^2}} \]  

it was calculated that the platinum $(200)_\alpha$ line should appear at an angle $\theta = 0.623320$, and the $(220)_\alpha$ line at $\theta = 0.971130$. $\Delta \theta$ thus is 0.347810 radians.

If the camera radius is taken as 50 millimeters as a standard, the distance between the two lines should be
\[ \Delta S (\text{mm}) = 200 \Delta \theta = 69.56 \text{ millimeters} \]  

If the measured distance on the film was other than 69.56 millimeters between the platinum lines, all the values were corrected in relation to this. Film shrinkage or effective variation in camera radius caused by misplacement of the specimen on the periphery was thus accounted for.

C. Calculation of Austenite Parameter

The austenite line, measured with respect to the platinum $(200)_\alpha$ line, was corrected for any deviations from the standard lengths as noted above.

For the austenite $(200)_\alpha$ line, the value of $a$ may be computed from the equation
\[ a = \frac{\lambda}{\sin \theta} \]  

where $\lambda$ is the wave length of chromium $K_\alpha$ radiation, 2.28503 Å, and $\sin \theta$ is obtained from
\[ \theta = 0.62332 + \frac{\Delta s}{200} \]  

(4)

\(\Delta s\) being the displacement in millimeters of the austenite \((200)_{\alpha}\) line from the platinum \((200)_{\alpha}\) line.

D. Calculation of Martensite Parameter

The martensite a parameter may be calculated in a similar way, using the displacement of the martensite \((110)_{\alpha}\) line from the standard platinum \((200)_{\alpha}\) line. In this case, the angle \(\theta\) is given by

\[ \theta(110)_{\alpha} = 0.62332 - \frac{\Delta s}{200} \]  

(5)

and used in the formula

\[ a_{\alpha} = \frac{\lambda}{\sqrt{2} \sin \theta(110)_{\alpha}} \]  

(6)

for obtaining the martensite \(a_{\alpha}\) dimension.

Having determined the value of martensite \(a\), the \(c\) parameter is calculated from the equations

\[ \frac{a^2}{a^2 + c^2} = \frac{\lambda^2}{4 \sin^2 \theta(101)_{\alpha}} \]  

(7)

and

\[ c^2 = \frac{a^2 \left( \frac{a^2}{a^2 + c^2} \right)}{a^2 - \left( \frac{a^2}{a^2 + c^2} \right)} \]  

(8)

The angle \(\theta\) again is obtained by measuring the distance, \(\Delta s\), in millimeters, between the martensite \((101)_{\alpha}\) and platinum \((200)_{\alpha}\) lines and using

\[ \theta(101)_{\alpha} = 0.62332 - \frac{\Delta s}{200} \]  

(9)
Appendix III
ERRORS IN PARAMETER DETERMINATIONS

A. Austenite

The austenite (200) line, used for its parameter measurement, was able to be measured on a special viewing box with vernier scale to an accuracy of within $\pm$ 0.02 millimeters. This corresponds to an error of $\pm$ 0.0001 in $\theta$ as obtained in equation 3, Appendix II.

If

$$a_j = \frac{\lambda}{\sin \theta}$$  \hspace{1cm} (1)

$$da_j = \frac{2.285 \cos \theta d \theta}{\sin^2 \theta}$$  \hspace{1cm} (2)

For $\theta$ of about 0.68 radians, $\cos \theta = 0.778$ and $\sin \theta = 0.629$, the error in the austenite parameter $a_j$ amounts to $\pm$ 0.00045 A.

B. Martensite

The $a_\alpha$ of martensite is calculated from the position of the line (110) $\alpha$. This line, usually somewhat diffuse, could be measured only to $\pm$ 0.05 millimeters, which would correspond to an error of $\pm$ 0.00015 in $\theta$. From equation 6, Appendix II,

$$a_\alpha = \frac{\lambda}{\sqrt{2} \sin \theta}$$  \hspace{1cm} (3)

$$da_\alpha = \frac{2.285 \cos \theta d \theta}{\sqrt{2} \sin^2 \theta}$$  \hspace{1cm} (4)

For $\theta = 0.60$ radians, $\cos \theta = 0.825$ and $\sin \theta = 0.565$. Thus the error in the martensite $a$ parameter becomes $da_\alpha = \pm$ 0.0006 A.
In a tetragonal lattice,
\[
\frac{1}{D^2} = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2}
\]
(5)

For the martensite (101) line, \( h = 1, k = 0 \) and \( l = 1 \), so
\[
c_{\alpha} = \frac{a_{\alpha} D}{\sqrt{a_{\alpha}^2 - D^2}}
\]
(6)

To compute the total error in \( c_{\alpha} \), it is necessary to add the errors due both to errors in \( a_{\alpha} \) and in \( D \).

For the effect of \( a_{\alpha} \),
\[
\frac{\partial c_{\alpha}}{\partial a_{\alpha}} = \frac{D^3}{(a_{\alpha}^2 - D^2)^{3/2}}
\]
(7)

\( D \) is approximately 2.09, \( a_{\alpha} = 2.85 \) and \( da_{\alpha} = \pm 0.0006 \text{ Å} \), so \( dc_{\alpha} \) (with respect to \( da_{\alpha} \)) = \( \pm 0.0008 \text{ Å} \).

For the effect of \( D \), we have, for the (101) line,
\[
D = \frac{\lambda}{2 \sin \theta}
\]
or
\[
dD = \frac{\lambda \cos \theta}{2 \sin^2 \theta} \frac{d \theta}{d \theta}
\]
(8)

If \( \lambda = 2.28 \), \( \cos \theta = 0.84 \), \( \sin \theta = 0.55 \), and the error in measurement is \( \pm 0.05 \text{ millimeters} \) (\( \pm 0.00015 \text{ in} \) \( \theta \)), \( dD = \pm 0.0005 \).

From equation 6 above,
\[
\frac{\partial c_{\alpha}}{\partial D} = \frac{a_{\alpha}^3}{(a_{\alpha}^2 - D^2)^{3/2}}
\]
(9)

whence, \( dc_{\alpha} \) (with respect to \( D \)) = \( \pm 0.0016 \text{ Å} \).

Thus, the total error in the \( c_{\alpha} \) measurement will be \( \pm 0.0024 \text{ Å} \).

Summarizing, the errors in parameter measurement are as follows:

Austenite \( a \) \( \pm 0.0005 \text{ Å} \)

Martensite \( a \) \( \pm 0.0006 \text{ Å} \)

\( c \) \( \pm 0.0024 \text{ Å} \)
Appendix IV

ERRORS IN RETAINED AUSTENITE CALCULATIONS

The formula, given on page 60, for calculating the amount of retained austenite is

\[ A = \text{per cent austenite} = \frac{\bar{v}_\alpha - \bar{v}_T}{\bar{v}_\alpha - \bar{v}_y} \times 100 \quad (1) \]

From this,

\[ \frac{(\bar{v}_j - \bar{v}_T) \, d\bar{v}_\alpha + (\bar{v}_\alpha - \bar{v}_y) \, d\bar{v}_T + (\bar{v}_\alpha - \bar{v}_T) \, d\bar{v}_y}{(\bar{v}_\alpha - \bar{v}_y)^2} \]

\[ dA = 100 \quad (2) \]

For an eutectoid steel containing about 20 per cent austenite, the values for the factors in this equation are \( \bar{v}_j = 0.1247 \), \( \bar{v}_\alpha = 0.1300 \) and \( \bar{v}_T = 0.1289 \). From the data in Appendix III, it is readily calculated that \( d \bar{v}_\alpha = 0.00016 \) and \( d \bar{v}_y = 0.00005 \). \( d \bar{v}_T \), measured, is about \( \pm 0.00003 \), after correcting for inclusions from the chemical analysis.*

We thus calculate that the maximum error in determining the amount of retained austenite, \( dA \), is \( \pm 3 \) per cent of austenite.

* The measured specific volume should be corrected for non-metallic inclusions. Assuming that the principal inclusions are MnS, a valid assumption for high carbon tool steels, the correction factor to be applied is that the measured specific volume should be reduced by 0.000033 cubic centimeters per gram for each 0.01 per cent sulfur present.
Since this error is calculated assuming all the errors act toward the same direction of deviation from the proper figure, and this would be a very exceptional case, the actual variation encountered is found to amount to 1 to 1.5 per cent of austenite. It appears that with so many different, but limited, sources of error, the chances of some of them tending to cancel the others are very good.
## Appendix V

**MISCELLANEOUS DATA ON ALLOYS AND STEELS USED**

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Carbon Weight %</th>
<th>Wt. (C in Solution)</th>
<th>Average Atomic Weight</th>
<th>Carbon Weight %</th>
<th>Atomic Weight (Ferrite)</th>
<th>Cementite</th>
<th>Atomic Weight</th>
<th>Carbon Atoms per Lattice Point</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>0.63</td>
<td>56.20</td>
<td>55.84</td>
<td>9.42</td>
<td>2.866</td>
<td>.0295</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>0.34</td>
<td>55.90</td>
<td>55.70</td>
<td>5.09</td>
<td>1.563</td>
<td>.0159</td>
<td></td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>0.95</td>
<td>56.38</td>
<td>55.84</td>
<td>13.21</td>
<td>4.272</td>
<td>.0446</td>
<td></td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>0.95</td>
<td>56.38</td>
<td>55.84</td>
<td>13.21</td>
<td>4.272</td>
<td>.0446</td>
<td></td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>0.78</td>
<td>56.28</td>
<td>55.84</td>
<td>11.67</td>
<td>3.529</td>
<td>.0566</td>
<td></td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>1.38</td>
<td>56.57</td>
<td>55.77</td>
<td>20.64</td>
<td>6.113</td>
<td>.0651</td>
<td></td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>1.44</td>
<td>56.62</td>
<td>55.80</td>
<td>21.54</td>
<td>6.366</td>
<td>.0680</td>
<td></td>
<td></td>
</tr>
<tr>
<td>17</td>
<td>1.17</td>
<td>56.47</td>
<td>55.81</td>
<td>17.50</td>
<td>5.221</td>
<td>.0551</td>
<td></td>
<td></td>
</tr>
<tr>
<td>18</td>
<td>0.70</td>
<td>56.18</td>
<td>55.78</td>
<td>10.47</td>
<td>3.176</td>
<td>.0328</td>
<td></td>
<td></td>
</tr>
<tr>
<td>19</td>
<td>0.67</td>
<td>56.17</td>
<td>55.79</td>
<td>10.02</td>
<td>3.043</td>
<td>.0314</td>
<td></td>
<td></td>
</tr>
<tr>
<td>21</td>
<td>0.92</td>
<td>56.31</td>
<td>55.78</td>
<td>13.76</td>
<td>4.142</td>
<td>.0432</td>
<td></td>
<td></td>
</tr>
<tr>
<td>22</td>
<td>0.57</td>
<td>56.00</td>
<td>55.79</td>
<td>5.54</td>
<td>1.699</td>
<td>.0173</td>
<td></td>
<td></td>
</tr>
<tr>
<td>23</td>
<td>0.79</td>
<td>56.28</td>
<td>55.83</td>
<td>11.82</td>
<td>3.573</td>
<td>.0371</td>
<td></td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>0.49</td>
<td>56.09</td>
<td>55.78</td>
<td>7.33</td>
<td>2.240</td>
<td>.0229</td>
<td></td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>0.94</td>
<td>56.30</td>
<td>55.76</td>
<td>14.06</td>
<td>4.229</td>
<td>.0442</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>1.02</td>
<td>56.32</td>
<td>55.71</td>
<td>15.26</td>
<td>4.576</td>
<td>.0480</td>
<td></td>
<td></td>
</tr>
<tr>
<td>D</td>
<td>1.26</td>
<td>56.47</td>
<td>55.72</td>
<td>18.85</td>
<td>5.605</td>
<td>.0594</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
BIографICAL NOTE

The author was born in Wilkinsburg, Pennsylvania, on January 20, 1918, but moved a few years later to New Kensington, Pennsylvania. He graduated from the New Kensington High School in 1934, and in the Fall of that year entered the Carnegie Institute of Technology. He received the degree of Bachelor of Science in Metallurgical Engineering from Carnegie Institute of Technology in 1938.

Following graduation, he was employed for a year on the technical staff of the Metallurgical Department of the Aluminum Research Laboratories, New Kensington, Pennsylvania.

In 1939 he was appointed an Assistant in Metallography at the Massachusetts Institute of Technology, and entered the Graduate School taking courses leading toward the degree of Doctor of Science in Metallurgy.

He is now a Research Assistant in the Department of Metallurgy at the Massachusetts Institute of Technology, conducting an investigation into the dimensional stability of metals.
Of the metallurgical materials in use today one of the most vital is tool steel. Of its many varieties the most widely used is plain carbon tool steel. In order to render plain carbon tool steel hard enough for practical use, it is necessary to quench it so that martensite is formed; to render it tough enough it must be tempered, or re-heated to a low temperature immediately after quenching. During the tempering treatment certain changes take place in the constituents making up the hardened steel. It is of utmost importance to understand the nature of these changes so that tempering may be more accurately controlled and the final properties desired more readily attainable.

The first step in this work was to establish the constitution of the steel as quenched, so that changes on tempering could be accurately interpreted. This was done by (1) quenching from such a temperature that only austenite and martensite could be present, (2) measuring the amount of each of these phases.

A new technique was developed for determining the amount of retained austenite. The lattice parameters of both austenite and martensite were measured by means of X-ray diffraction, and the specific volume of each of them calculated therefrom, the compositions being known. By correlating this figure with the actual specific volume of a sample as measured, the amount of austenite was easily obtained.
Calculations of the errors inherent in these measurements show that the maximum error is ± 3 per cent of austenite; actually the values obtained checked much closer than that, for all the errors may not operate in the same direction.

In order to determine the effect of normal alloying elements, such as manganese and silicon, in commercial steels, a number of high purity alloys were made by melting together electrolytic iron and graphite in a vacuum induction furnace. These alloys were then forged to sizes for use in the experimental apparatus.

Tempering of quenched steels and high purity iron-carbon alloys having carbon contents from 0.63 per cent to 1.38 per cent was carried out, during which magnetization, length changes, specific volume, and in some cases hardness and X-ray diffraction patterns were observed. Measurements were made of magnetization (at applied fields of 1000 and 265 gauss) and of dilatation during continuous heating and cooling for a variety of cycles, and also during tempering at various constant temperatures. These data were correlated with the results of magnetization, specific volume, X-ray diffraction patterns, and hardness measurements made at room temperature after tempering at various temperatures for various times.

It was found first that the high purity alloys behaved no differently than the commercial steels, save for reactions taking place slightly more rapidly. Therefore most of the work was concentrated on the commercial steels.

Tempering of plain carbon steels appears to result in a three-stage structural change, during which the original austenite-martensite mixture is transformed to a ferrite-cementite aggregate.
The first decomposition, which takes place in martensite alone, is located approximately between 90 and 160°C (195 and 320°F) and results in the formation of a transition precipitate from the martensite. This sub-precipitate is shown definitely to be not cementite, as heretofore supposed by one school of thought. The presence of the sub-precipitate causes a diminishing amount of carbon in the matrix, and therefore results in the loss of tetragonality of the martensite, which degenerates into an ill-defined cubic structure in which some carbon is undoubtedly still dissolved. Martensite does not collapse from a tetragonal to a cubic structure merely by a shift of the carbon atom in the lattice without any precipitation, as has also been postulated.

The second decomposition, which involves austenite, takes place approximately between 230 and 310°C (450 and 590°F) on continuous heating. During this range of temperatures the retained austenite decomposes to a structure not unlike that of tempered martensite. It is ferritic in nature, but contains some sort of carbon-rich (with respect to ferrite) sub-precipitate which has also been shown not to be cementite.

The third stage of decomposition during tempering, taking place between 265 and 360°C (510 and 675°F), involves the gradual diffusion of carbon out of the ferritic matrix to form cementite from the sub-precipitate existing heretofore. On continuous heating cementite was not found to exist as such below about 360°C (675°F).
The anomalous behavior of the magnetization curves at low fields in the temperature range of 160 and 230° C (195 to 450° F) has been attributed to the relief of stresses both in martensite and in its decomposition product on heating.

Some indications were obtained that the first decomposition of martensite results in slightly increased hardness, while the effect of stress-relief is to lower hardness. This is contrary to the general conception of the effects operating on hardness in this type of material. Further and more complete hardness work should be carried out to clarify this point.

Other phenomena observed during the course of this study were that the amount of retained austenite increases sharply with carbon content, and supercooling to liquid nitrogen temperatures decreases the amount of retained austenite in all except the 0.63 per cent carbon alloy.

All the temperatures quoted above were obtained on heating at a rate of 3° C (5.4° F) per minute; the same reactions would take place at somewhat lower temperatures if the heating rate were slower, or if the steel were held for a long time at the lower temperature. All the reactions are thus indicated to involve a certain amount of diffusion.