A transmission electron microscopy study of some high strength plain carbon steels

George Joseph Vytanovych

Follow this and additional works at: http://scholarsmine.mst.edu/masters_theses

Part of the Metallurgy Commons

Department: Materials Science and Engineering

Recommended Citation

A TRANSMISSION ELECTRON MICROSCOPY
STUDY OF SOME HIGH STRENGTH
PLAIN CARBON STEELS

BY

GEORGE J. VYTANOVYCH

A

THESIS

submitted to the faculty of

THE UNIVERSITY OF MISSOURI AT ROLLA

in partial fulfillment of the requirements for the

Degree of

MASTERS OF SCIENCE IN METALLURGICAL ENGINEERING

Rolla, Missouri

1967

Approved by

Fred Kiphinga (Advisor)

Thomas O'Keefe

L. Moeller
ABSTRACT

Methods of preparing foils of high strength, heat treated, plain carbon steels for examination in the electron microscope by the transmission technique were perfected and are described. Two processes for the initial thinning of a bulk sample were successful. A chemical process was found to be more rapid but not satisfactory for small samples. A mechanical process was slower, but was applicable to the smaller specimens. Electro-polishing the thinned material yielded acceptable foils from which photomicrographs of good quality were obtained.

The microstructure of the high strength steel samples showed typical tempered martensite. No reasons for the differences in ductility of different heats of steel or for the differences in ductility of a given steel, when heat treated differently, were found.
ACKNOWLEDGEMENT

The author wishes to express his gratitude to Dr. Fred Kisslinger for his guidance, advice, encouragement, and assistance during the preparation of this thesis.

The author is grateful for the help of Dr. H. P. Leighly, Jr. in the transmission electron microscopy work.

The author wishes to thank Robert Hollenbeck, who supplied some of the heat treated and tensile tested samples.

The author also wishes to express his gratitude to the staff of the Metallurgical Engineering Department for their assistance and cooperation.
<table>
<thead>
<tr>
<th>TABLE OF CONTENTS</th>
<th>PAGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>LIST OF FIGURES...............................................</td>
<td>v</td>
</tr>
<tr>
<td>LIST OF TABLES..................................................</td>
<td>vii</td>
</tr>
<tr>
<td>I. INTRODUCTION..................................................</td>
<td>1</td>
</tr>
<tr>
<td>II. LITERATURE SURVEY...........................................</td>
<td>3</td>
</tr>
<tr>
<td>A. Specimen Preparation........................................</td>
<td>3</td>
</tr>
<tr>
<td>B. Tempering of High Strength Steel.........................</td>
<td>7</td>
</tr>
<tr>
<td>C. Hardness of Tempered Martensite.........................</td>
<td>11</td>
</tr>
<tr>
<td>II. EXPERIMENTAL PROCEDURE.....................................</td>
<td>13</td>
</tr>
<tr>
<td>A. Materials....................................................</td>
<td>13</td>
</tr>
<tr>
<td>B. Specimen Preparation for Transmission Electron Microscopy</td>
<td>16</td>
</tr>
<tr>
<td>C. Electron Microscopy..........................................</td>
<td>32</td>
</tr>
<tr>
<td>IV. EXPERIMENTAL RESULTS AND DISCUSSION.....................</td>
<td>37</td>
</tr>
<tr>
<td>A. General........................................................</td>
<td>37</td>
</tr>
<tr>
<td>B. Interpretation of Photomicrographs........................</td>
<td>40</td>
</tr>
<tr>
<td>1. As-Quenched Specimens.......................................</td>
<td>40</td>
</tr>
<tr>
<td>2. N-Series Specimens...........................................</td>
<td>47</td>
</tr>
<tr>
<td>3. R-Series Specimens...........................................</td>
<td>56</td>
</tr>
<tr>
<td>C. Correlation of Microstructure with Changes in Mechanical Properties</td>
<td>64</td>
</tr>
<tr>
<td>V. CONCLUSIONS....................................................</td>
<td>70</td>
</tr>
<tr>
<td>BIBLIOGRAPHY......................................................</td>
<td>72</td>
</tr>
<tr>
<td>VITA...............................................................</td>
<td>76</td>
</tr>
</tbody>
</table>
# LIST OF FIGURES

<table>
<thead>
<tr>
<th>FIGURE</th>
<th>PAGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Mechanical Thinning Device</td>
<td>19</td>
</tr>
<tr>
<td>2. Polishing Cup With Specimen In Place</td>
<td>20</td>
</tr>
<tr>
<td>3. Shaft Assembly</td>
<td>21</td>
</tr>
<tr>
<td>4. Circuit Diagram For Relay On Mechanical Thinning Device</td>
<td>24</td>
</tr>
<tr>
<td>5. Electropolishing Apparatus</td>
<td>27</td>
</tr>
<tr>
<td>6. Electropolishing Cell Showing Arrangement Of Sample And Electrodes Used For Final Polishing Operation</td>
<td>28</td>
</tr>
<tr>
<td>7. Bollman Method Of Preparing Thin Foils</td>
<td>29</td>
</tr>
<tr>
<td>8. The Hitachi llA Electron Microscope</td>
<td>33</td>
</tr>
<tr>
<td>9. Sectional Diagram Of Microscope Column</td>
<td>34</td>
</tr>
<tr>
<td>10. Specimen 2NM</td>
<td>41</td>
</tr>
<tr>
<td>11. Specimen 3NM</td>
<td>42</td>
</tr>
<tr>
<td>12. Specimen ANM</td>
<td>43</td>
</tr>
<tr>
<td>13. Specimen 2RM</td>
<td>44</td>
</tr>
<tr>
<td>14. Specimen 3RM</td>
<td>45</td>
</tr>
<tr>
<td>15. Specimen 2N4</td>
<td>48</td>
</tr>
<tr>
<td>16. Specimen 2N5</td>
<td>49</td>
</tr>
<tr>
<td>17. Specimen 3N4</td>
<td>50</td>
</tr>
<tr>
<td>18. Specimen 3N5</td>
<td>51</td>
</tr>
<tr>
<td>19. Specimen AN4</td>
<td>52</td>
</tr>
<tr>
<td>20. Electron Diffraction Pattern of Specimen 2N4</td>
<td>53</td>
</tr>
<tr>
<td>FIGURE</td>
<td>Description</td>
</tr>
<tr>
<td>--------</td>
<td>--------------------------------------------------</td>
</tr>
<tr>
<td>21.</td>
<td>Electron Diffraction Pattern of Specimen 2N5</td>
</tr>
<tr>
<td>22.</td>
<td>Electron Diffraction Pattern of Specimen 3N4</td>
</tr>
<tr>
<td>23.</td>
<td>Electron Diffraction Pattern of Specimen AN4</td>
</tr>
<tr>
<td>24.</td>
<td>Specimen 2RY</td>
</tr>
<tr>
<td>25.</td>
<td>Specimen 2RZ</td>
</tr>
<tr>
<td>26.</td>
<td>Specimen 3RY</td>
</tr>
<tr>
<td>27.</td>
<td>Specimen 3RZ</td>
</tr>
<tr>
<td>28.</td>
<td>Electron Diffraction Pattern of Specimen 2RY</td>
</tr>
<tr>
<td>29.</td>
<td>Electron Diffraction Pattern of Specimen 2RZ</td>
</tr>
<tr>
<td>30.</td>
<td>Electron Diffraction Pattern of Specimen 3RY</td>
</tr>
<tr>
<td>31.</td>
<td>Electron Diffraction Pattern of Specimen 3RZ</td>
</tr>
</tbody>
</table>
# LIST OF TABLES

<table>
<thead>
<tr>
<th>TABLE</th>
<th>PAGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>I. CHEMICAL COMPOSITIONS OF STEELS STUDIED</td>
<td>14</td>
</tr>
<tr>
<td>II. HEAT TREATMENT AND TENSILE TEST RESULTS FOR STEELS STUDIED</td>
<td>15</td>
</tr>
</tbody>
</table>
I. INTRODUCTION

A considerable amount of work has been performed to develop a high strength carbon steel by the use of heat treatment. During these investigations, it was found that steels of the same nominal chemical composition and similar mechanical properties in a soft condition, when heat treated to high strength showed a disparity in their mechanical properties. This was observed in the variations of tensile strength and ductility.

The structure of high strength carbon steel normally is composed of a dispersion of ε-carbide or cementite in a matrix of martensite, or a combination of both carbides in a martensite matrix, depending on the time and temperature of tempering. This structure is much too fine to be resolved and identified by optical microscopy or, in its earlier stages, by x-ray diffraction. However, with the advent of the electron microscope, the resolution of the structure has become possible.

Transmission electron microscopy is probably the best method to examine, in great detail, the internal structure of high strength steels, and to investigate the reason for differences in mechanical properties which can result from differences in structure. Metal in the thickness range of a few thousand angstroms becomes transparent to electrons, and due to certain diffraction conditions, contrast is obtained in the image. Any lattice displacement, such as imperfections
or second phases, produces a phase contrast effect, making it possible to reveal most of the structural features that exist in metals. It is especially applicable to the study of precipitate morphology, coherency, and distribution.

The purpose of this thesis was to investigate the differences in high strength carbon steels of the same nominal chemical composition and heat treatment, but displaying different mechanical properties. The electron microscope was used in this study, and an attempt was made to correlate the microstructure of the steels with the differences in the tensile properties. A large portion of the work had to be devoted to the development of a specimen preparation technique because, to a large extent, transmission electron microscope specimens were obtained from tensile test samples, in order to have material of known properties.
II. LITERATURE REVIEW

A. **Specimen Preparation**

The requirements for a transmission electron microscope specimen are the following: its sides should be approximately parallel, thin—five hundred to five thousand angstroms, and have an uncontaminated surface (1). The degree of transparency to electrons will depend on the atomic number of the material. The heavier metals must be thinner, while the lighter metals, such as aluminum, will be transparent up to a few microns thick. A clean surface is also very important because a thin layer of amorphous material that shows no contrast, can reduce the transparency of a specimen very markedly by giving a strong diffuse scattering of the electrons.

In general, the various specimen preparation techniques can be divided into three main groups (2):

a) Deposition

b) Deformation

c) Dissolution

Deposition methods consist of procedures for condensing metal vapors in a vacuum, precipitating thin crystals from aqueous solutions, and casting foils from the liquid state.

Takahashi and Ashinuma (3) have prepared thin foils by dipping a small ring below the surface of a metal which is held just above its melting point and then withdrawing it. The liquid attached to the ring by surface tension is thin
enough in some places for electron microscopy. Duwez, Willens, and Klement (4) developed a technique consisting of pneumatically propelling a drop of molten metal onto a cold surface. The metal is rapidly chilled and contains thin areas. This procedure has been called splat cooling. Both Weil and Read (5), and L. Reimer (6) prepared foils by electroplating nickel on copper or zinc, and stripping the thin electroplate from the cathode. Transmission foils were prepared by evaporation in a vacuum by Price (7) - zinc and cadmium, Takahashi and Trillat (8) - aluminum-copper alloys, and Pitsch (9) - iron. Specimens prepared by the deposition techniques are generally of limited use, since their transmission micrographs are seldom typical of bulk material.

A deformation process consisting of cutting the metal with diamond-bladed ultramicrotomes has been used, especially for the examination of multi-phase alloys. Reimer (10) has prepared foils of aluminum, nickel, iron, copper, gold, silver and platinum. This procedure gives a very severely-deformed sample.

For the most part, the above-mentioned techniques were utilized for specific alloys and produced specimens ready for transmission microscopy. However, in most cases, specimens are produced from bulk material by thinning in several steps. In the first step, the material is reduced to 0.001 - 0.010 inches thickness by a mechanical method such as grinding or machining. These procedures can deform the surfaces and, in some instances, the deformed layer can be quite deep. The
Material thinned in the first step is subsequently reduced to a thickness suitable for a transmission electron microscope sample, frequently by electropolishing.

It is possible to thin a bulk material by chemical etching without deforming the specimen surfaces. Keon and Pickering (11) used aqueous solutions of nitric (50%) and hydrofluoric (10%) acids for carbon and low alloy steels, and of nitric (45%), hydrofluoric (10%), and hydrochloric (15%) acids for stainless and high alloy steels. Cole, Bucklow, and Grigson (12) utilized a spark machining apparatus using a slotted rotating disk electrode five inches in diameter with the specimen facing the outer regions of the disk. The method has produced sheets 0.01 inches thick, and is suitable for aluminum alloys, tungsten, titanium, and austenitic and ferritic stainless steels. Kelly and Nutting (13) developed an electrolytic jet technique which, using hydrochloric acid and aqueous copper chloride, was able to thin bulk material at the rate of ten microns per minute over an area one-inch square. This method is especially useful for steel and other hard alloys.

The most straightforward and generally-used method for the final thinning procedure is electropolishing. Heidenreich (14) was the first to develop an electropolishing technique for use on aluminum and aluminum-copper alloys. He electropolished 0.005 inch disks in a solution of nitric and hydrochloric acids in methanol. The electropolishing produced holes at the center of the specimen, and the areas around the holes were thin.
enough to be transparent to electrons. Bollman (15) used pointed cathodes mounted close to the center of a metal disk. The specimen was electropolished until a hole appeared in the center, then the electrodes were moved away one to two centimeters and polishing continued. Perforation occurred at the edge of the lacquered coating around the disk, and continued toward the center of the hole. Foils were cut from the region near the junction of the two holes. The preferential polishing of a vertical specimen due to the formation of a heavy viscous layer has been utilized in the "window" technique, developed by Nicholson, Thomas, and Nutting (16) for use with aluminum alloys. Later, Tomlinson (17) used this method for making thin foils of magnesium, nickel, copper, iron and cobalt. This method consists of lacquering the edges of a thin sheet, so that only a one-inch square (window) is left uncoated, and mounting it vertically with a vertical cathode in an electropolishing solution. Perforation occurs at the top edge adjacent to the lacquer coating and advances downward. When perforation has extended about half-way down, the specimen is removed and washed, and foils cut from the edge of the hole. Another technique was developed for iron by Brandon and Nutting (18), utilizing the viscous layer. Using the "window" method, a sheet is polished down to about 20 microns. Then on one surface, an outline of a "figure of eight" is painted with a non-conducting lacquer. Electropolishing is continued until perforations occur at the top and sides of the specimen.
To overcome the relatively slow electropolishing of the material, Philips and Hugo (19, 20, 21) used an electrolytic jet technique. This method utilized the Diza-Electropol instrument and various Diza electrolytes to prepare copper alloy foils. This technique can be employed for thinning most metals.

One of the best handbooks on specimen preparation techniques for electron microscopic examination has been written by I. S. Brammar (22). It contains, in table form, detailed summaries of specimen preparation methods for a great number of metals for use with both the transmission and replica techniques of electron microscopy. Other articles by Kelly and Nutting (2), Thomas (23), and Hirsch and co-workers (1) summarize a number of techniques for the preparation of foils for use in transmission electron microscopy.

B. Tempering of High Strength Steel

Originally, Hanemann and Trager, as reported by Tekin and Kelly (24), suggested that three stages exist in the tempering of steel:

1. The decomposition of martensite and precipitation of \(\varepsilon\)-carbide.

2. The transformation of retained austenite.

3. The transition of \(\varepsilon\)-carbide to cementite.

On tempering an 0.9% C steel, Heidenreich (25) found a precipitate which was isomorphous with \(\varepsilon\)-Fe\(_3\)N and which
transformed to cementite at 350°C. Using x-ray diffraction, Jack (26) observed that the loss of tetragonality of martensite during the first stage of tempering (80°C - 160°C) was caused by the precipitation of a hexagonal, close-packed carbide, ε-carbide. During the third stage of steel tempering (260°C - 360°C) ε-carbide transforms to give a fine dispersion of thin platelets of cementite. Employing the replica method of electron microscopy, Cohen and co-workers (27) observed the formation of ε-carbide during the tempering of steel at 150°C - 250°C. The ε-carbide then progressively dissolved in the low carbon martensite matrix while tempering at 205°C - 315°C. The formation of cementite began at tempering temperatures of 230°C to 260°C. These tempering stages are expected to vary with tempering time and composition of steel (28), and all three stages might easily overlap.

In the early stages of the tempering of steel, the precipitate normally observed is ε-carbide (29). In spite of the fact that ε-carbide is known to exist in high silicon steels up to 650°C (30,31), cementite is normally the only carbide found above 300°C (29). Between the two stages where ε-carbide and cementite exist separately, there exists a range over which they co-exist. On the other hand, Eguchi and co-workers (32) observed, in an 0.4% steel, that ε-carbide dissolved completely below 300°C before cementite first appeared. Irvine and co-workers (33), however, observed some autotempered cementite in the as-quenched specimens.
Cementite, \(\varepsilon\)-carbide and \(\alpha\)-Fe have crystallographic similarities. Thus, the transformation of \(\varepsilon\)-carbide to cementite in situ is at least theoretically feasible; first by the rearrangement of the crystal lattice of \(\varepsilon\)-carbide to that of cementite, and then by gradual change in carbon concentration of the carbide by diffusion, bringing the composition to Fe\(_3\)C (26). However, recent work implies that the transformation does not take place in situ, but involves the gradual resolution of \(\varepsilon\)-carbide and simultaneous precipitation of cementite in different areas (32,34).

Since the late 1950's, the development of high-resolution electron microscopes and advances in specimen preparation techniques have given a great impetus to the study of tempering of high strength steels using transmission electron microscopy. Kelly and Nutting (35), and others (36, 37, 38) investigated the morphology of martensite, and concluded that there exist two types of martensite in plain carbon steels. In high carbon steels, the martensite consists of internally twinned plates. In low carbon steels, the martensite consists of single crystal needles. The absence of twinning in these needles is reflected in the Widmanstatten form of the carbide produced on tempering. Due to the high Ms temperature, the martensite needles formed just below the Ms temperature in low carbon steels temper on subsequent cooling during the quench. After tempering at 100°C - 300°C for one hour, little growth of the precipitate can be observed, but all the needles will contain the precipitate.
Tekin and Kelly (24) found very little significant precipitation of carbides at room temperature in high-carbon steel (0.8%), but tempering for two hours at 100°C - 150°C produced \( \varepsilon \)-carbide precipitates between the twins. After tempering two hours at 200°C, the \( \varepsilon \)-carbide particles were larger and fewer in number. This treatment also caused cementite to form on and across the twins. With increased tempering temperature, the total number of precipitate particles decreased, cementite particles coarsened, and the twins disappeared gradually.

Baker, Lauta, and Wei (39) studied the relationship between microstructure and toughness of steels and concluded that low fracture toughness in lightly tempered steels was the result of a high defect density and the occurrence of carbide films at the martensite plate and twin boundaries. Only when both the defects and carbide films were removed or modified did toughness increase. Tekin and Kelly (24) reported that in the very early stages of tempering the twinned martensite increased in hardness due to the formation of a fine coherent precipitate of \( \varepsilon \)-carbide. Further tempering caused the \( \varepsilon \)-carbide to coarsen and lose its coherency. This decreased the precipitation hardening effect, and as carbon continued coming out of solution, an overall softening occurred. The \( \varepsilon \)-carbide dissolved during further tempering, and the twins disappeared. This caused more softening of the structure.
C. Hardness of Tempered Martensite

A number of factors contribute to the hardness of martensite in plain carbon steel. Kelly (37) divided these factors into those that do not vary with carbon content, and those that do. The factors influencing the hardness of a given martensite were given as:

a) Basic hardness of the metal.
b) Grain size effect.
c) Work hardening from deformation caused by the transformation.

The carbon dissolved in the martensite has three additional hardening effects:

a) At low carbon contents, the carbon increases the hardness by pinning the dislocations produced during the austenite to martensite transformation.
b) Once the dislocations are saturated with carbon, a further increase in the dissolved carbon will increase the hardness by introducing internal strain.
c) Hardening due to the presence of internal twinning becomes more prevalent as carbon increases up to 0.8% C.

Furthermore, Kelly (37) stated that the relative number of twinned martensite plates varies sigmoidally from nearly zero at 0.1% carbon to 100% at 0.8% carbon and above. Therefore, the hardening effect caused by twinning should increase with increasing carbon content.
During the very early stages of tempering, the hardness of the martensite increases as a result of a precipitation hardening effect associated with the formation of a fine, coherent $\varepsilon$-carbide precipitate. As the precipitation process progresses, the solid solution hardening effect of carbon decreases. While the twin boundaries, themselves, interfere with movement of dislocations, twin boundaries containing fine precipitated carbides are even more effective in preventing the movement of dislocations. These hardening effects of the precipitated carbides counterbalance the softening resulting from the carbon coming out of solution. As tempering continues, the $\varepsilon$-carbide dispersion coarsens, and the precipitate begins to lose its coherency. Loss of coherency decreases the precipitation hardening effect, and with further decrease in the solid solution hardening effect due to continued carbide precipitation, there is an overall loss of hardness. Eventually, with further tempering, the $\varepsilon$-carbide dissolves and cementite platelets begin to form. These platelets grow with additional tempering and finally spheroidize. Softening of the structure continues throughout this part of the tempering process.
III. EXPERIMENTAL PROCEDURE

A. Materials

The compositions of the three steels used in this study are given in Table I. The structure of the steels in the as-received condition consisted of ferrite and coarse pearlite. Table II lists the samples studied, outlines their heat treatment and gives the tensile test data to be expected or actually obtained on the samples.

In the N-series of heat treatments, Steels No. 2 and 3 were austenitized for 20 minutes at 1450°F, quenched in oil at 140°F, and then tempered for 60 minutes at 400°F or 500°F. This heat treatment was selected from the preliminary work performed by Hollenbeck (40), who studied high strength, heat treated, plain carbon steels. Hollenbeck investigated six different heats of AISI 1065 steel supplied by Interlake Steel Corporation. Steel No. 3 was more ductile at high hardness than Steel No. 2, and tended to give much better properties at high strength levels.

Hollenbeck found that the heat treatments used on specimens 2N4, 2N5, and 3N4 produced tensile test samples that failed in the jaws of the tensile tester at relatively low loads and showed no ductility. The specimen 3N5 treatment gave a tensile strength of about 250,000 psi, but no ductility.

Hollenbeck developed a rapid heating hardening process which produced carbon steel specimens of about 300,000 psi
# TABLE I
CHEMICAL COMPOSITIONS OF STEELS STUDIES

<table>
<thead>
<tr>
<th>Steel Number</th>
<th>C</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
<th>Si</th>
<th>Cu</th>
<th>Ni</th>
<th>Cr</th>
<th>Mo</th>
<th>Sn</th>
<th>Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>.71</td>
<td>.68</td>
<td>.020</td>
<td>.040</td>
<td>.04</td>
<td>.01</td>
<td>.01</td>
<td>.01</td>
<td>.005</td>
<td>.006</td>
<td>.005</td>
</tr>
<tr>
<td>3</td>
<td>.65</td>
<td>.70</td>
<td>.014</td>
<td>.013</td>
<td>.05</td>
<td>.01</td>
<td>.01</td>
<td>.01</td>
<td>.009</td>
<td>.008</td>
<td>.005</td>
</tr>
<tr>
<td>A</td>
<td>.49</td>
<td>.78</td>
<td>.006</td>
<td>.022</td>
<td>.19</td>
<td>.06</td>
<td>.02</td>
<td>.05</td>
<td>--</td>
<td>.007</td>
<td>--</td>
</tr>
<tr>
<td>Sample Number</td>
<td>Hardening Time</td>
<td>Tempering Time</td>
<td>Mode of Failure</td>
<td>T.S. 1000 psi</td>
<td>Elongation Percent</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>---------------</td>
<td>----------------</td>
<td>----------------</td>
<td>-----------------</td>
<td>---------------</td>
<td>-------------------</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Min. °F</td>
<td>Min. °F</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2N4</td>
<td>20</td>
<td>1450</td>
<td>60</td>
<td>400</td>
<td>C</td>
<td>Nil</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2N5</td>
<td>20</td>
<td>1450</td>
<td>60</td>
<td>500</td>
<td>C</td>
<td>Nil</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3N4</td>
<td>20</td>
<td>1450</td>
<td>60</td>
<td>400</td>
<td>C</td>
<td>Nil</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3N5</td>
<td>20</td>
<td>1450</td>
<td>60</td>
<td>500</td>
<td>C</td>
<td>Nil</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>AN4</td>
<td>15</td>
<td>1550</td>
<td>60</td>
<td>400</td>
<td>S</td>
<td>300</td>
<td>2.3</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2NM</td>
<td>20</td>
<td>1450</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3NM</td>
<td>20</td>
<td>1450</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ANM</td>
<td>15</td>
<td>1550</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Rapid Heating to 1500 °F

<table>
<thead>
<tr>
<th>Sample Number</th>
<th>Hardening Time</th>
<th>Tempering Time</th>
<th>Mode of Failure</th>
<th>T.S. 1000 psi</th>
<th>Elongation Percent</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Min. °F</td>
<td>Min. °F</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2RY</td>
<td>&quot;</td>
<td>10</td>
<td>550</td>
<td>C</td>
<td>220</td>
</tr>
<tr>
<td>2RZ</td>
<td>&quot;</td>
<td>20</td>
<td>550</td>
<td>C/S</td>
<td>302</td>
</tr>
<tr>
<td>3RY</td>
<td>&quot;</td>
<td>10</td>
<td>550</td>
<td>S</td>
<td>296</td>
</tr>
<tr>
<td>3RZ</td>
<td>&quot;</td>
<td>20</td>
<td>550</td>
<td>S</td>
<td>286</td>
</tr>
<tr>
<td>2RM</td>
<td>&quot;</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>3RM</td>
<td>&quot;</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

* C - cleavage, S - shear, C/S - partial cleavage and partial shear.
with a limited amount of elongation. In this heat treatment, designated R., the specimens were heated in a furnace held at 1550°F. When the specimens reached a temperature of 1500°F, they were taken out of the furnace and quenched in the warm oil. Subsequently, the specimens were tempered for periods of 10 or 20 minutes at 550°F as indicated in Table II.

The third steel, designated A, was heat treated according to the procedure used by Chien (41), which gave tensile strengths of about 300,000 psi with 2% to 3% elongation in this AISI 1042 steel. This process consisted of austenitizing at 1550°F for 15 minutes, quenching in water, and then tempering for 60 minutes at 400°F.

Samples of the three steels were hardened as indicated for specimens 2NM, 3NM, and ANM. The first two samples were quenched in warm oil, while the last was quenched in cold water.

All the N-designated samples were heat treated by the author. The R-series specimens were the failed tensile test samples, which had been heat treated and tensile tested by Hollenbeck. All heat treating was performed in an air atmosphere.

B. Specimen Preparation for Transmission Electron Microscopy

It is considered desirable to examine specimens of known properties, and, in order to do this, it is desirable to be able to prepare electron microscope transmission specimens from the pieces of a tensile test sample after the test. The procedure for doing this must, of course, thin the very hard steel
without heating or deforming it. The initial thinning can be done by either a mechanical or a chemical process, and each has been used in this study.

Chien (41) first undertook at this university to mechanically thin the high strength steel specimens for transmission electron microscopy. He first tried to thin specimens on a surface grinder; however, the magnetic chuck was not able to hold the samples. It was believed that heat from the grinding action caused the sample to expand, and this expansion was responsible for the grinding wheel "grabbing" the sample. Chien attempted to avoid the problems with the surface grinder by building a machine which was supposed to wear away material at a slow rate, and the action was intended to be sufficiently mild to prevent heating or deformation.

A specimen was fastened at the bottom of a metal polishing cup filled with an abrasive suspension. Then a shaft connected to a small electric motor by means of a rubber hose in order to have a flexible coupling, was mounted over the cup. The end of the rotating shaft rubbed against, and was supposed to thin, an area on the sample. The relatively slow rotation and the abrasive suspension prevented any heating of the specimen. However, Chien had little success with his thinning machine. The thinned area was thick in the center, where the relative movement of the shaft was small, and thinner at the outer edges, where the movement of the shaft was much greater. Furthermore, it was not possible to control the force exerted by the shaft
on the sample, and the thinning rate was not the same each time the machine was started. The device had to be stopped in order to determine how the thinning was proceeding, and then started again. The thinning action was supposed to produce an area a few thousandths of an inch thick. Usually the action was rather slow, but occasionally it was rapid and, therefore, the most frequent experience with this machine was that thinning was done very slowly on a given specimen for a week or more and then the rate became unexpectedly high, yielding a hole rather than a thin section.

Chien's machine was completely redesigned. The new design included features which would: a) produce a uniformly-thin area, b) allow the force of the shaft on the sample to be controlled, and c) stop the machine when a thin section had been produced. The new mechanical thinning device, shown in Figure 1, consisted, basically, of five parts: A-motor, B-pulley system, C-shaft assembly, D-polishing cup, and E-relay.

A specimen, Figure 2, was placed in the polishing cup D, and machine oil, in which 400 grit silicon carbide was suspended, was added. The specimen measured 4.5 x 0.75 x 0.037 inches, and the polishing cup was about six inches in diameter. The shaft assembly, Figure 3, was then placed over the polishing cup. This assembly was composed of the shaft F supported in the bearing plates G, and tipped with a hardened and replaceable tip H. The bearing plates held the shaft perfectly vertical, and the tip flat against the area of the specimen to be
Figure 1. Mechanical Thinning Device.
Figure 2. Polishing Cup with Specimen in Place.
Figure 3. Shaft Assembly.
thinned. Two brass bearings located at I and J permitted easy rotation. The hardened tip prevented wear on the shaft and had a grinding surface of 3/8 inches in diameter. A set of cross-shaped slots were cut in to the end of the tip to allow access to the abrasive.

The copper strip K was added to stir the oil and keep the abrasive in suspension. The collar L was fastened to the shaft with a set screw and used as a weight. The collar and the adjustable screw M acted as contacts in the relay circuit, described below, to determine the depth of penetration of the shaft into the specimen.

In Figure 1, the motor A was equipped with a gear box, which reduced the speed, and the pulley B. Two belts, P and R, turned the shaft and the polishing cup in opposite directions. The centers of rotation of the shaft and the polishing cup were off-set by 1/8 inch in order to obtain a more nearly-uniform thickness of the thinned area. The off-set did not allow the center of the shaft to grind on the same spot of the sample constantly, and gave a more nearly-uniform grinding action over the whole area. Pulley diameters on the shaft and the polishing cup were such that the shaft speed was 60 revolutions per minute, and the polishing cup speed was 14 revolutions per minute.

The relay E, Figure 1, stopped the thinning device when contact was made between collar L and screw M, Figure 3. This allowed the device to be set to thin a specimen to a pre-determined thickness, at which time the device stopped itself.
The relay was a modified double pole, normally open relay, with a low voltage control circuit. Figure 4 shows a diagram of the relay circuit. Closing the double pole toggle switch activated the voltage relay coil closing the relay which connected terminal 1 to 2 and terminal 3 to 4. Connecting terminal 1 to 2 kept the relay coil activated and held the relay in the closed position after the toggle switch was opened. Connecting terminal 3 to 4 closed the 110-volt circuit on the motor of the thinning device which started the grinding action. The grinding action was stopped by shorting out the relay coil causing the relay to open, which disconnected terminals 1 from 2 and 3 from 4. If the toggle switch were open when the relay opened, it stayed open until the toggle switch was closed manually. The second pole on the toggle switch merely turned on the warning light, which tended to prevent the operator from leaving with the toggle switch closed. Shorting out the coil with the toggle switch closed would have placed the secondary of the transformer in a short-circuited condition. The relay coil was shorted out through a set of terminals which were added to the relay and are designated A on the circuit diagram. These added terminals were connected to the thinning device, one to the base which is electrically in contact with the collar L, Figure 3, and the other to a contact M on the thinning device (screw M in Figure 3 which was in a threaded nylon bushing and electrically insulated from the rest of the device). Screw M, Figure 3, could be adjusted to allow collar L on the shaft to
Figure 4. Circuit Diagram for Relay on Mechanical Thinning Device.
make contact when the shaft ground into the specimen and moved down a predetermined amount. In this manner, the mechanical thinning device stopped automatically and did not grind away a thin section after it was produced.

The mechanical thinning device thinned an area 5/8 inches in diameter and could be made to produce areas of a relatively uniform 0.001 inches thickness. The problems encountered by Chien had been eliminated. However, the device described here depended upon spliced drive belts which were found to be rather fragile and did not allow much load to be applied to the shaft, or high speeds. For this reason, the thinning action was slow. Thinning one sample required one to eight days, depending on the hardness of the sample. An improved drive system would permit more grinding force and higher speeds if precautions were taken to keep the abrasive suspension out of the bearings. This should appreciably reduce the thinning time.

In the chemical thinning method, a continuously-stirred aqueous solution of 40% concentrated nitric acid and 10% hydrofluoric acid was used to rapidly thin a specimen to a thickness of from 0.005 to 0.007 inches. Then, a 2:1 solution of orthophosphoric acid and hydrogen peroxide (40% by volume) was used to thin the specimen to about 0.001 inches. To prevent the preferential attack on the edges of the specimen by the chemical solutions, the edges were coated with a protective lacquer. The lacquer consisted of styrene dissolved in trichloroethylene. The specimen was coated on both sides, so that
only a 1 by 2 centimeter rectangle in the center of the specimen remained accessible to the chemical solutions. The specimen was uniformly thinned in this unlacquered area. The chemical method was much faster, normally requiring only 20 to 30 minutes. The thinned area was somewhat wedge-shaped, the center being thinner than the edges. However, near the center of the thinned area, an adequate uniformity of thickness was found over a relatively extensive region.

The chemical thinning process produced a wedge-shaped, thinned region. This caused difficulty with small or narrow specimens. In small specimens, the thickness gradient was large and restricted the finished, thin foil to a very narrow band. Usually, this band was too narrow to permit a satisfactory examination in the electron microscope. The mechanical thinning procedure was useful because it could produce a thin region of uniform thickness on small specimens.

The final thinning which gave samples suitable for transmission studies in the electron microscope was performed by electropolishing in the apparatus shown in Figure 5. This apparatus consisted of: S-D.C. power supply, T-cooling bath, U-electropolishing cell, and V-voltmeter. Figure 6 shows the electropolishing cell with a pointed cathode on each side of the specimen. The voltmeter was used to measure the voltage drop across the cell. The Bollman method (15) for electropolishing was utilized, Figure 7. A specimen was coated with
Figure 5. Electropolishing Apparatus.
Figure 6. Electropolishing Cell Showing Arrangement of Sample and Electrodes Used for Final Polishing Operation.
Figure 7. Bollman Method of Preparing Thin Foils.
a) Initial window, b) Close-up position of electrodes for first stage of thinning, the
gap is symmetrical and the electrodes are
lacquered except at the tips, c) The central perforation at the end of the first stage of
thinning, d) The wide-spaced electrode position for the second stage of thinning, e) The final
state of the specimen. (42)
a stop-off lacquer leaving only a 1.5 centimeter square or circle uncovered. This specimen, anode, was then placed between two closely-spaced, stainless steel, pointed cathodes in an electropolishing solution. The cathodes were coated with stop-off lacquer except for their tips. A gradually-increasing potential was applied until a plateau on the current-voltage curve was reached. This occurred between 12 and 18 volts with about 0.1 amp per square centimeter current density during polishing. With these conditions, the specimen was evenly thinned and not etched or pitted. Thinning was continued until a perforation occurred, usually in the center, close to the cathodes. Then the cathodes were moved about 4 inches apart and thinning was continued until further perforations developed. Usually a thin region was found between the perforations, from which a specimen could be cut with scissors or scalpel (rectangular area outlined in Figure 7e) ready for transmission electron microscopy. The conditions for the complete electropolishing operation were as follows:

- Electrolyte solution: 90% acetic 10% perchloric acids.
- Cathodes: Stainless steel
- Temperature: 15 - 20°C
- Voltage: 12 - 18 volts
- Current density: 0.1 amp per square centimeter.

The temperature of the electropolishing solution must be held below 30°C, because above this temperature there is a danger of explosion. The cooling of the electrolytic cell was accomplished by keeping it in an ice-water bath as shown in Figure 6.
Both the "window" (16) and "figure of eight" (18) methods were investigated. However, neither of these methods produced as large an area of uniform thickness as did the Bollman method. In both of these methods a large, single, stainless steel cathode is used, and the unlacquered surface of the specimen is in the shape of a rectangle, window, or a "figure of eight". For more uniform thinning, the specimen is inverted periodically. Transmission specimens are cut from the edges of the perforated "window" or "figure of eight".

A second electropolishing solution was investigated. This solution consisted of 135 ml acetic acid, 25 grams chromium trioxide, and 7 ml water. Electropolishing in this solution progressed very slowly, and since the solution was dark in color, the appearance of perforations was not readily detected. This frequently resulted in the polishing away of thin material around perforations before its presence was known. This solution was not used more extensively because of its slow action and its more-or-less-opaque nature.

Usually, the preparation process yielded one or two pieces of foil for examination in the microscope from each of the steel specimens. These were obtained from within the thinned and polished area which was approximately one-fourth of a square inch. The pieces of foil taken from this area were about 3/32-inches square. A number of spots in these foils yielded good images which could be examined visually or photographed.
The photomicrographs used in this thesis were selected as the best of several taken of each specimen. The photomicrographs in the thesis are considered the most clear and the most representative of the structure of the specimen. It should be remembered that all the areas examined from a given specimen came from the thinned area of about one-fourth square inch, and were, at most, only about one-half inch apart. More remote portions of the specimen could have had different structures.

C. Electron Microscopy

For transmission electron microscopic examination of the steel specimens, a Hitachi H1A Electron Microscope was utilized, Figure 8. A 100-KV voltage was used to provide maximum specimen penetration and a vacuum better than $10^{-5}$ mm Hg was maintained in the microscope column. The resolution of this microscope is about 6 Å, and maximum magnification is around 300,000X.

The microscope column, Figure 9, is divided into three main systems. The illuminating system is composed of the electron gun which provides the electron beam, and a double condenser lens which focuses the electron beam down to a 2-micron square on the specimen. This small spot is necessary to minimize heat effects and contamination. The image-forming system consists of the objective, intermediate and projection lenses. These three magnetic lenses provide a three stage magnification in which a change in lens' current varies their focal lengths. The third system is the viewing system and
Figure 8. The Hitachi 11A Electron Microscope. (Hitachi, Ltd.)
Figure 9. Sectional Diagram of Microscope Column. (Hitachi, Ltd.)
consists of a viewing chamber, camera chamber, and exposure meter. The viewing chamber contains a fluorescent screen on which an image is produced by the transmitted electron beam. By raising the fluorescent screen, a film plate is exposed, providing a record of the image. An automatic exposure meter, utilizing a CdS cell as a light detector, furnishes a correct automatic exposure for a wide density variation of the illuminating beam.

Two molybdenum apertures are used in the column, one above and one below the specimen. They have the function of removing stray electrons, and of extracting, from the specimen, that part of the beam that is needed. An 0.3 mm aperture of the second condenser lens was used to introduce onto the specimen electrons having uniform speed. The 30-micron aperture of the objective lens was used to improve contrast by eliminating the elastically-scattered electrons, thus allowing only the direct beam and any low angle inelastically-scattered electrons to reach the final image.

In general, there were two main problems during the examination of the steel specimens. The abnormally-rapid burning-up of the tungsten filaments was reduced by lowering the tungsten filament tip from the grid cap to prevent arcing, and by adjusting the beam current to the start of the saturation condition, since a higher beam current heated up the filament and shortened its life by its partial evaporation. Furthermore, additional cleaning and a better vacuum also helped. The other
problem was the contamination of the specimen by carbonaceous material which developed from the bombardment of hydrocarbon particles by the electron beam. The sources of the hydrocarbon particles were the organic solvents used in cleaning the microscope parts and the diffusion pump oil. The contamination from both of these sources can be reduced by a cold trap utilizing liquid nitrogen.

An effort has been made to photograph and identify electron beam diffraction patterns of components of the steel specimens.
IV. EXPERIMENTAL RESULTS AND DISCUSSION

A. General

The interpretation of transmission electron photomicrographs is somewhat more involved than that of photomicrographs taken with a light microscope. The transmission pictures are the result of absorption and diffraction effects, and show a two-dimensional projection of a three-dimensional sample.

In this study, interpretation of the transmission electron photomicrographs was based upon the following:

a) Current knowledge of the morphology of martensite and tempered martensite.

b) Knowledge of the composition and heat treatment of the steel samples being examined.

c) Comparison of photomicrographs with those of similar steels to be found in the literature (24, 32, 35, 36, 38, 39).

d) Electron diffraction patterns (24, 32, 38).

Transmission electron microscopy has been used in recent years to study martensite and tempered martensite, and has yielded new information on the structure of martensite and the changes taking place on tempering. The literature on this subject has been reviewed in the section, Literature Review. Our current knowledge of the morphology of martensite and tempered martensite can be combined with a knowledge of the
composition and treatment given the sample to aid in the interpretation of its photomicrographs. Use of this information will indicate the possible microconstituents.

Various workers have studied high strength steels and have presented various transmission electron photomicrographs in the literature. These photomicrographs have been used to determine the appearance of the various microconstituents. Furthermore, the photomicrographs obtained in this study have been compared, extensively, with those in the literature to help identify the various microconstituents.

The transmission electron photomicrographs in the literature show ε-carbide as a fine, almost unidirectional, needlelike precipitate. Cementite forms as a more massive, almost elliptical platelike precipitate. Both carbides appear as almost continuous films when precipitated on martensite plates and twin boundaries in large amounts.

The electron microscope can be used to obtain diffraction patterns of a sample. These patterns can be analyzed to determine crystallographic structure of the material or if the structure of a phase is known, the pattern can be used to indicate the presence of the phase. The electron diffraction patterns in the literature (24, 32) have been used as reference patterns to which those made from the samples studied in this investigation were compared. No attempt was made in this work to analyze any diffraction patterns. However, the diffraction patterns of the two carbides appear to be sufficiently different to permit a rather positive
identification of the carbides, when they are present separately in a sample. It might have been possible to fail to detect the presence of \(\varepsilon\)-carbide in some of these samples when both carbides were present simultaneously. The \(\varepsilon\)-carbide gave only a few diffraction spots and, if a diffraction pattern of cementite was superimposed on it, there could be difficulty in distinguishing which diffraction spots were caused by which carbide. The interpretation of the patterns when both carbides were present would require a thorough analysis of the crystallography of the microconstituents and the knowledge of foil orientation.

Twins in the as-quenched martensite plates appear as parallel bands extending out from the plate boundaries. Alternate bands, twins, show up in the transmission electron photomicrographs as lighter and darker bands. However, it is difficult to detect the presence of twins in an as-quenched specimen. The twins are only visible in certain martensite plates because the martensite plate must be oriented in a particular manner with regard to the electron beam to reveal the twins. Twins are visible when \(\{112\}_M\) lies in the plane of the sample (37). If the martensite plates which contain the twins are incorrectly oriented, with regard to the electron beam, the twins might appear as a "mottling" effect or as a dark, unresolved mass. This mottling could be mistakenly identified as precipitate or dislocation tangles.

During the early stages of tempering, \(\varepsilon\)-carbide precipitates on twin boundaries. Since the fine carbides are rather
easily detected, their presence delineates any twins that may be present. Thus, twins are more readily revealed in lightly tempered steels than they are in as-quenched steels.

In the photomicrographs, dislocations appear as fine gray or dark lines, separate or tangled together. In as-quenched martensite plates the dislocations exist in great numbers within the plates while in tempered steels they sometimes surround the precipitated particles. The visibility of the dislocations depends on the orientation of the foil relative to the electron beam.

B. Interpretation of Photomicrographs

1. As-Quenched Specimens

Figures 10 through 14 show the as-quenched structures of specimens 2NM, 3NM, ANM, 2RM, and 3RM. The austenitizing and quenching procedures were those stated under the photomicrographs. All the specimens showed very similar martensite structures. The martensite appeared to have a platelike morphology with a high dislocation density within the plates. None of the as-quenched specimens exhibited twins with the possible exception of specimen 2RM in Figure 13.

In Figure 13 twins are probably present to the right of A. Twins might well be present in this sample in other areas, however, due to either martensite plate orientation or thickness of foil, they are not visible. The parallel bands, alternately gray and black running downward and to the right from A, could be twins which
Figure 10. Specimen 2NM. Austenitized for one hour at 1450°F and quenched in warm oil. Structure shows martensite plates with high dislocation density.

Top: X90,000    Bottom: X198,000
Figure 11. Specimen 3NM. Austenitized for one hour at 1450°F and quenched in warm oil. Structure shows martensite plates with high dislocation density. X140,000
Figure 12. Specimen ANM. Austenitized for one hour at 1550°F and quenched in water at room temperature. Structure shows martensite plates with a high dislocation density.

Top: X70,000  Bottom: X165,000
Figure 13. Specimen 2RM. Sample heated up to 1500°F and quenched in warm oil. Structure is composed of martensite plates with high dislocation density and some internal twins at A. X107,000
Figure 14. Specimen 3RM. Sample heated up to 1500°F, and quenched in warm oil. Structure shows martensite plates with high dislocation density. X70,000
show up because of some precipitated carbides. It is possible that some heating during sample preparation caused the precipitate. A very fine carbide dispersion formed at a very low temperature, often shows up as "mottling" similar to that seen in Figure 13. The fine carbides outline and reveal the twins in the martensite plates because they precipitate on the twin boundaries. The structure of specimen 2RM in Figure 13 is very similar to structures found during the early stages of tempering of martensite. Thus, it is believed that this structure does not represent the true as-quenched condition.

Specimen 3NM showed the junction of three martensite plates, Figure 11. One plate is visible in the upper portion of the photomicrograph near the center and the other two plates are to the right and left of it. The dark areas surrounding the plates are martensite plate boundaries. Within the plates, a fine network of lines is visible. This probably is a tangle of dislocations. The upper left corner of the photomicrograph shows a dark region. This was probably due to the specimen thickness being too great to allow penetration of the electrons.

In Figures 10(Top), 12(Top), and 14, the different contrasts in the martensite plates was due to the difference in orientation of the martensite plates and, possibly, to a difference of specimen thickness.
2. N-Series Specimens

The structures of the tempered N-series specimens were those shown in Figures 15 through 19. Figures 20 through 23 show the diffraction patterns made by these specimens. The specimens were quenched to give a martensite structure and then were tempered at 400°F or at 500°F as indicated on the figures.

Specimen 2N4, Figure 15(Top), appeared to contain two types of precipitate. Most of the precipitate consisted of long, thin platelets forming a cross-hatched pattern within the martensite plates. This precipitate appeared to be $\varepsilon$-carbide. The cross-hatched pattern probably resulted from the precipitation of $\varepsilon$-carbide on different families of planes in the martensite. The electron diffraction pattern obtained from this specimen, Figure 20, was very similar to one identified as $\varepsilon$-carbide by Eguchi (32). During the early stages of tempering, $\varepsilon$-carbide precipitate can be mistaken for tangles of dislocations. However, the very high magnification photomicrograph of Figure 15(Bottom) tends to show the presence of precipitate platelets instead of dislocation tangles.

In Figure 15(Bottom) the prominent dark streak, starting at the top a little to the left of the center of the picture and running downward to the right, appeared to be a martensite plate boundary. To the
Figure 15. Specimen 2N4. Sample tempered for 60 minutes at 400°F. A cross-hatched pattern of ε-carbide is shown in a matrix of martensite. Possibly some cementite is seen beginning to form at A.

Top: X110,000    Bottom: X250,000
Figure 16. Specimen 2N5. Sample tempered for 60 minutes at 500°F. Structure shows cementite formed on and between the twins in the martensite plates. Dislocations surround the cementite platelets.

Top: X123,000   Bottom: X172,000
Figure 17. Specimen 3N4. Sample tempered for 60 minutes at 400°F. Structure shows the formation of cementite platelets in martensite plates. X133,000
Figure 18. Specimen 3N5. Sample tempered for 60 minutes at 500°F. Structure consists of cementite in a matrix of martensite plates.

Top: X128,000  Bottom: X182,000
Figure 19. Specimen AN4. Sample tempered for 60 minutes at 400°F. Structure shows the beginning of formation of cementite in a matrix of martensite.

Top: X129,000   Bottom: X165,000
Figure 20. Electron Diffraction pattern of specimen 2N4.

Figure 21. Electron Diffraction pattern of specimen 2N5.
Figure 22. Electron Diffraction pattern of specimen 3N4.

Figure 23. Electron Diffraction pattern of specimen AN4.
right and left of this plate boundary appear elongated spots which are probably precipitated platelets of $\varepsilon$-carbide. Surrounding some of these precipitated carbides, there are fine networks, light gray in color in the photomicrograph, which could be either a finer precipitate of $\varepsilon$-carbide or dislocations.

The second type of precipitate shows up in Figure 15(Top), as the large dark spots such as those to the left of the letter A. They could be the beginning of cementite precipitation. At the tempering temperature of 400°F used on this specimen, there is the possibility of the existence of both $\varepsilon$-carbide and cementite. It is also possible that the dark spots at A, Figure 15(Top) are some inclusions or contamination in the steel but they are considered to be rather small even if they were inclusions sometimes referred to as "submicroscopic in size".

The specimens of this series, Figure 16, through 19, appeared to show precipitated cementite platelets, sometimes surrounded by dislocations, in a matrix of martensite. Figure 18(Top and Bottom), showed some dark spots, cementite, surrounded by lighter areas. These lighter areas probably were areas containing dislocations. The electron diffraction patterns in Figures 21 through 23 were very similar to patterns produced by cementite in a martensite matrix (32, 24).
In carbon steels with silicon contents under 0.25%, cementite starts to precipitate at about 400°F. The amount of cementite increases with both tempering time and tempering temperature.

Specimen ANM, Figure 19, showed very little precipitate that appeared to be cementite; however, it gave an electron diffraction pattern of cementite, Figure 23. Normally, the cementite precipitates as small particles within the martensite plates and as almost continuous films along the martensite and twin boundaries. Figure 16(Bottom) shows a martensite boundary running diagonally from the upper right-hand corner of the photomicrograph down to the lower left-hand corner. On this boundary, an almost continuous film of cementite is visible. Specimens 2N5 and 3N5, Figures 16(Top) and 18(Top), were tempered at 500°F and show more cementite precipitate than specimens 2N4 and 3N4, Figures 15(Top) and 17, which were tempered at 400°F. In the photomicrograph of Figure 15(Top), most of the visible precipitate is ε-carbide. In the other photomicrographs of the N-series tempered specimens, the dark spots are cementite precipitate and their relative numbers represent the amount of cementite present.

3. R-Series Specimens

Samples of Steels No. 2 and 3 were rapidly heated to 1500°F and immediately quenched in warm oil. These specimens were then tempered at 550°F for 10 or 20 minutes.
The resulting microstructures are shown in Figures 24 through 27. The structure of these samples appeared to consist of cementite platelets precipitated between and along twin and martensite boundaries.

Figure 27 shows a martensite plate boundary starting 3/4-inches below the upper right-hand corner of the photograph and running diagonally downward and to the left. The parallel bands running away from this plate boundary at approximately right angles are twin boundaries. On both the martensite and twin boundaries precipitated, cementite appears in the form of dark spots or clusters. The formation of the precipitate on these boundaries made them easily visible.

Electron diffraction patterns of these specimens, Figures 28 through 31, indicated the precipitate was cementite. Furthermore, Tekin and Kelly (24) reported that similar steel specimens (0.8%C) tempered at 500°F showed only cementite precipitate present. Specimens 2RZ and 3RZ, Figure 25 (Top and Figure 27, which were tempered for 20 minutes, showed more carbide precipitate than specimens tempered for 10 minutes, Figure 24 (Top) and Figure 26. Clusters of carbide particles which showed up in these photomicrographs as dark areas were the cementite precipitate.
Figure 24. Specimen 2RY. Sample tempered for 10 minutes at 550°F. Structure shows the formation of cementite in martensite plates.

Top: X90,000   Bottom: X205,000
Figure 25. Specimen 2RZ. Sample tempered for 20 minutes at 550°F. Structure is composed of cementite platelets in a martensite matrix.

Top: X103,000 Bottom: X165,000
Figure 26. Specimen 3RY. Sample tempered for 10 minutes at 550°F. Structure shows a number of cementite platelets within martensite plates. X64,500.
Figure 27. Specimen 3RZ. Sample tempered for 20 minutes at 550°F. Structure consists of cementite platelets within the martensite plates. X77,000
Figure 28. Electron Diffraction pattern of specimen 2RY.

Figure 29. Electron Diffraction pattern of specimen 2RZ.
Figure 30. Electron Diffraction pattern of specimen 3RY.

Figure 31. Electron Diffraction pattern of specimen 3RZ.
C. Correlation of Microstructures with Changes in Mechanical Properties

Hollenbeck (40) examined six heats of AISI 1065 steel which included Steels No. 2 and 3, and concluded that there was no relationship between composition and mechanical properties. These six steels were all made by the same mill and were the same grade of steel. Steel No. 3 was found to be more ductile than Steel No. 2 when they were heat treated to high hardness or high strength levels. Steel No. A was an AISI 1042 steel and was obtained from a different source. Chien (41) found it to be relatively ductile at high strength levels. Steel No. A, with 0.49% carbon, had a lower carbon content than Steels No. 2 and 3 with 0.71% carbon and 0.65% carbon, respectively. Hollenbeck concluded that carbon contents lower than that of Steels No. 2 and 3 would give better ductility at the 300,000 psi tensile strength level.

He also found that better tensile properties were obtained in Steels No. 2 and 3 when they were hardened by rapid heating. That is, the R-series samples had higher strength and ductility than the N-series samples. He proposed that the difference might be due to the relative amount of carbon dissolved in the austenite at the start of the quenching procedure. This would have resulted in the formation of different types of martensite (lower or higher carbon martensite) which, after tempering for optimum mechanical properties, produced different values of tensile strength and ductility.
High carbon martensite contains a large proportion of twinned plates (100% at 0.8%C) (37). The twin boundaries block dislocation movement and thus restrain deformation. Carbides precipitate on the twin boundaries during tempering, and make these boundaries more effective as barriers to the movement of dislocations. Martensite plates, formed from austenite with lower carbon content, form more untwinned martensite plates which do not inhibit deformation as much as twinned plates. Low carbon austenite (about 0.1%C) transforms into a needlelike martensite structure with no internal twins, and is relatively ductile.

The N-series specimens were held a relatively long time, 15 or 20 minutes, at the austenitizing temperature. This should have allowed the carbon to diffuse throughout the austenite producing a homogeneous, or nearly homogeneous, high carbon austenite. This high carbon austenite would be expected to transform into a predominantly-twinned type of martensite which, after low temperature tempering, would lack ductility.

On the other hand, according to Hollenbeck, the R-series specimens spent a very short time at temperatures in the austenite range. The short time could have limited the amount of carbon dissolved and the degree of homogeneity attained by the austenite. Thus, the austenite near the original cementite sites could have been high in carbon while the austenite at a distance from the cementite would have been relatively low in carbon. An appreciable portion of the austenite could have
been well below the approximately 0.65% - 0.70% carbon present in these steels. This lower carbon austenite should have transformed into a martensite with fewer twins than that in the N-series samples. A less twinned martensite would be more ductile after tempering and this more ductile tempered martensite would permit the application of greater loads during the tensile test.

It might be possible to confirm or refute Hollenbeck's ideas by examination of the samples by transmission electron microscopy. For example, the remains of the undissolved carbide particles might be found in the rapidly heated samples, the R-series samples. These undissolved carbide particles should have appeared on the photomicrographs as relatively large dark areas, much larger than any precipitate clusters.

During the examination of the R-series specimens by transmission electron microscopy, no undissolved carbides were observed. These carbides may not have been found because they were not of interest at the time most of this work was done. Hollenbeck put forth his ideas as this work was nearly complete. Since the undissolved carbide particles could have been much larger than any precipitated carbides, it is possible that the very high magnifications used in this transmission technique were too high to reveal them. These large carbides may have been as large as a field of view and passed over without being identified, being considered thick areas of the foil or some spurious effect. It may be better to look for
these carbides using the replica technique at a much lower magnification which would permit a much greater area of the specimen to be examined in one field. The size and distribution of particles observed at the lower magnification might be correlated with the known original microstructure of the specimen to indicate the presence of undissolved carbides in the rapidly-heated specimens.

Another way to test Hollenbeck's theory would be to look for carbon concentration gradients in the R-series specimens. The carbon concentration gradients could be indicated by the proportion of twinned to untwinned martensite plates. The high carbon areas would consist of predominantly twinned martensite plates, while the low carbon areas would contain a smaller proportion of twinned to untwinned martensite plates.

Examination of the photomicrographs for carbon concentration gradients of both R-series and N-series specimens was not fruitful. Both series of specimens showed twinned and untwinned martensite plates but no determination of their relative proportions could be made because of the small specimen area covered by the photomicrographs and the limited number of thin foils available. The determination of the relative amounts of twinned to untwinned martensite plates might be accomplished most readily by examining lightly tempered specimens. The precipitated carbides form preferentially during tempering on the twin and martensite plate boundaries, outlining them and making them visible. A sufficient number of foils should be prepared and examined by
transmission electron microscopy to permit study of a representative area of the sample. A larger area might be examined successfully if the photomicrographs are taken at low magnification and subsequently enlarged for examination.

It would appear that it is possible to test Hollenbeck’s explanation for the differences in mechanical properties of the N-series and R-series samples by the proper metallographic examination of specimens using an electron microscope. While some of his samples were studied, it would appear that the proper examination was not conducted because no pertinent evidence bearing on his explanation has been produced. However, Hollenbeck’s ideas are considered to be reasonable and further work using the techniques developed in this thesis project should confirm or disprove his explanation.

The reason for the difference in ductility of the steels was not apparent. Steels No. 3 and A are considered to be more ductile than Steel No. 2. With one exception, all the tempered specimens appeared to have similar microstructures, cementite in a tempered martensite matrix. Specimen 2N4 was the exception. This sample had ε-carbide in a tempered martensite matrix. No significance can be attached to this one observation, but it suggests that the tempering process does not proceed as rapidly in the less ductile steels.

The major effort in this project was devoted to the development of a sample preparation procedure for making thin foil samples of hard metal for examination by a transmission
electron microscopic technique. Two processes for thinning bulk material without changing its structure have been used successfully. One process employs a chemical polishing solution which thins rather rapidly. The other process uses an improved model of a mechanical device originally proposed by Chien (41). This machine is slower than the chemical process, but it can be used on small samples which cannot be thinned by the chemical process. An electropolishing procedure has been applied to hard steel samples as the final thinning process. The samples prepared by these processes were successfully examined with the new electron microscope at the University of Missouri at Rolla. This examination involved some "de-bugging" of the instrument.
The work in this thesis was directed toward the establishment of procedures and techniques for the transmission electron microscopic examination of high carbon steels. Specimen preparation techniques were developed for making transmission foils from relatively hard, high carbon steels in bulk form. A certain amount of work was devoted to the "de-bugging" of the electron microscope. Photomicrographs were obtained of metal microstructures and were analyzed for various structural constituents. These photomicrographs compared, very favorably, with similar photomicrographs found in the literature.

Examination of heat treated, high strength steel specimens by transmission electron microscopy did not reveal reasons for differences in properties of different heats of steel. The examination did not reveal the reason why different austenitizing procedures in the heat treating operation produced different tensile properties in a given steel.

Study of the microstructure of high strength steels using the electron microscope should be continued. It is reasonable to believe that this will yield useful information on the reason why rapid heating in the hardening process produces a more ductile material than slower heating and holding at the austenitizing
temperature. It is not clear that this type of study will indicate why some heats of steel are more ductile than others when they are heat treated to high strength levels.

Hollenbeck's explanation of the causes of the differences in mechanical properties of N-series and R-series samples appears to be reasonable. While it may be possible to test his explanation by the proper metallographic examination of samples using an electron microscope and while some of his samples were studied, it would appear that the proper kind of examination was not conducted. The results of this study did not confirm or disprove Hollenbeck's explanation.
BIBLIOGRAPHY


VITA

George Joseph Vytanovych was born August 9, 1938 in Lviv, Ukraine. He came to the United States in March, 1949, and completed his primary and secondary education in Chicago, Illinois.

In September 1956, he entered the Navy Pier Branch of the University of Illinois, Chicago, pursuing course work in Chemical Engineering. In February 1959, he entered the University of Illinois in Champaign, changing his field of study to Metallurgical Engineering. He received his Bachelor of Science Degree in Metallurgical Engineering in June 1961.

After graduation, he worked for a short time at the Republic Steel Corporation in Chicago until entering the army for six months active duty. After his military service, he worked as the plant metallurgist at Rauland Corporation in Chicago, Illinois.

In September 1965, he entered the University of Missouri at Rolla as a graduate student.