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The precipitation hardening response of copper bearing HSLA steels

Azucena Perez Cabello

University of Wollongong

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THE PRECIPITATION HARDENING RESPONSE OF COPPER BEARING HSLA STEELS

A thesis submitted in partial fulfilment of the requirements for the award of the degree

Doctor of Philosophy

from

UNIVERSITY OF WOLLONGONG

by

AZUCENA PEREZ CABELLO, B. Met

Department of Materials Engineering

1995

MAY 1995
DECLARATION

I hereby declare that this submission is my own work and that, to the best of my knowledge and belief, it contains no material previously published or written by another person nor material which to a substantial extent has been accepted for the award of any other degree or diploma of the university or other institute of higher learning, except where due acknowledgement is made in the text. The work presented in this thesis was carried out by the candidate in the laboratories of the Department of Materials Engineering at the University of Wollongong.

Azucena Perez Cabello

May 1, 1995
ACKNOWLEDGEMENTS

The author wishes to express sincerest thanks to several people without whose expertise, assistance and support, this work would not have been completed.

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The metallographic content of this work owes much of its quality to the efforts of two expert technicians who have assisted me greatly. Special thanks go to both, Mr P. Renwick for his expertise and assistance with the transmission electron microscopy undertaken in this work and to Mr A. Sly for his optical metallographic skills.

I am indebted to BHP for sponsoring my studies over the years and most particularly to Mr J. G. Williams and Mr L. Moll for their understanding and support in allowing me the time and resources to complete this work.

Finally, words are insufficient to thank my dearest husband Jose Luis and my son. I dedicate this thesis to my husband, friend and confidante for his intelligence, endless support and, encouragement which were often above and beyond the call of duty and to my son whose laughter and sweetness are “...the wind beneath my wings.”.

A. M. D. G.
ABSTRACT

This thesis reports a detailed investigation of the precipitation hardening response of a series of Cu bearing HSLA steels typical of the commercial grades represented by the ASTM specification A710, the military specification MIL-S-16216 and the classification HSLA 80. During the commercial production of these types of steels there are two stages during their thermal history wherein the process operator can influence the nature of the Cu precipitation and hence the ultimate strength of these steels. The first of these stages is directly after thermo-mechanical control processing (TMCP) during cooling of the steel plate from the rolling temperature and the second stage is during the subsequent ageing treatment.

The ferritic microstructure, the precipitate size and distribution and the volume fraction of ε Cu precipitates in the TMCP condition were first established. The effect of laboratory normalising at 900 °C and cooling at rates of 0.2, 4 and 70 °C/s was then determined. It was found that ageing of the TMCP steel and ageing of the normalised and slow cooled steels (0.2 °C/s) resulted in a step shift in the particle size distribution curve to smaller sizes. The results of this work confirm that the amount of Cu retained in solution is strongly dependent on cooling rate.

The impact of cooling rate and the resulting change in particle distributions on the Vickers hardness and Charpy impact toughness has been established. Although the final steel hardness was increased by increasing the cooling rate from the normalising temperature, the associated decrease in impact toughness properties indicates that there is little advantage to be gained in the overall mechanical property performance by quenching a steel that was originally designed for the TMCP process route.

The effect of the subsequent ageing on the precipitation hardening response was established by examining the results of a series of isothermal ageing treatments. The activation energy for the precipitation hardening process was calculated from the data to be 157,940 J/mol, which is much lower than the published value for bulk diffusion of Cu in ferrite. The lower value is consistent with a strong contribution by grain boundary and dislocation pipeline diffusion.
Correlation equations between the Vickers hardness and tensile properties for the Cu bearing experimental steels in both the TMCP and the TMCP and aged condition, have been determined which have high correlation ratios \( R^2 > 0.92 \). In addition, the relationship between the Cu content of the steel and the magnitude of the strength increment observed on ageing has been established.

Applying the principle that the most effective barrier to dislocation motion will determine the yield stress, a number of strength models were examined in an attempt to determine which single mechanism best fitted the experimental measurements of the strength of the fully aged and overaged steels. It was found that when using the experimentally determined and estimated volume fractions of Cu in its various forms, each of the models examined significantly underestimated the yield strength of the aged Cu bearing HSLA steels. A derivative of the Orowan model was found to produce estimates closest to the experimental results, but even in this case the experimental yield strengths of the 1% Cu steels were underestimated by up to 45 MPa.

A shortcoming of these calculations is the assumption that the effective precipitates were nearly pure copper, as there is evidence in the literature that the coherent \( \varepsilon \) Cu and Cu rich clusters, are probably metastable solid solutions of Fe and Cu. Therefore the estimates of the volume fraction of these precipitates calculated from the particles visible in the TMCP and the TMCP and aged condition and the chemical compositions of the experimental steels, are likely to seriously underestimate the actual values. If a correction for the particle composition, together with a more accurate estimate of the shear modulus for the precipitates is applied then, in principle, this allows predictions close to the experimental measurements.

Considering alternatively, that the observed strength is associated with the contributions of a series of discrete strengthening methods, the Pythagorean addition rule and the additive rule were used to predict the observed strengths. Although both the Pythagorean and the linear addition rules overestimated the experimental yield strength of the aged 1% Cu bearing steels, the linear addition rule produced estimates which were closer to the experimental results than the Pythagorean rule.
If linear addition is appropriate, as is frequently assumed, then incoherent ε Cu particles would account for up to about 40% of the observed strength increment on ageing, the formation of Cu rich zones or clusters would account for up to 55%, and solid solution strengthening by Cu would account for less than about 5% of the strength increment on ageing. However, it must be recognised that the strength increment on ageing accounts for < 12% of the final steel strength, with the balance being due to grain refinement, dislocation structure and solid solution strengthening following TMCP.

Two factors limited the testing of various models for the strengthening mechanism in aged steels, the lack of an accurate measure of the shear modulus of a metastable Fe/Cu solid solution and a more accurate estimate of the volume fraction of fine particles (<5nm).

It is concluded that the data obtained were inadequate to test the validity of the various models proposed to account for the strengthening obtained on age hardening. However, the analysis allowed the relative contributions of the various types of copper based strengthening mechanisms to be estimated; and indicated that for specific coherency strengthening models the values of key variables, which were needed to obtain good agreement with measured yield strengths, were not unrealistic.
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PUBLICATIONS
The family of plate steels represented by the ASTM specification A710, is finding increasing commercial applications. These low carbon, Cu-Ni-Cr-Mo-Nb precipitation hardened steels, were first commercially produced in the 1970s and were known as IN-787 (1). ASTM specifications were subsequently developed for structural (A710) and pressure vessel (A736) applications. Application of these steels by the US Navy in their frigate and cruiser replacement programme in the 1980s lead to the development of a military specification MIL-S-24645(SH), also initially known as HSLA-80. Significant tonnage has been produced for the US Navy as a replacement for HY80 (MIL-S-16216) in cruiser deck and bulkhead applications (8).

The strength and toughness in steels such as HY80 is obtained with the use of relatively high amounts of alloying elements combined with a quench and temper (Q&T) heat treatment. The result is a martensitic steel structure which requires the use of stringent welding process controls and specially designed filler materials to retain adequate properties in the as welded condition.

Precipitation hardening HSLA steels can potentially deliver similar strength and toughness properties to HY80 steel, but are obtained by a combination of small amounts of microalloying elements which produce a "leaner" steel than that designed for the Q&T process route. These steels are produced by thermo-mechanical controlled processing (TMCP) followed by an ageing process, resulting in a ferritic microstructure which is more easily welded than that of the HY80 type steels.

This class of steel depends upon the proper control of post thermo-mechanical heat treatments which enable the precipitation of copper in the ferritic matrix of the steel to increase its mechanical strength. The mechanism of precipitation hardening in copper bearing steels has been the subject of numerous studies. The large body of work which exists contains contradictions and conflicts as to the mechanism which is predominantly responsible for strengthening in Fe-Cu alloys. Furthermore, although
a number of models exist to explain the observed increment on ageing in these steels, because of the effects which other alloying elements have on the nature and kinetics of precipitation in the Fe-Cu system, what holds true for any one particular steel chemistry may be altered by alternative microalloying additions. Therefore, the accuracy of these models when applied to specific examples of commercial age hardenable Cu bearing HSLA steels needs to be reviewed.

Although the precipitation hardening capacity of Cu has long been recognised, it has only more recently been used to strengthen low alloy steels. The kinetics of precipitation is sensitive to composition and knowledge of the ageing response of lean HSLA 80 type chemistries is limited. Therefore, this investigation evaluates the precipitation hardening responses of a series of Cu bearing HSLA-80 type steels developed by BHP SPPD Port Kembla, as well as those of other commercially available steels.
1.0 LITERATURE REVIEW

1.1 Historical Development

The exact historical origin of the deliberate addition of copper to iron cannot be pinpointed with any great degree of accuracy. One can say with some confidence that it dates back to the early 18th century to the production of malleable iron in England. When an intricate casting was made requiring particularly good properties, large Cu coins referred to as "Boulton Pennies" were sometimes added to the melt.

Experimentation with the addition of Cu to structural steels for its ability to impart good weathering properties, began in 1916 in the USA (3, 141). It was first commercially used in this way from 1933 to 1935. Use of this type of material around the world has included bridges, laboratory and office buildings, multi storey carparks and some very recent deep sea oil rigs of Japanese origin. For example, Cu bearing steels have been used in the USA in the construction of the US. Steel Corporation high rise in Pittsburgh, the Chicago Civic Centre building and the Saimen designed John Deer Headquarters in Wisconsin. In Australia examples of the use of this material can be found in BHP Melbourne Laboratories, BHP House in Victoria as well as Tullamarine airport which has used Austen 50 type weathering steel in critical exposed parts of their complex. The ability of Cu bearing steel to withstand atmospheric corrosion is not the major factor which provides the impetus for the development of these steels today. Until recently it was less well recognised that, as well as improved corrosion resistance, the precipitation of Cu can make a significant contribution to the mechanical properties of steel.

The first major developments of Cu bearing high strength steels, which could be age hardened to high strength levels with toughness extending to very low temperatures, came in the early 1960s. During the early development and the first commercial production in the 1970s, these Cu steels were known as IN-787 and Nicuage (trademark of International Nickel Company) (1,2).
References in the literature to the effect of Cu on steel begin in the early 1920s when the austenitic stainless steels were evolving, and Cu additions were sometimes made to the 18-8 and chromium ferritic grades (142, 143). Closely following this development came Pheil's study in 1929 of hot oxidation (144) and Nehl's 1930 paper on precipitation hardening (3).

The first significant summary of the metallurgy of Cu and Fe alloys was given in the 1934 monograph by Gregg and Daniloff (4). The first general text was that prepared by Lorig and Adams (5). Since these early works, extensive studies have been carried out on Cu containing steels, eventually leading to the publication of "Copper in Iron and Steel" (6). The first "International Conference on Cu in Steel" was held in Luxembourg in 1983 (7).

1.2 Development of Copper Bearing HSLA Steels.

Interest has recently been rekindled in the design of HSLA alloys which exploit Cu as an alloying element (8-11, 15). The use of Cu as an alloying element has the advantage of increased strength due to the precipitation of Cu, whilst still retaining good toughness, weldability (13-15) and formability (16), even at low temperatures. Furthermore, these steels have a reported high resistance to fatigue crack growth (17); the ability to suppress hydrogen induced cracking (18, 19); excellent corrosion resistance (20); and when Cu is combined with other microalloying elements such as B or Mo, an acicular or bainitic structure can be produced (21).

1.2.1 Commercially Available Copper Bearing Steels.

A number of HSLA steels have been developed which depend upon Cu to meet their specified properties. Table 1.1 lists the more significant alloys, their carbon equivalents (CEQ) and typical applications.
<table>
<thead>
<tr>
<th>STEEL TYPE</th>
<th>TYPICAL COMPOSITION</th>
<th>APPLICATIONS</th>
<th>IIW CEQ</th>
<th>REF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn-Mo-Cu</td>
<td>.14 C, .31 Si, 1.4 Mn, .03 Al, .1 V, .03 Nb, .22 Mo, .48 Cu</td>
<td>Pipeline Fittings</td>
<td>.45</td>
<td>18</td>
</tr>
<tr>
<td>Experimental</td>
<td>.024 C, .19 Si, 1.17 Mn, .04 Al, .041 Nb, .19 Ni, .29 Cu, .0015 B</td>
<td>Sour Gas Linepipe</td>
<td>.25</td>
<td>19</td>
</tr>
<tr>
<td>WEL-TEN 80</td>
<td>.14 C, .27 Si, .9 Mn, .04 V, .9 Ni, .6 Cr, .43 Mo, .2/.5 Cu, .001 B</td>
<td>Elevating racks for offshore platforms</td>
<td>.58</td>
<td>22</td>
</tr>
<tr>
<td>CRYALSIM</td>
<td>.08 C, .35 Si, 1.2 Mn, .02 Nb, .25 Ni, .30 Cu</td>
<td>Shipbuilding, storage tanks</td>
<td>.33</td>
<td>102</td>
</tr>
<tr>
<td>OFFSHORE Type 1</td>
<td>.10 C, .45 Si, 1.25 Mn, .015 Nb, .18 Ni, .28 Cu</td>
<td>Offshore structures</td>
<td>.33</td>
<td>102</td>
</tr>
<tr>
<td>Cu-B-Nb</td>
<td>.04 C, .01 Si, 1.3 Mn, .01 Al, .06 Nb, 1.0 Ni, 1.85 Cu, .0009 B, .03 Ti</td>
<td>Linepipe, naval structures</td>
<td>.44</td>
<td>24</td>
</tr>
<tr>
<td>A710 STEELS NI-COP</td>
<td>.04 C, .28 Si, .48 Mn, .038 Al, .038 Nb, .90 Ni, .70 Cr, .19 Mo, 1.16 Cu</td>
<td>Fittings, machinery, ships, offshore structures</td>
<td>.43</td>
<td>23</td>
</tr>
<tr>
<td>AMAX</td>
<td>.07 C, .4 Si, .4/.7 Mn, .02/.06 Nb, .7/.10 Ni, 1.0/1.3 Cu, .15/.25 Mo, .6/.9 Cr</td>
<td>Shipbuilding</td>
<td>.49</td>
<td>103</td>
</tr>
<tr>
<td>LUKENS</td>
<td>.029 C, .21 Si, 1.46 Mn, .025 Nb, .94 Ni, 1.1 Cu, .012 Ti, .72 Cr</td>
<td>Shipbuilding</td>
<td>.55</td>
<td></td>
</tr>
<tr>
<td>NIPPON STEEL CORPORATION</td>
<td>.06 C, .2 Si, 1.42 Mn, .01 Nb, .73 Ni, 0.9 Cu, .03 Al</td>
<td>Offshore structures</td>
<td>.40</td>
<td>31</td>
</tr>
<tr>
<td>NIPPON KOKAN</td>
<td>.06 C, .30 Si, 1.40 Mn, .03 Nb, .70 Ni, 1.2 Cu, .025 Al</td>
<td>Pipe fittings</td>
<td>.42</td>
<td>28</td>
</tr>
</tbody>
</table>

*NOTE*  

\[
IIW\ CEQ = C + Mn/6 + (Cr + Mo + V)/5 + (Cu + Ni)/15
\]
The family of steels represented by the ASTM Specification A710 and listed in Table 1.1, is finding increasing applications (8). Recent interest in and application of this family of steels by the US. Navy has led to the development of a military specification MIL-S-24645 (SH), also known as HSLA80. A significant tonnage is being produced for the US Navy as a replacement for HY80 (MIL-S-16216) in cruiser deck, bulkhead and hull applications (8).

### 1.2.2 Alloy Design

At this point, a discussion of the optimisation of the general chemistry for the ASTM A710 and HSLA80 family of steels is appropriate. Three different categories of ASTM A710 Grade A are commercially available. These categories correspond to different types of heat treatment which produce steels of several strength and toughness combinations over a wide range of plate thicknesses. These combinations are listed in Table 1.2.

#### TABLE 1.2: Specifications for ASTM A710 Grade A type steel

<table>
<thead>
<tr>
<th>CLASS</th>
<th>PROCESS ROUTE</th>
<th>THICKNESS (mm)</th>
<th>SPECIFICATION</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>STEP 1</td>
<td>STEP 2</td>
<td>STEP 3</td>
</tr>
<tr>
<td>1</td>
<td>As Rolled</td>
<td>Precipitation Hardened (Age 540 to 650 °C)</td>
<td>4.8 - 7.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>&gt;7.9-19</td>
</tr>
<tr>
<td>2</td>
<td>Normalised 870 to 930 °C</td>
<td></td>
<td>4.8 - 25</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>&gt;25 - 51</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>&gt;51</td>
</tr>
<tr>
<td>3</td>
<td>Austenitised 870 to 930 °C</td>
<td>Water Quenched</td>
<td>Precipitation Hardened (Age 540 to 665 °C)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>&gt;51</td>
</tr>
</tbody>
</table>

Whilst a 585 MPa yield ASTM A710 Grade A steel plate can be produced via the quench and age processing route, its weldability and low temperature toughness are not as good as those of steels with
similar strength produced by the Thermo-Mechanical Control Rolled Process (TMCP) \( (8, 21, 23, 24, 25) \). Although ASTM A710 includes an as rolled and aged version (Class 1), the alloy design is more suited to the quench and age processing route (Class 3), due to the high quench hardenability provided by the Ni, Cr and Mo additions.

Accordingly, various steelmakers have designed leaner chemistries more appropriate to the TMCP route. Figure 1.1 shows the general metallurgical approach adopted for producing high strength steel with good weldability and low temperature toughness \( (26) \), such as those listed in Table 1.1.

Ultimately the microstructure which forms in these low carbon, copper bearing steels is highly sensitive to microalloy composition, thermo-mechanical treatment and cooling rate. This fact is reflected in the morphology of the transformation product, the mechanism of its formation and ultimately the wide variety of mechanical properties which can be produced. Thus when steelmakers undertake the design of these HSLA steels, they must take the influence of each of these factors into account. The following sections will
examine the effect of composition, thermo-mechanical treatment and cooling rate on Cu bearing HSLA steels.

1.3 Effect of Composition on Cu bearing Steels.

1.3.1 Design of Optimum Chemistry

The chemistry selected as the optimum by a particular producer depends greatly upon the manufacturing process available in the plant. Generally, the steels are designed to have a low CEQ to facilitate welding (<0.5 for IIW CEQ - see note on Table 1.1) (25, 28, 29, 30, 31, 145). They contain sufficient Cu to cause precipitation hardening (>0.8%)(29); Ni to prevent hot shortness due to the high Cu; and Mo, Cr and Nb to improve the low temperature toughness. A more detailed discussion follows on steel composition and particularly the effects of microalloy additions.

Figure 1.2 shows the relationship between the CEQ (IIW CEQ) and the mechanical properties of a hot rolled and formed 0.14%C - 0.3%Si - 1.45%Mn - 0.03 Nb steel in the normalised and aged condition (28). Additions of Mo, Cr, Ni and/or V have been made alone or in combination in order to vary the CEQ. It is evident that strength appears to increase with increasing carbon equivalent while toughness (50%FATT) remains fairly constant. These results indicate that a steel with a minimum yield of 550 MPa cannot be produced without increasing the carbon equivalent to above 0.5 which is generally considered to be detrimental to the weldability of the steel (25, 28, 29, 30, 31, 145). In the leaner A710 steels being produced today the utilisation of strengthening by the precipitation hardening of Cu is effective in improving the strength whilst maintaining good toughness properties and weldability (low CEQ).
FIGURE 1.2 Relationship between carbon equivalent (CEQ) and mechanical properties, in the normalised and aged condition (28).

The Fe-Cu phase diagram is shown in Figure 1.3 and indicates that there are three invariant reactions which occur in the Fe - Cu binary system. These are the peritectic reactions at about 1484 °C and 1094 °C and a eutectoid reaction at about 850 °C. The products of the eutectoid reaction are ε Cu and ferrite. The equilibrium ε Cu phase is FCC Cu with a small amount of iron in solution, whilst the ferrite contains a
small amount of Cu in solution. Recent work by Goodman, Brenner and Lowe (93) has shown that the composition of these particles can vary, with as little as 50% Cu being present in the particle in the peak hardened condition. The maximum solubility limit of Cu in ferrite is 2.1% at about 850 °C. The decreasing solubility with temperature allows subsequent processing by precipitation hardening, provided that the content is above 0.4% which is the solubility limit of Cu in ferrite at room temperature. Takahashi et al. (29) have reported that the practical limit for precipitation hardening is approximately 0.8% Cu.

![Fe - Cu phase diagram](image)

FIGURE 1.3 The Fe - Cu phase diagram, based on data from references (12, 32, 33)

The effect of Cu on the mechanical properties of C-Mn steels is illustrated in Figure 1.4 (28). It is evident that in both the normalised condition and in the normalised plus aged condition, an increase
in the Cu content is accompanied by an increase in the strength, with the strength increase being particularly large for Cu > 1.2%. This result is consistent with those published earlier by Hurley and Shelton (34) who reported significant increases in strength with increases in Cu content (up to about +120 MPa in both the normalised and the normalised plus aged conditions). Strength increases occurred up to an optimum Cu level of 1.32%, after which further additions had little or no added effect on strength.

FIGURE 1.4 The effect of Cu content on mechanical properties of a C-Mn steel (28)
More recent results published by Tomita et al. (31) indicate that the base steel strength (350 MPa) of a 0.05 %C / 1.5 %Mn steel in the control rolled condition, was increased by approximately 120 MPa (ie. to 470 MPa) with the addition of 1.5 %Cu. Various authors have proposed a number of explanations for the dramatic effect of Cu on the base strength of steel. These are discussed further in Section 1.7.

Toughness in the normalised condition appears to be affected little by Cu contents up to about 1.2% (Figure 1.4). This observation is in agreement with the results published by Tomita et al. (31) who found from Charpy impact and CTOD tests performed on Cu bearing steels used in offshore structures, that Cu has little effect on HAZ toughness of welded steel regardless of heat input.

The relatively low melting point of the ε phase (approximately 1094 °C) (Figure 1.3) means that potential problems with hot shortness exist during reheating and hot working where there has been extensive segregation (≥0.8%) of Cu (35, 36). The phase boundaries of the Fe-Cu system are affected by the presence of additional alloying elements and it should be borne in mind that the binary Fe-Cu diagram only provides rough estimates of phase boundaries and reaction temperatures for commercial steels, which are complex multi-component systems.

Figure 1.5 shows the liquidus for the Fe-Ni-Cu system, as originally determined by Guertler et al. (38). This phase diagram shows the Fe-Cu binary peritectic P1 (1094 °C) extending into the Fe-Cu-Ni ternary system and terminating in a critical tie line at 1220 °C. Clearly, as the %Ni increases the temperature of the peritectic reaction is raised. Because of this effect Ni is often added to high Cu bearing steels to prevent hot shortness. The general rule often applied by producers is that the minimum amount of Ni addition to prevent hot shortness due to Cu is half the Cu content. More complete Fe-Ni-Cu ternary system data have been prepared by Koster and Dannöhl (41).
In conjunction with its effect on the peritectic reaction, Ni has a profound effect on the decomposition of austenite in Fe-Cu alloys (43). Ricks et al. (43) showed that for high purity alloys of Fe-Cu and Fe-Cu-Ni, the kinetics of the austenite to ferrite transformation, the transformation structures and the associated precipitation morphologies formed by isothermal transformation are sensitive functions of the Ni content. Specifically, the results show that the addition of Ni increases the time for polymorphic transformation and also leads to the change in the resultant ferrite morphology from equiaxed to Widmanstätten to bainitic with a concomitant increase in the partially coherent interphase boundary growth mode. The increase in the transformation time allows the precipitation of Cu to occur at the advancing ferrite/austenite interface, which can lead to both coherent and incoherent interphase precipitation and to precipitation in the matrix from supersaturated ferrite after transformation.
Although the addition of Ni has little direct effect on strength, it does provide a clear improvement in material toughness (28, 34). Generally, Ni is added for its ability to prevent hot shortness and for the secondary purpose of increasing toughness.

Addition of Nb is mainly for its ability to retard austenite recrystallisation and subsequent grain refining effect on the microstructure, resulting in improvement of strength (147-152). However, it has been reported that Nb levels of > 0.13% do have detrimental effects upon the parent plate and HAZ toughness (25, 28, 31, 34). Therefore, the level is typically between .02 and .05 wt%.

The addition of Mn has a number of benefits. Mn strengthens the ferrite matrix whilst improving the HAZ toughness, providing its level is kept below 1.5%. Furthermore, Mn depresses the austenite to ferrite transformation temperature which makes the steel more amenable to TMCP, promotes ferrite grain refinement and slows down the precipitation of Cu during plate cooling after rolling (23, 153).

The addition of the alloying elements Cr and Mo increase steel strength, but it is generally accepted that they are deleterious to low temperature toughness properties (152).

Figure 1.6 (28) summarises the effects of these various microalloying elements on strength and toughness.
1.3.2 Transformation Kinetics and Hardenability of Cu Bearing Alloy Steels.

Each of the chemical elements in steel has an influence on the transformation kinetics and on the hardenability of the steel. The magnitude of the effect is dependent upon the element or combination of elements in question.

To date, limited information is available regarding the effect of Cu on the transformation kinetics and hardenability of steels. It is known that Cu lowers the $Ae_3$ and Ms temperatures, the extent of the effect being proportional to the Cu content as shown by Habraken and Gready (Figure 1.7)(44). Thus Cu acts as a mild austenite stabilising element and delays its decomposition (44, 45, 46).
Cu also appears to act in a synergistic manner in combination with other alloying elements. A recent report by Krishnadev indicates that combined additions of Cu and B to low carbon steels results in a lowering of transformation temperatures to an extent which was much greater than that which would be expected from a summation of the individual effects (Table 1.3) (47). This synergistic effect of Cu and B can result in reduction of the austenite transformation temperature by about 100 °C.
TABLE 1.3: Effect of Cu on the transformation kinetics of low carbon Boron steel (47).

<table>
<thead>
<tr>
<th>MATERIAL</th>
<th>COOLING RATE (°C/min)</th>
<th>COOLING MEDIUM</th>
<th>Ar₃ - Ar₁ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1A</td>
<td>19</td>
<td>Furnace</td>
<td>779 - 749</td>
</tr>
<tr>
<td></td>
<td>295</td>
<td>Air</td>
<td>700 - 628</td>
</tr>
<tr>
<td></td>
<td>1080</td>
<td>Forced Air</td>
<td>590 - 555</td>
</tr>
<tr>
<td></td>
<td>5420</td>
<td>Oil</td>
<td>532 - 416</td>
</tr>
<tr>
<td>5A</td>
<td>17</td>
<td>Furnace</td>
<td>689 - 666</td>
</tr>
<tr>
<td></td>
<td>230</td>
<td>Air</td>
<td>616 - 666</td>
</tr>
<tr>
<td></td>
<td>1030</td>
<td>Forced Air</td>
<td>530 - 508</td>
</tr>
<tr>
<td></td>
<td>6420</td>
<td>Oil</td>
<td>490 - 381</td>
</tr>
</tbody>
</table>

NOTE: Chemical Analysis of Material

1A 0.053 % C, 0.26 % Si, 1.62 % Mn, 0.023 % Al, 0.037 % Ti, 0.001 % B

5A 0.039 % C, 0.25 % Si, 1.52 % Mn, 0.018 % Al, 0.035 % Ti, 0.0009 % B, 1.79 % Cu

Siebert et al. (48) suggested that in calculations of hardenability the sum of Cu and Ni present must be used with an appropriate multiplying factor. An increase in the hardenability corresponding to increases in alloying elements has been reported by Irani et al. in their studies of Cu, Cu+Ni+Mo and Cu+Ni+Mo+B additions to low C-Mn steels (Figure 1.8) (49).
1.4 Thermo-mechanical Treatment

Thermo-mechanical Controlled Processing (TMCP) is a method whereby reheating practice, rolling reduction and hot rolling temperature are controlled to optimise strength and low temperature toughness for a given combination of microalloys. Most of the benefits which come from TMCP are the result of the refinement of the transformed microstructures, the most important of which is ferrite grain size. The grain size of ferrite produced from deformed austenite depends on:

- the transformation temperature (153),
- the prior austenite grain size (153),
- the morphology of the austenite grains (153) and
- the deformation substructures and precipitates which may nucleate ferrite (154, 155).

Ultimately the purpose of TMCP is to optimise the effect of microalloying on the mechanical properties. Literature on this subject is readily available. Copper in steel at levels below 0.4 weight % is generally not
considered to be a very influential microalloying addition in terms of its strengthening effect in ferrite (Refer to Section 1.3.1) or its grain refinement abilities.

In steels containing sufficient Cu to produce precipitation hardening (> 0.4 wt%), TMCP is important only in so far as it influences the ferritic microstructure of these steels and assists in producing a high base strength. Therefore, in the context of the current work a detailed discussion of TMCP methods is not warranted. However, a brief overview of the process as generally applied by BHP to HSLA 80 type steels is useful in assisting in the interpretation of the TMCP microstructures. This process is summarised in Figure 1.9.
FIGURE 1.9  Thermo-mechanical controlled processing as applied by BHP to HSLA 80 steel to optimise base steel strength prior to post TMCP ageing.
1.5 Effect of Cooling Rate on High Cu Bearing Steels.

The definition of hardenability is primarily concerned with the capacity of a steel to develop a martensitic microstructure. The cooling rate from the solution temperature is obviously an important factor in determining hardenability and it is therefore appropriate to discuss the effect of the cooling rate on the microstructure of Cu bearing steels.

1.5.1 Air and Accelerated Cooling

The microstructure of normal reheated (solution treated), rolled and aged A710 alloys (classified commercially as ASTM A710 Class 1 (Table 1.2), consists of fine equiaxed ferrite grains (ASTM 8 to 13) with islands of pearlite and grain boundary carbides (25, 28, 51, 52, 53). These steels are generally produced via the TMCP processing route or by air or accelerated cooling. Creswick (51) likened the microstructure to that of a .05%C plain carbon steel processed similarly except for a slightly dull appearance of the saturated ferrite at high magnification.

1.5.2 Quenching

It is appropriate when discussing the quenching of steels to first define the martensitic microstructures which may be produced. Martensite is the generic term for microstructures formed by diffusionless phase transformation, in which the parent and the product phases have a specific crystallographic relationship. Martensite can be produced in steels or iron based alloys by rapid quenching of the parent austenite phase. The morphology typically consisting of lath shaped or plate shaped martensite units in low and high carbon steels respectively.

Lath martensite tends to form in alloys containing up to 0.6% C. Laths are grouped into larger sheaves or packets, in which the individual units have closely similar orientations and are separated by low angle
boundaries (54). Adjacent aggregates are separated by high angle boundaries and may be twin related (56, 57). The substructure of lath martensite consists of a high density of dislocations some of which form laths or cells. Plate martensite forms as isolated lenticular crystals with a substructure consisting of fine transformation twins which do not generally extend to the plate edge, but which degenerate into a complex array of dislocations (58). Both martensites are associated with surface relief effects directly related to the transformation crystallography (59, 60) and it has been reported that both types partition the austenite during transformation (61).

After water quenching the microstructure of low to medium carbon steels with 1% to 1.5% Cu consists of martensite laths and cementite precipitates (52, 62). Krishnadev and Le May (63) reported that in a commercial 2% Cu HSLA steel the water quenched microstructure (ASTM A710 Class 3) consisted of a mixture of massive and acicular martensite with traces of proeutectoid ferrite. The terms massive and acicular martensite are understood in the context of this reference to be synonymous with lath and plate martensite, respectively. Their electron microscopy revealed the microstructure to be composed essentially of lath martensite of high dislocation density. This observation is consistent with results published by Ricks et al. (43) for high purity Fe-Cu and Fe-Cu-Ni alloys.

Examination of quenched and tempered plates of ASTM A710 by Hicho et al. (53) found the microstructure to be fine grained equiaxed ferrite. The grain boundaries in these water quenched and tempered steels were found to be highly irregular compared to those of air cooled ASTM A710 Class 1 type plates, consistent with the transformation from martensite to ferrite upon tempering with associated recovery and/or recrystallization. The rate of cooling, the austenite grain size and the chemistry, all combine to determine the amount of quasi polygonal and polygonal ferrite that forms in these alloys (64).

1.6 Ferritic Microstructures in Cu Bearing Steels

The morphology of the transformation product which forms in these low carbon, copper bearing steels is highly sensitive to cooling rate as discussed in Section 1.5. However, because these alloys are complex
multi-component systems, which can be subjected to a variety of thermal treatments, the variety of ferrite morphologies is wide. It is simplistic to categorise the products of these transformations as simply polygonal ferrite, bainite or martensite. Certainly, at low cooling rates polygonal equiaxed ferrite grains would be favoured, whilst at high cooling rates such as those produced by rapid quenching, lath martensite is likely to be produced. However, because of the operation of diffusion, partitioning of alloying elements will occur, the extent of which will be dependant on the severity of cooling. Thus a variety of intermediate stage products or "Zwischen - stufe" (Zw) will be generated during the cooling of these low carbon microalloyed steels.

The variability of the structure with composition and cooling rate can lead to a wide variation in mechanical properties. Hence to enable the clear interpretation of the relationship between the various morphological aspects of these non classic transformation products and the resultant mechanical properties, it is important to identify the transformation products present using terms which are clearly defined and universally understood. Current literature contains examples of several terminologies being applied to the same morphological aspect (156 - 158) which can lead to confusion. Therefore, a review of nomenclature for ferritic transformation product in low carbon steels is appropriate at this point.

A recent paper by Dunne and Pang (159) which discusses the types of ferrite aggregate structures found in ferrous weldments of low carbon steels, neatly summarises the interrelationships of the various nomenclature currently used. Their correlation of literary classifications of ferritic transformation product forms the basis of Table 1.4, which lists the various classifications as a function of decreasing temperature of formation. Furthermore, this table contains a description of the microstructural appearance and in some cases, where clarification is required, a cross reference is given to appropriate photomicrographs.

The proposals included in Table 1.4 are those by Bhadeshia (160), the IIW (161) and the Bainite Committee of the Iron and Steel Institute of Japan (162). Bhadeshia's terminology is based on studies of transformation mechanisms, the ISIJ nomenclature is based on the structures produced in low carbon microalloyed steels transformed under defined conditions following TMCP or normalising and the IIW classification is based on optical microscopic observations of weld metal microstructures.
### TABLE 1.4 Classifications for transformation products in low carbon steels

<table>
<thead>
<tr>
<th>General Description</th>
<th>Classifications</th>
<th>Characteristics</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Bha- deshia (160)</td>
<td>IIW (161)</td>
</tr>
<tr>
<td><strong>Reconstructive Transformations</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Polygonal Ferrite</td>
<td>( \alpha )</td>
<td>( \alpha_p )</td>
</tr>
<tr>
<td></td>
<td></td>
<td>PF(G)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Idiomorphic Ferrite</td>
<td>( \alpha_i )</td>
<td></td>
</tr>
<tr>
<td>Quasi Polygonal Ferrite</td>
<td>( \alpha_q )</td>
<td></td>
</tr>
<tr>
<td><strong>Displacive Transformations</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Widmanstätten Ferrite</td>
<td>( \alpha_w )</td>
<td>F(SP)</td>
</tr>
<tr>
<td>Acicular Ferrite</td>
<td>( \alpha_a )</td>
<td>AF</td>
</tr>
<tr>
<td>Granular Bainite</td>
<td>( \alpha_{gb} )</td>
<td>FS(NA)</td>
</tr>
<tr>
<td>Bainitic Ferrite</td>
<td>( \alpha_b )</td>
<td>FS(A)</td>
</tr>
<tr>
<td>Martensitic Ferrite</td>
<td>( \alpha' )</td>
<td>M(L)</td>
</tr>
</tbody>
</table>

**NOTE 1:** Acicular: A term applied to needle crystals found in ferromanganese, basic slags etc. and to ferrite in weld metals and wrought oxide inoculated steels (159). It has been applied erroneously to describe the appearance of sections of plates and wedge shaped crystallites in certain TMCP metals and alloys (162).
The ISIJ classification also includes a series of minor ("second") phases: Retained Austenite ($\gamma_r$), Martensite - Austenite constituent (MA), Auto-tempered Martensite (aTM), Upper Bainite (BII, B2, Bu), Lower Bainite ($B_L$), Pearlite (P), Degenerated Pearlite (P'), Cementite ($\theta$). The twinned martensite M(T) in the IIW classification is also likely to fit this description of a minor phase.
FIGURE 1.10 a and b. Examples of ferritic transformation products in low carbon steels using the ISIJ nomenclature (162).

a. Polygonal Ferrite ($\alpha_p$) (x200)

b. Quasi Polygonal Ferrite ($\alpha_q$)
FIGURE 1.10c and d. Examples of bainitic transformation products in low carbon steels according to the ISIJ nomenclature (162).

c. Lower Bainite/Bainitic Ferrite ($\alpha^B$)

d. Upper Bainite/Granular Bainite ($\alpha_g$)
FIGURE 1.10 e and f. Examples of martensitic transformation products in low carbon steels according to the ISIJ nomenclature (162).
1.7 Strengthening in Iron Copper Alloy Systems.

1.7.1 Strengthening Mechanisms

In the following discussion of strengthening in Fe - Cu based alloys, the term "strength" will be used to express a materials resistance to plastic flow. Since the discovery of dislocations by Taylor (65), Orowan (66) and Polanyi (67) in the early 1930s and the earliest theories of age hardening using the concept of the dislocation by Mott and Nabarro (135), it has been recognised that dislocations are responsible for the phenomenon of slip by which most metals deform plastically. Thus, all strengthening mechanisms in metals have in common the reduction of the mobility of dislocations and the increase of the stress required to move dislocations through the material (68). The commonly recognised methods of metal strengthening include:

* Grain Size Refinement (Base Strength)
* Solid Solution Strengthening.
* Dispersion of a second phase
* Precipitation Hardening.
* Dislocation Hardening.

In Copper bearing steels such as ASTM A710 the strengthening mechanism of particular concern is "Precipitation Hardening".

1.7.1.1 Precipitation strengthening - Background

A number of noteworthy reviews of various aspects of the history of precipitation hardening have been produced since 1940, by authors such as Mehl and Jetter (136), Smith (137), Kelly and Nicholson (138), Brown and Ham (139) and Ardell (140).
The earliest of these reviews, by Mehl and Jetter (1940), is a history of the progression of thought on the
mechanism of precipitation from solid solution strengthening through the late 1930s. However, one major
deficiency of the review is that it makes no reference to the possible role of dislocations, even though the
existence of dislocations had been recognised in the literature from 1934 (65, 66, 67). The earliest attempts
to explain the role of dislocations in age hardening were made by Mott and Nabarro (135). They suggested
that the interaction between dislocations and the internal stresses produced by misfitting coherent
precipitates were responsible for the strengthening observed. Furthermore, they recognised that
precipitation hardening involved the shearing of coherent precipitates by dislocations. The next major
development came in 1948 when Orowan derived his equation relating the strength of an alloy containing
hard particles to the ratio of the shear modulus of the dislocation and the average planar spacing of the
particles (132).

Surprisingly, the 1950 article by Smith (137) which dealt specifically with the progress in the
understanding of precipitation hardening omits reference to both the work of Mott and Nabarro published in
1940 (135)and the later work by Orowan (1948) (132). This would tend to indicate that the understanding
of the details of this process were not generally widespread during the 1940s and 1950s.

The 1963 review by Kelly and Nicholson (138) discusses the early attempts at formulating theories of
precipitation hardening. The mechanical behaviour of precipitation hardened alloys and the theories of
yield strength are discussed at length. Furthermore, the profound impact of the application of TEM to the
advances in the understanding of the mechanism of precipitation hardening is highlighted.

In 1971 an article published by Brown and Ham (139) discussed the advances in understanding made
throughout the 1960s. It was during this decade that the theories of coherency strengthening, order
strengthening, modulus hardening, stacking fault strengthening and spinodal decomposition were
formulated and proposed.

In 1985 an admirable review paper was published by Ardell (140) in which the progress made in the
previous decade or so in understanding the statistics of dislocation - particle interactions and the
mechanisms of age hardening were discussed in some detail. Most importantly for the analysis of data generated in the current work, he showed that when compared to linear supposition and the law of mixtures, Pythagorean superposition (Appendix 6.6) for strengthening by random mixtures of localised obstacles of different strengths provides the best agreement between theory and experiment.

As noted earlier in Cu-bearing steels such as ASTM A710 the strengthening mechanism of particular concern is "Precipitation Hardening". In the following discussion only those mechanisms with significant strengthening contributions (ie. >10 MPa) in Fe-Cu based systems will be reviewed.

1.7.1.2 Base strength (grain size refinement) in TMCP Cu bearing steels

The Hall Petch equation predicts the yield stress which applies to steels strengthened by the direct effects of lattice friction, solute elements and grain boundaries. The relationship between polygonal ferrite grain size (d) and the discontinuous yield stress ($\sigma$) (69, 70) is written;

$$\sigma = \sigma_0 + k_y \times d^{-\frac{1}{2}}$$

where

$\sigma_0$ = a stress constant associated with the effects of lattice friction and solute atoms, and

$k_y$ = the grain size coefficient, which is related to the stress concentration required to activate slip-dislocation sources.

The work of Gladman and Dulieu in the mid 1970s (71) produced a more detailed quantitative equation which relates various microstructural and compositional factors to strength. The basic equation pertaining to plain C/Mn steels which have been slowly cooled from the austenite range is:

$$\sigma(MPa) = K + 37(\%Mn) + 83(\%Si) + 2918(\%N_{free}) + 15.1d^{-\frac{1}{2}}$$
where \[ K = 88 \text{ MPa} \text{ for an air cooled steel and } 62 \text{ MPa for furnace cooled steel.} \]
\[ d = \text{the mean linear intercept of the polygonal grains expressed in mm.} \]

1.7.1.3 Solid solution strengthening

Solid Solution Strengthening (SSS), often referred to in literature as matrix strengthening, refers to the increased resistance to the movement of dislocations, through their interaction with the stress field surrounding solute atoms.

The magnitude of the solid solution strengthening effect is dependent on the following factors:

1. the difference in size between the solute and the solvent atoms. In general, the rate of change of strength with concentration is given by;
\[
\frac{d\tau}{dc} \approx \alpha \left( \frac{1}{\alpha} \times \frac{dc}{da} \right)^n
\]

where \( \tau \) is the shear stress, \( \alpha \) is the lattice parameter of the solid solution and \( c \) is the solute concentration. Data have been obtained which support this theory of the effect of atom size difference for copper alloys (72) and for ferrite - pearlite steels (73).

2. Disturbances to the electronic structure, often expressed in terms of the difference in shear modulus between the solute and the solvent.

In dilute solutions the effect of substitutional and/or interstitial solutes can be simplified to a linear dependence of solid solution strengthening upon the atomic percentage of solute, or, in some cases where solvent and solute do not differ markedly in atomic weight, to a linear dependence upon weight percent solute. Data obtained for ferrite and austenite are shown in Figures 1.11 (73) and 1.12 (74).
The effectiveness of either of the mechanisms described above (1 and 2) is limited by the amount which can be maintained in solution. In steels such as HSLA80 and A710 the degree of solid solution strengthening by Cu as a substitutional solute would be expected to be relatively small because of the
limited solubility of Cu in ferrite. This conclusion is supported by data presented in Figure 1.11 which indicates that a low C ferritic steel with the addition of 1.1 weight % Cu (which is typical of HSLA80 and A710) would experience a strength increase of approximately 30 MPa from substitutional SSS.

There is however, some contradictory evidence relating to the magnitude of the effect of SSS by Cu on the strength of steel. Baird et al. (75) report that the SSS effect can account for an increase in the yield point of ferrite of approximately 38% for each 1% of Cu added. Assuming that the major proportion of strengthening comes from SSS then according to Baird's analysis, the base strength reported by Tomita (31) of 350 MPa would be increased by approximately 200 MPa with the addition of 1.5% Cu. Tomita's reported final strength of 470 MPa approaches the estimate of 550 MPa based on the solid solution strengthening effect predicted by Baird et al. (75). Despite this proposal that SSS is significant, it has been observed (7) that Cu bearing steels respond strongly to ageing, resulting in strength increases well above the solution treated level. Therefore, precipitation hardening must be a major factor in the strengthening increment due to Cu.

1.7.1.4 Dispersion Strengthening

Dispersed particles cause strengthening by restricting the distance within a crystal through which a mobile dislocation can travel under the influence of an applied stress. The various models which describe dispersion strengthening differ in two aspects,

1. the mechanism by which the slip dislocations overcome particle resistance and
2. the assumed distribution of obstacles to slip.

Of the models available, the Ashby Orowan model (76) is widely applied to steels because it associates the yield stress increment with randomly distributed carbonitride dispersions in ferrite.

The Ashby Orowan model modified to include particle fraction and size can be expressed quantitatively as,
\[ \sigma (\text{MPa}) = \frac{5.9 \sqrt{f}}{x} \ln \frac{x}{5 \times 10^{-4}} \]

where

- \( \sigma \) = yield stress in tension
- \( f \) = volume fraction of precipitate particles and
- \( x = \frac{D}{(\frac{2}{\sqrt{3}})^{\frac{1}{2}}} \) where
- \( D \) = the mean precipitate diameter observed in a thin foil specimen.

Fuji et al. (77) have in fact found that "... the yield stress of alloys at overaged states could well be explained by simple Orowan theory". Most importantly for the application of the Orowan theory in these steels they found that, "Transmission electron microscope observations on the interaction between moving dislocations and precipitates showed the operation of the bypass process in these alloys...".

1.7.1.5 Hardening by Cu Precipitation

As mentioned previously, the solubility of Cu with decreasing temperature decreases significantly and the FCC \( \varepsilon \) phase can be precipitated on slow cooling or on ageing of supersaturated ferrite, provided of course that the level is >0.4%. It has been reported by Fletcher et al.(88) that precipitation can result in increases in strength of up to 248 MPa for each 1% of Cu and because of this potential for substantial strengthening, attempts have been made to identify the operative mechanism.

a. Hardening Due to Incoherent \( \varepsilon \) Cu Precipitates

Due to the complexity of the interaction between particle and dislocation, hardening due to incoherent \( \varepsilon \) Cu precipitates is one of the most difficult to treat theoretically. A number of authors have constructed theories of precipitate hardening using their own calculations of the interaction forces. Those most applicable to the
Cu bearing HSLA steels are those proposed by Knowles and Kelly (80) who showed their equations could be fitted to data on Fe - 1.5% Cu, Fe - 0.9% Cu alloys; and a model proposed by Russell and Brown (81) which was shown to be consistent for peak aged and overaged Fe - 0.9%, 1.68% and 3.95% Cu alloys. In later sections of this report (Section 4.3.2.3), the theories of Russell and Brown are applied to the experimental steels examined in this work. Therefore, a more detailed review of their work is warranted at this point.

Russell and Brown (81) have devised a model in which the strengthening observed upon ageing of Fe - Cu alloys is wholly accounted for by the difference in elastic modulus between copper and iron. In this system the attraction (between dislocation and obstacle) results from the fact that the Cu precipitates are elastically softer than the ferrite matrix.

For the overaged condition, where the precipitates are incoherent with the ferrite matrix, the strength of the alloy is calculated following the methods of Brown and Ham (82) based on Foreman and Makins’ numerical solution for stress at which a dislocation can move large distances through an array of obstacles (83). The shear stress is given by

\[
\tau = 0.8 \frac{Gb}{L} \left[ \cos \frac{\phi}{2} \right] \quad \text{for} \quad \phi \leq 100^\circ \tag{1.4a}
\]

\[
\tau = 0.8 \frac{Gb}{L} \left[ \cos \frac{\phi}{2} \right]^{3/2} \quad \text{for} \quad \phi \geq 100^\circ \tag{1.4b}
\]

where

\[ L = \text{obstacle spacing in the slip plane,} \]
\[ \phi = \text{critical angle at which a dislocation can cut an obstacle,} \]
\[ G = \text{shear modulus of the obstacle and} \]
\[ b = \text{Burgers vector of the dislocation.} \]

Russell and Brown deduce that when the energy of the dislocation is lower in the precipitate \( (E_1) \) than it is in the matrix \( (E_2) \), then the angle \( \phi \) has a minimum value and \( \tau \) a maximum value. When the dislocation is about to break away from the precipitate, the strength of the material is given by
Russell and Brown argue that it is possible by this mechanism to produce high strength levels in the overaged condition without the usually expected work hardening because no Orowan loops are left behind when the dislocation cuts the precipitate. Despite the claims of Fujii et al. (77) results of electron microscopy of deformed overaged alloys published in existing literature (77, 85, 86) do not show the pronounced tangling and prismatic loop production characteristic of deformation in other alloy systems.

Nevertheless, Fujii, Nemoto, Suto and Monma (77) in their paper on "Precipitation Hardening of Iron Copper Alloys", claim that the strengthening by the incoherent copper particles arises mainly from the by-passing process and that contributions from other mechanisms such as the above and similar elastic modulus difference models (79, 81) and chemical strengthening as proposed by Kelly and Nicholson (78) are almost negligibly small. Therefore, Fujii et al. have proposed that the yield stresses of these alloys in the overaged state can be explained most effectively using the simple Orowan theory (87) in which the stress required to bypass the particles is given by,

\[
\tau = 0.8 \frac{G b}{L} \left[ 1 - \frac{E_1}{E_2} \right]^{1/2} \text{ for } \sin^{-1} \frac{E_1}{E_2} \leq 50^\circ \tag{1.5a}
\]

\[
\tau = 0.8 \frac{G b}{L} \left[ 1 - \frac{E_1}{E_2} \right]^{3/4} \text{ for } \sin^{-1} \frac{E_1}{E_2} \geq 50^\circ \tag{1.5b}
\]

\[
\tau = 0.8 \frac{G b}{L} \left[ 1 - \frac{E_1}{E_2} \right]^{1/2} \text{ for } \sin^{-1} \frac{E_1}{E_2} \leq 50^\circ \tag{1.5a}
\]

\[
\tau = 0.8 \frac{G b}{L} \left[ 1 - \frac{E_1}{E_2} \right]^{3/4} \text{ for } \sin^{-1} \frac{E_1}{E_2} \geq 50^\circ \tag{1.5b}
\]

\[
\tau = 0.8 \frac{G b}{L} \left[ 1 - \frac{E_1}{E_2} \right]^{1/2} \text{ for } \sin^{-1} \frac{E_1}{E_2} \leq 50^\circ \tag{1.5a}
\]

\[
\tau = 0.8 \frac{G b}{L} \left[ 1 - \frac{E_1}{E_2} \right]^{3/4} \text{ for } \sin^{-1} \frac{E_1}{E_2} \geq 50^\circ \tag{1.5b}
\]

\[
\tau = 0.8 \frac{G b}{L} \left[ 1 - \frac{E_1}{E_2} \right]^{1/2} \text{ for } \sin^{-1} \frac{E_1}{E_2} \leq 50^\circ \tag{1.5a}
\]

\[
\tau = 0.8 \frac{G b}{L} \left[ 1 - \frac{E_1}{E_2} \right]^{3/4} \text{ for } \sin^{-1} \frac{E_1}{E_2} \geq 50^\circ \tag{1.5b}
\]

\[
\tau = 0.8 \frac{G b}{L} \left[ 1 - \frac{E_1}{E_2} \right]^{1/2} \text{ for } \sin^{-1} \frac{E_1}{E_2} \leq 50^\circ \tag{1.5a}
\]

\[
\tau = 0.8 \frac{G b}{L} \left[ 1 - \frac{E_1}{E_2} \right]^{3/4} \text{ for } \sin^{-1} \frac{E_1}{E_2} \geq 50^\circ \tag{1.5b}
\]

\[
\tau = 0.8 \frac{G b}{L} \left[ 1 - \frac{E_1}{E_2} \right]^{1/2} \text{ for } \sin^{-1} \frac{E_1}{E_2} \leq 50^\circ \tag{1.5a}
\]

\[
\tau = 0.8 \frac{G b}{L} \left[ 1 - \frac{E_1}{E_2} \right]^{3/4} \text{ for } \sin^{-1} \frac{E_1}{E_2} \geq 50^\circ \tag{1.5b}
\]

\[
\tau = 0.8 \frac{G b}{L} \left[ 1 - \frac{E_1}{E_2} \right]^{1/2} \text{ for } \sin^{-1} \frac{E_1}{E_2} \leq 50^\circ \tag{1.5a}
\]

\[
\tau = 0.8 \frac{G b}{L} \left[ 1 - \frac{E_1}{E_2} \right]^{3/4} \text{ for } \sin^{-1} \frac{E_1}{E_2} \geq 50^\circ \tag{1.5b}
\]

\[
\tau = 0.8 \frac{G b}{L} \left[ 1 - \frac{E_1}{E_2} \right]^{1/2} \text{ for } \sin^{-1} \frac{E_1}{E_2} \leq 50^\circ \tag{1.5a}
\]

\[
\tau = 0.8 \frac{G b}{L} \left[ 1 - \frac{E_1}{E_2} \right]^{3/4} \text{ for } \sin^{-1} \frac{E_1}{E_2} \geq 50^\circ \tag{1.5b}
\]

\[
\tau = 0.8 \frac{G b}{L} \left[ 1 - \frac{E_1}{E_2} \right]^{1/2} \text{ for } \sin^{-1} \frac{E_1}{E_2} \leq 50^\circ \tag{1.5a}
\]

\[
\tau = 0.8 \frac{G b}{L} \left[ 1 - \frac{E_1}{E_2} \right]^{3/4} \text{ for } \sin^{-1} \frac{E_1}{E_2} \geq 50^\circ \tag{1.5b}
\]

\[
\tau = 0.8 \frac{G b}{L} \left[ 1 - \frac{E_1}{E_2} \right]^{1/2} \text{ for } \sin^{-1} \frac{E_1}{E_2} \leq 50^\circ \tag{1.5a}
\]

\[
\tau = 0.8 \frac{G b}{L} \left[ 1 - \frac{E_1}{E_2} \right]^{3/4} \text{ for } \sin^{-1} \frac{E_1}{E_2} \geq 50^\circ \tag{1.5b}
\]

\[
\tau = 0.8 \frac{G b}{L} \left[ 1 - \frac{E_1}{E_2} \right]^{1/2} \text{ for } \sin^{-1} \frac{E_1}{E_2} \leq 50^\circ \tag{1.5a}
\]

\[
\tau = 0.8 \frac{G b}{L} \left[ 1 - \frac{E_1}{E_2} \right]^{3/4} \text{ for } \sin^{-1} \frac{E_1}{E_2} \geq 50^\circ \tag{1.5b}
\]

\[
\tau = 0.8 \frac{G b}{L} \left[ 1 - \frac{E_1}{E_2} \right]^{1/2} \text{ for } \sin^{-1} \frac{E_1}{E_2} \leq 50^\circ \tag{1.5a}
\]

\[
\tau = 0.8 \frac{G b}{L} \left[ 1 - \frac{E_1}{E_2} \right]^{3/4} \text{ for } \sin^{-1} \frac{E_1}{E_2} \geq 50^\circ \tag{1.5b}
\]
b. Precipitation Hardening due to Coherent Cu Rich Zones or Clusters

Dispersed particles or precipitates cause strengthening by restricting the distance within a crystal through which a mobile dislocation can travel under the influence of an applied stress. For strong coarse impenetrable particles the dislocations will bow out until they bypass the particles by looping, as described by the Orowan type mechanism (87). When the dispersed particles are coherent or partially coherent the hardening is usually referred to as precipitation or age hardening. In the case of weak or fine coherent particles the dislocation may cut straight through them.

Many theories have been proposed to explain precipitation hardening and a concise review has been published by L.M. Brown (89). The theories discussed in some detail here are those by Russell and Brown (81) and Hornbogen (90).

Russell and Brown (81) have proposed that the peak strength is determined by taking account of the dependence of the energy of the dislocation inside the precipitate upon the radius of the precipitate. Thus the strength in the underaged condition can be determined if the precipitate spacing (L) is known. They begin with an expression for the ratio of the energy of the dislocation in the precipitate and in the matrix \( \frac{E_1}{E_2} \) as a function of the radius of the precipitate (r).

\[
\frac{E_1}{E_2} = \frac{E_1^o \log \frac{R}{r_o} + \log \frac{R}{r}}{E_2^o \log \frac{R}{r_o} + \log \frac{R}{r}} \tag{1.7}
\]

where

- \( R \) = outer cut off radius of the dislocation,
- \( r_o \) = inner cut off radius of the dislocation and
- \( E_1^o, E_2^o \) = energy per unit length of the dislocation in infinite media.

If equation 1.5 is combined with equation 1.7 it is found that a critical precipitate size exists for which the strength is a maximum. For a void \( \frac{E_1}{E_2} = 0 \), and the maximum stress is predicted to occur when the voids have a radius equal to \( 2r_o \), which in the Fe-Cu system occurs when \( \frac{E_1^o}{E_2^o} = 0.6 \). Through
experiment and a review of existing literature Russell and Brown produce an equation in which the
maximum strength which can be achieved is inversely proportional to the square root of the volume fraction
of precipitate.

\[ \tau_{\text{max}} = 0.041 \frac{Gbf^{1/2}}{r_o} \]

Thus they derive a relatively simple model which can be applied to all systems with attractive particles.

An alternative mechanism for the cutting of particles or clusters has been suggested by Hornbogen (90),
who claimed that the most likely cause of strengthening in alloys containing Cu clusters could be due to
Cu induced vacancies causing jogs on screw dislocations. These jogs would decrease the mobility of the
dislocations. Hornbogen suggested that vacancies are randomly distributed as Cu-vacancy pairs in the
homogeneous solid solution and that when clusters form the vacancies also segregate in their vicinity.
A screw dislocation passing through the random solid solution would only acquire step jogs rather than
the large jogs it may acquire from the vacancy concentrations in the clusters. Hence clusters would be far
more effective in hindering dislocation movement.

Hornbogen further suggested that during the stages between clustering and the development of
course particles by overaging, hardening was produced by a combination of mechanisms involving both
the clusters and the fine particles together. Cu precipitates, because of their relative 'softness' compared to
NbCN and TiCN particles, would not conceivably form impenetrable particles but rather would be most
likely cut by dislocations. When small, the cutting of the particles by the dislocations is facilitated as they
are still coherent with the ferrite matrix and the slip systems in the FCC particle and the BCC matrix
are parallel. Thus in this case, strengthening would be a combination of jogged screw dislocations
caused by the remaining clusters and by particle cutting.

A number of authors (65, 91, 92) support this theory of particle shearing as the most probable mechanism
of strengthening. Goodman et al. (93, 94), through their work with field ion microscopy and atom probe
analysis have evidence to suggest that during the early stages of ageing, the strength increment may be due to the fact that the precipitates are highly supersaturated Cu-Fe solutions rather than the nearly pure Cu. These particles are reported to have a shear strength in excess of 980 MPa and as such would offer considerable resistance to shear (93).

1.7.1.6 Dislocation hardening associated with rapid cooling.

Cooling directly after TMCP from the austenitic field introduces dislocations in the supersaturated solid solution, which cause hardening in the alloy. However, subsequent ageing treatments gradually eliminate the majority of these dislocations. It was found by Fujii et al. (77) when tempering an Fe - 1.4% Cu alloy at temperatures between 300 and 700 °C for various periods, that the contribution of these dislocations to the yield stresses was about 5 kg/mm$^2$ at most. On this basis, the effect of these dislocations has not been considered in this work.

1.7.2 Precipitate Morphology

The sequence of morphological changes on ageing Cu supersaturated ferrite involves firstly the formation and growth of metastable BCC Cu rich clusters which are coherent with the ferrite matrix (118). Recent investigations by Soylu and Honeycombe (163) indicate that these coherent bcc zones transform into stable fcc particles with a substructure of fcc plates which are twin related to each other. These particles have a Kurdjumov - Sachs (KS) orientation relationship with the bcc ferrite (164) $\text{[110]}_{\text{FCC}} || \text{[110]}_{\text{BCC}}$, $\text{[110]}_{\text{FCC}} \parallel \text{[111]}_{\text{BCC}}$.

Goodman, Brenner and Low (93) have predicted that those clusters present at the ageing temperature are nucleated at the ageing temperature and did not originate from quenched in clusters. They found that these clusters and presumably the coherent fcc particles identified by Soylu and Honeycombe (163) grow and transform into incoherent fcc Cu precipitates when they reach a critical size. Goodman et al. calculate that
loss of coherency will occur when the particle diameters are about 40Å. This estimate was supported by their experimental results which indicated that when particles reached a diameter > 50Å they became incoherent with the ferrite matrix. These particles gradually coarsen with prolonged ageing into rod like precipitates (63).

Current literature contains much conflicting information with regard to the morphology and distribution of ε Cu. Cox (95) reported that in a 0.3%C-1.5% Cu alloy, ε phase precipitation takes place predominantly along dislocation boundaries. However, a number of authors (63, 91) have reported that ε precipitation in low carbon steels takes place uniformly through the matrix. This difference may be due to the carbon content, with the low carbon steels altering the degree of supersaturation sufficiently to change the energy criterion for nucleation. Uniform precipitation through the matrix in low carbon steels (.05C-.06C) is further supported by the observations of Tsukada et al. (28).

Ricks, Howell and Honeycombe (43) reported that ε Cu appears to be the only precipitate to form in association with ferrite. In a 2%Cu, 2%Ni alloy the precipitation of Cu was found to occur in three distinct distributions. One consisted of regularly spaced sheets of ε Cu precipitates (Figure 1.13) (43). This form is analogous to the interphase precipitation described by Honeycombe for low alloy steels containing strong carbide forming elements (96). The presence of these sheets of regularly spaced carbides is a consequence of a ledge mechanism of growth of immobile, partially coherent phase boundaries (97, 98). Ricks et al. described this type of precipitate distribution as "coherent interphase precipitation" (43).

The second distribution consisted of either curved sheets of irregularly spaced precipitates or a seemingly random precipitate distribution (A and B respectively in Figure 1.14) (43). Ricks et al. suggested that the growth of these precipitates is a result of incoherent or disordered phase boundary growth. This form of precipitate morphology was therefore termed "incoherent interphase precipitation". An interphase bowing mechanism has been suggested by Honeycombe (96) to account for this type of precipitation.
The third form of Cu precipitation consisted of particles which formed from supersaturated ferrite at grain boundaries, matrix dislocations and within the matrix (Figure 1.15) (43).

**FIGURE 1.13** Precipitate centred dark field micrograph showing coherent interphase precipitation formed in the Fe-2Cu-2Ni by isothermal transformation at 720 °C for 5 minutes (43).
FIGURE 1.14 Bright Field electron micrograph showing incoherent interphase precipitation formed in the Fe-2Cu-2Ni alloy by isothermal transformation at 720 °C for 5 minutes. This precipitate dispersion can develop as curved sheets (eg. at A) or in a virtually random manner (eg. at B) (43).

FIGURE 1.15 Bright field electron micrograph showing precipitation of s Cu from supersaturated ferrite in the Fe-2Cu-2Ni alloy isothermally transformed at 700 °C for 5 minutes (43).
As mentioned earlier, whichever form of precipitation these Cu particles take, they eventually coarsen with prolonged ageing into rod-like precipitates (63). Two possible explanations exist for the formation of the rod-like precipitates on prolonged ageing. Nabarro (99) suggested that the rod form is due to the minimisation of strain energy while Speich (100) attributed it to an anisotropy of surface energy. Speich also reported the length to radius ratio of these rod-like particles to be constant at about 10. However, Krishnadev (101) reported precipitates with ratios in the range 20 to 50.

1.8 Scope of Present Work.

It is evident from this review of the existing literature that uncertainty remains as to the mechanism of strengthening which is mainly responsible for the strengthening in Fe-Cu alloys. Furthermore, although a number of models exist to explain the observed strength increment in Cu bearing HSLA steels, because of the effects of other alloying elements on the nature and kinetics of precipitation in the Fe-Cu system, the type and the amount of microalloying addition could affect the operative model. Therefore, the accuracy of these models when applied to a particular commercial age hardenable Cu bearing HSLA steel is unknown.

Where the development and eventual commercial production of any steel is concerned, the metallurgist must be well informed of the metallurgical peculiarities of the steel in question. In this way it is possible to design the most economically feasible means of producing a new steel grade. When BHP SPPD undertook the development of a new high copper bearing steel to meet market demands, it was necessary to understand the metallurgical characteristics of the particular developmental chemistry in question.

Because of the sensitivity of the kinetics of precipitation to alloy variations, it was not sufficient to rely purely on published data relating to steels of similar chemistry. Therefore, an investigation was undertaken to examine the precipitation hardening response and the morphology of the precipitates produced in Cu bearing HSLA80 type steels developed by BHP SPPD. It is this work which forms the basis of this thesis.
2 EXPERIMENTAL MATERIALS AND PROCEDURES

2.1 Introduction

The primary aim of this work was to examine in detail, Cu precipitation in a range of Cu bearing steels being investigated as candidate steels for a TMCP production route. The experimental work was designed to quantify the effect of:

i. cooling rate from the solution temperature on the precipitate morphology and distribution;

ii. ageing time and temperature on the precipitation hardening response of Cu; and

iii. Cu precipitation on the mechanical properties of the steel.

The melting procedure used and the alloys investigated are outlined in Section 2.2. Flow diagrams of the procedures involved in the above investigations are given in Section 2.3 in Figures 2.2(a) and (b). The thermo-mechanical control processing details are given in Section 2.4. Heat treatment and mechanical testing are described in Section 2.5 and metallographic methods are outlined in Section 2.6.
2.2 Production of Laboratory Melts.

All steels examined during the course of this work were produced at BHPR-ML using vacuum induction melting as detailed in Figure 2.1.

FIGURE 2.1 Flow diagram of procedure for the production of laboratory melts.
The alloys produced and investigated during the course of this work are summarised in Table 2.1.

### TABLE 2.1 Check spectrographic analyses of experimental steels, produced as laboratory melts in an induction furnace.

<table>
<thead>
<tr>
<th>STEEL TYPE</th>
<th>CHEM. wt% CODE</th>
<th>C</th>
<th>P</th>
<th>Mn</th>
<th>Si</th>
<th>S</th>
<th>Ni</th>
<th>Cu</th>
<th>Cr</th>
<th>Mo</th>
<th>Al</th>
<th>Nb</th>
<th>Ti</th>
<th>N ppm</th>
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<td>.007</td>
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</tbody>
</table>

**NOTE**  
IIW CEQ = C + Mn/6 + (Cr + Mo + V)/5 + (Cu + Ni)/15
Steels A1, A2, B1, B2 and C are copies of commercially available ASTM A710 type grades listed in Table 1.1 (Section 1.2.1). These steels were used as reference grades for the assessment of steels D through to G, which are different versions of the developmental BHP SPPD grade HSLA80. Steel D is the BHP laboratory version of the commercially available HSLA80 steel specification. Steel E1 had essentially the same chemistry as D, but contained a phosphorous level more consistent with commercially achievable levels. Steels F & G were designed to allow the examination of the effects of low Nb (.008) and medium Ni/Cu (.4/.5), on the base chemistry grade (E1) which acted as the control.

The chemistry of the BHP experimental HSLA80 steels D to G in some cases varied significantly from the grades currently available commercially. These modifications were based on the following considerations.

i. Cr and Mo additions were not used. This steel grade was to be produced by Thermo-mechanical Controlled Processing (TMCP) in order to achieve a minimum yield strength of 550 MPa as specified for ASTM A710. In addition, the high hardenability which would be needed for a quenched and tempered type steel was not required. The elimination of Cr and Mo would result in a reduction of the carbon equivalent (IIWCEQ) which according to a number of authors should improve weldability (25, 28, 30, 31). Furthermore, their elimination should provide significant benefits in steelmaking such as increased hot ductility during casting and lower production costs.

ii. The increased Mn content would have a number of benefits. It would partly offset the strength reductions arising from the elimination of the Cr and Mo additions. Furthermore, Mn depresses the austenite to ferrite transformation temperature (Ar3) which renders the steel more amenable to TMCP, promotes ferrite grain refinement and reduces the precipitation of Cu during plate cooling after rolling (23). Moreover, it has been reported that Mn is less deleterious to HAZ toughness than the carbide formers Cr and Mo (29).
The Nb level was reduced and a small Ti addition was made to enhance the HAZ toughness (117). Due to a malfunction of the spectrometer when the check analysis was being carried out during vacuum melting of the experimental steels, steels A through to G had low carbon levels of between .018 and .031. Since carbon levels of between .04 and .05 are more typical of levels achieved in commercial steels of this type, three steels A2, B2 and E2 were remade with carbon levels between .035 and .075 C. The first attempt to make A2 resulted in a steel with a Cu content of 1.7 wt% and this steel was renamed A2'. A second ingot (A2) contained the required Cu level of 1.15 wt%.
2.3 Summary of Experimental Procedures

Figure 2.2(a) Flow diagram showing the overall procedure followed in order to determine the effect of cooling rate from the solution temperature on the precipitation morphology and distribution of Cu bearing steels.

Figure 2.2(b) Flow diagram showing the overall procedure followed in order to determine the effect of ageing time and temperature on the precipitation hardening response of TMCP Cu bearing steels.
2.4 Thermo-Mechanical Controlled Processing

The ingots were reheated to 1250 °C and subjected to thermo-mechanical controlled processing (TMCP) to 12 mm x 180 mm x 1710 cm plate with an aim finish temperature of approximately 800 °C. The TMCP schedule is summarised in Figure 2.3, whilst actual entry and finish rolling temperatures and reduction schedules used are summarised in Table 2.2(a) and (b), respectively.

![Figure 2.3 Schematic diagram of thermo-mechanical controlled processing schedule for laboratory melts.](image)

### TABLE 2.2(a) Thermo-mechanical controlled processing - temperature details.

<table>
<thead>
<tr>
<th>STEEL TYPE</th>
<th>CODE</th>
<th>ENTRY TEMP. TO FINISH MILL (°C)</th>
<th>FINISH ROLLING TEMP. (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AMAX</td>
<td>A1</td>
<td>840</td>
<td>790</td>
</tr>
<tr>
<td>NKK/NSC</td>
<td>B1</td>
<td>830</td>
<td>790</td>
</tr>
<tr>
<td>LUKENS</td>
<td>C</td>
<td>822</td>
<td>790</td>
</tr>
<tr>
<td>BHP HSLA80</td>
<td>D</td>
<td>823</td>
<td>752</td>
</tr>
<tr>
<td>BHP HSLA80</td>
<td>E1</td>
<td>825</td>
<td>780</td>
</tr>
<tr>
<td>MOD1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BHP HSLA80</td>
<td>F</td>
<td>821</td>
<td>770</td>
</tr>
<tr>
<td>MOD2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BHP HSLA80</td>
<td>G</td>
<td>825</td>
<td>786</td>
</tr>
<tr>
<td>MOD3</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>AMAX REMAKE</td>
<td>A2</td>
<td>835</td>
<td>790</td>
</tr>
<tr>
<td>NKK/NSC REMAKE</td>
<td>B2</td>
<td>841</td>
<td>795</td>
</tr>
<tr>
<td>BHP HSLA80</td>
<td>E2</td>
<td>828</td>
<td>785</td>
</tr>
<tr>
<td>MOD1 REMAKE</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### TABLE 2.2(b) Thermo-mechanical controlled processing - roughing and finishing pass schedule.

<table>
<thead>
<tr>
<th>REDUCTION (%)</th>
<th>INGOT THICKNESS (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reheat to 1275 °C</td>
<td>114.3</td>
</tr>
<tr>
<td>13.4</td>
<td>99</td>
</tr>
<tr>
<td>14.0</td>
<td>85</td>
</tr>
<tr>
<td>21</td>
<td>67</td>
</tr>
<tr>
<td>21</td>
<td>53</td>
</tr>
<tr>
<td>24.5</td>
<td>40</td>
</tr>
<tr>
<td>Hold to 920 °C</td>
<td>30.5</td>
</tr>
<tr>
<td>24</td>
<td>23.9</td>
</tr>
<tr>
<td>25</td>
<td>17.2</td>
</tr>
<tr>
<td>20</td>
<td>13.8</td>
</tr>
<tr>
<td>16</td>
<td>11.6</td>
</tr>
<tr>
<td>Finish at 800 °C</td>
<td></td>
</tr>
</tbody>
</table>
2.5 Heat Treatment and Mechanical Testing

The steels produced were subjected to a variety of heat treatments and mechanical property tests which are described below.

2.5.1 Effect of Cooling from Solution Temperature

2.5.1.1 Thermal treatment

10mm cubes were machined from each plate in the TMCP condition. A number of cubes from each steel type were retained in the TMCP condition to use as a control whilst the remainder were subjected to various thermal treatments, as indicated in Figure 2.4 (for actual cooling curves see Appendix 3, Figures A3.1 to A3.3). For all ageing treatments a 10mm cube with a thermocouple inserted into its centre was introduced into the furnace to monitor and verify the temperatures and cooling rates. The solution treatment consisted of a hold of 30 minutes at 900 °C in an argon purged furnace. These samples were then cooled using various cooling rates as outlined in Figure 2.4. An age hardening treatment was then carried out at 550 °C for 60 minutes.

![FIGURE 2.4 Heat treatment procedure for laboratory melts. Cooling rates refer to the cooling rate between 800 °C and 500 °C.](image-url)
2.5.1.2 Hardness testing

Hardness tests were carried out on all samples, as indicated in Figure 2.2 a. In preparation for testing, all samples were cut slightly off centre, the larger portion was mounted with the cut face up, ground down to expose the centre plane, polished and hardness tested using a Vickers Hardness Tester with a 10kg load. Five separate hardness indentations were performed close to the centre on each sample, the mean hardness and the standard deviation were then calculated. These mean hardnesses and standard deviations are summarised in Tables 3.3 and A3.1.

2.5.1.3 Impact testing

Charpy transition curves were determined for each steel in both the TMCP condition and the TMCP/solution treated/control cooled/aged condition.

For the ageing treatments, a control blank and the test blanks (all 60mm x 190mm x 12mm) were placed in a muffle furnace, which had been preheated to a selected ageing temperature (450 to 600 °C). The time for blanks to reach the required temperature was determined by measuring the temperature at the centre width/thickness position of the control blank. This temperature was recorded by a thermocouple as shown in Figure 2.5. The blanks were held at temperature for 60 minutes, then removed from the furnace and placed on wire racks to cool.
EXPERIMENTAL MATERIALS AND PROCEDURES

Sample Size

TEMPERATURE

450 to 600 °C
60 Minutes

60 mm

250 mm

12 mm

Thermocouple insert in centre of sample.

FIGURE 2.5 Heat treatment procedure for impact test and tensile test blanks.

Charpy test pieces were machined and tested according to Australian Standards as per Appendix 4.1.

A standard testing temperature (-85 °C) was selected for inclusion in all transition curves because this temperature has been specified by NAVSEA (134) as a standard testing temperature for A710 and HSLA 80 type steels (MIL - S - 24645(SH)).

2.5.2 Determination of Optimum Ageing Conditions (Temperature and Time).

2.5.2.1 Thermal treatment

10mm cubes were machined from each plate in the TMCP condition. A number of cubes from each steel type were retained in the TMCP condition to use as a control whilst the remainder were subject to various ageing treatments directly after TMCP. The ageing procedure consisted of holding the samples at temperatures between 500 and 650 °C for various times of between 5 minutes and 3 hours followed by air cooling. Selected samples were aged for 100 hours to examine the effect of overageing.
2.5.2.2 Hardness testing

The samples were prepared for hardness testing according to the procedure outlined in 2.5.1.2 and tested using a Vickers Hardness tester with a 30 kg load.

2.5.2.3 Tensile testing

Tensile tests were performed for each steel selected, to examine the effect of ageing time and temperature (Figure 2.2b) in both the TMCP and TMCP and aged conditions.

Ageing treatments were performed in the same manner discussed in Section 2.5.1.3 for impact tests.

Tensiles were machined and tested according to the Australian Standard described in Appendix 4.2.
EXPERIMENTAL MATERIALS AND PROCEDURES

2.6 Metallographic Examination

2.6.1. Optical Microscopy

Samples in both the TMCP and the solution treated and aged condition (Section 2.5.1.1) were prepared for metallographic examination as described in Section 2.5.1.2 followed by etching. These samples were examined using an Olympus optical microscope prior to Vickers hardness testing. Photomicrographs were taken using a Carl Zeiss / Jena Neophot 2 Microscope and intercept grain sizes were determined using a Reichert-Jung MeF3 microscope and / or a Biquant Image Analyser.

Since image analysis equipment operates by distinguishing the differences between various shades of grey, contrast is of the utmost importance. Standard etching techniques usually accent grain boundaries which presents problems when trying to etch martensite and bainite. The procedure outlined in section 2.5.1.1 produced martensitic and bainitic microstructures (see sections 3.1.1 and 4.2.1) and in order to produce the necessary contrast in these samples two different etchants, Nital (165) and Le Pera's (166) were used. The composition of these etchants, their method of application and their specific attributes are summarised in Table 2.3.

<table>
<thead>
<tr>
<th>ETCH</th>
<th>COMPOSITION</th>
<th>METHOD</th>
<th>PURPOSE</th>
</tr>
</thead>
<tbody>
<tr>
<td>NITAL (165)</td>
<td>3% Nitric Acid ($HNO_3$) in Ethyl alcohol</td>
<td>• Immerse at room temperature.</td>
<td>Etches the grain boundaries of ferrite and attacks ferrite grains except those with {100} parallel to the section surface. Reveals Cementite, etches untempered martensite.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• Rinse in Ethyl alcohol.</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>• Blow dry.</td>
<td></td>
</tr>
<tr>
<td>LePera (166)</td>
<td>1% sodium metabisulphite ($Na_2S_2O_3$) in distilled water. 4% picric acid ($C_6H_2(NO)_3OH$) in ethyl alcohol (SDA 32)</td>
<td>• Etch 6-8s using 4% picral rinse in water</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>• polish using 0.3 micron alpha alumina to remove frosted appearance.</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>• immerse in blended etchant for 5-10s and oscillate</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>• rinse in ethyl alcohol</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>• blow dry</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
2.6.2. Electron Microscopy

2.6.2.1 Foil preparation

Foils for transmission electron microscopy were prepared using the procedure shown in Figure 2.6. The foils were examined using a JEOL 2000 FX microscope.

![Flow diagram of foil preparation procedure](image_url)

FIGURE 2.6 Flow diagram of procedure and apparatus used in foil preparation.
2.6.2.2. Precipitate species identification

In this study the precipitate species of particular interest were identified using a combination of conventional "convergent beam" and "selected area" diffraction techniques.

The procedure used for indexing and identifying the diffraction patterns produced was as follows.

1. The camera constant $\lambda L$ was determined using a gold standard (as in Appendix 1 - Figure A1.1 and Table A1.1) through the Bragg relationship for interplanar spacing ($d_{hkl}$).

$$d_{hkl} = \lambda L / R_{hkl} \quad 2.1$$

where

- $\lambda$ = wavelength of the diffracted beam.
- $L$ = the effective camera constant.
- $R_{hkl}$ = measured distance between the diffraction pattern spot in question and the spot made by the direct beam.

2. A prepared foil of the experimental steel was inserted into the TEM and a diffraction pattern was produced from the precipitate species in question (Appendix 1 - Figure A1.2).

3. The d spacing was determined from selected spots appearing on the diffraction pattern through the relationship in equation 2.1 (Appendix 1-Figure A1.3 and Table A1.2).

4. The d spacings were compared to known d spacings from the literature (104) and a tentative identification was made.

5. The tentative identification was checked using known d spacing ratios and angles between planes. If a good correlation was found for a plausible precipitate species, the tentative identification was accepted as the correct identification.
2.6.2.3 Foil thickness determination

The image formed in a transmission electron microscope is a magnified two dimensional projection of the object. In order to enable the accurate determination of population density of precipitates as discussed in the following section (2.6.2.4), it was first necessary to determine the volume of the imaged region by obtaining an accurate measurement of foil thickness.

There are many ways in which the foil thickness can be measured in the TEM. The method used here is that pioneered by Sadhukhan (105) and Von Heimendahl (106) and quoted by Scott and Love in their review paper (107). In this method, artificially produced features are applied to both foil surfaces.

The features in this case are small cones or spots of contamination produced using a highly focused electron beam and deposited on the upper surface of the foil where the electron beam impinges and on the lower surface where the beam emerges. Tilting the foil causes the spots to separate and a thickness value can be determined directly from the angle of tilt and the separation between the surfaces of the projected spot.

Rae et al. (108) have described several sources of error associated with this technique, the most important being that it is not always obvious between which contamination spot features one should measure. To minimise this error, Rae et al. have recommended that the contamination spots be made as small as possible and that the minimum distance between spots should be 3 \( \mu \text{m} \) to avoid overlapping discs of contaminant. It has been found by other authors (109), in a study of uranium alloy foils, that the contamination spot method overestimates the foil thickness by about 10%.

Whilst a number of alternative techniques are available which enable the foil thickness to be measured, some of which have potentially smaller sources of error, the "contamination spot" technique was considered the most appropriate for this study because of its simplicity, compatibility with available equipment and the fact that volume fraction determination is relatively insensitive to foil thickness measurements particularly within the ±10% error expected of this technique.
Based on the geometric considerations outlined in Figure 2.9 the foil thickness was determined for each foil used in the precipitate counting exercise. Complete thickness profiles for the transparent and therefore useable area of the foil were produced for each foil. From this profile an average foil thickness $\bar{t}$ was determined.

![Figure 2.9](image)

**FIGURE 2.9** Schematic diagram showing the method of contamination spot foil thickness determination.

2.6.2.4 Precipitate population distributions

All of the Series 1 and Series 2 steels with the exception of the low Cu steel G (0.49 wt% Cu) and the high Cu steel A2' (1.9 wt% Cu), contained similar amounts of Cu (1 wt%). During preliminary examinations of foils produced from each steel type, it became apparent that those steels with around 1 wt% Cu, showed similar precipitate sizes and distributions for the same conditions of cooling and ageing. Due to the large amount of work involved in the manual determination of precipitate distributions, it was decided to measure
only steel E2 in detail as being representative of the other steels. Checks of the precipitate distributions of
the other 1 wt% Cu experimental steels were carried out using random fields from each steel type.

The precipitate point count procedure was carried out using methods outlined in ASTM E562 - 89 and as
discussed at some length by E. E. Underwood in his text "Quantitative Stereology" (110).

Various studies have been carried out on the accuracy and efficiency of systematic point count analysis (111, 112, 113), outlining the various sources of error apparent in this and similar techniques. In this study an
attempt has been made to account for and eliminate errors where possible. Two major areas of consideration
were:

a. **Point Count Procedure**

The accuracy of the point count procedure can be assessed from the relationship given by De Hoff (114);

\[
P_i = \left[ \frac{200}{\text{accuracy}} \times \sigma (P_p) \right]^2
\]

where

- \( P_i \) = Total Number of point elements or test points.
- \( P_p \) = Point Fraction, Number of Points per test point.
- \( \sigma \) = Standard Deviation

b. **Particle Truncation and Overlap**

A correction for particle truncation and overlap was made by applying Underwood's model (110) which is
based on a procedure used by Cahn (115) and Hilliard (116) in which:

\[
f = \left[ -2 \ln \left( 1 - \Lambda^R \right) \right] \left[ \frac{D}{D + 3t} \right]
\]
where \( f \) = Volume fraction

\( A^R \) = Area fraction of projected areas of selected feature (Relative Area)

\( D \) = Particle diameter of a spherical particle

\( t \) = Foil thickness

This equation is used in Appendix 2 to determine actual volume fractions. The procedure followed to determine the volume fractions appears in Appendix 2.2 using the terms defined in Table A2.1.
3 RESULTS

3.1 Metallography

3.1.1 Photomicrographs of Experimental Steels Subject to Various Thermal Treatments

Optical and transmission electron micrographs of the experimental steels, subjected to various TMCP and ageing conditions are as shown in Figures 3.1 to 3.6. Figures 3.1 and 3.2 show the "base or control structure" typical of the experimental steels prior to normalising and ageing i.e. in the TMCP condition, whilst Figures 3.3 through to 3.6 show the effect of different cooling rates from the solution temperature on the microstructure and the state of precipitation. Theoretical estimates of the yield strength of a number of the experimental steels have been made using various models. This theoretical analysis required that the grain size of these steels in the TMCP condition be measured in order for the yield strength to be estimated. The ferrite and in some cases the austenite grain size measurements appear in Table 3.1a and b. The results of this theoretical analysis appear in Section 4.3.2.1.
RESULTS

FIGURE 3.1  Optical micrographs showing the microstructures typical of the Series 2 experimental steels in the TMCP condition prior to solution treatment and ageing (x 500).

NITAL ETCH (165)  Le PERA ETCH (166)
FIGURE 3.2a  Transmission electron micrographs typical of the Series 2 steels in the TMCP condition (x100K).

FIGURE 3.2b  Transmission electron micrographs typical of the Series 2 steels in the fully aged condition (x100K).
RESULTS

NITAL ETCH (165)

Le PERA ETCH (166)

70 °C/s 4 °C/s 0.2 °C/s

FIGURE 3.3a Optical micrographs of Series 2 steel A2 in the solution treated condition, showing the effect of cooling rate on the optical microstructure (x 500).
FIGURE 3.3b Optical micrographs of Series 2 steel B2 in the solution treated condition, showing the effect of cooling rate on the optical microstructure (x 500).
FIGURE 3.3c Optical micrographs of Series 2 steel E2 in the solution treated condition, showing the effect of cooling rate on the optical microstructure (x 500).
FIGURE 3.3 d Optical micrographs of Series 2 Steels A2, B2 and E2 in the solution treated condition, showing the optical microstructure produced using a 0.2 °C/s cooling rate (Slow Cool). Prepared using Nital etch (165) and low magnification to show banding (x 200).

FIGURE 3.3 e Optical micrographs of Series 1 steel E1 in the solution treated condition, showing the effect of cooling rate on the optical microstructure. Prepared using Nital etch (165) (x 500).
**TABLE 3.1a** Microstructural analysis of Series 2 experimental steels. Condition: TMCP and solution treated at 900 °C for 30 minutes and cooled at various cooling rates.

<table>
<thead>
<tr>
<th>STEEL</th>
<th>MICROSTRUCTURE</th>
<th>TMCP</th>
<th>Solution Treated at 900 °C and Cooled at Various Cooling Rates</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.2 °C/s</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>α_p</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>α_q</td>
</tr>
<tr>
<td>NUMBER OF OBSERVATIONS</td>
<td>520</td>
<td>530</td>
<td>535</td>
</tr>
<tr>
<td>MEAN GRAIN SIZE (μm)</td>
<td>7.4</td>
<td>6.8</td>
<td>6.2</td>
</tr>
<tr>
<td>STANDARD DEVIATION</td>
<td>3.2</td>
<td>3.4</td>
<td>4.0</td>
</tr>
</tbody>
</table>

**NOTE:**
* Prior Austenite grain size

All nomenclature used corresponds to ISIJ classifications listed in Table 1.4 and repeated below.

- \( \alpha_p \) = Polygonal Ferrite
- \( \alpha_q \) = Quasi-Polygonal Ferrite
- \( \alpha_B \) = Granular Bainitic Ferrite
- \( \alpha'_B \) = Bainitic Ferrite
- \( \alpha_M \) = Martensite

B = Upper Bainite
Residual Phases = ( )

MA = Martensite - Austenite Constituent
P = Pearlite
TABLE 3.1b  Microstructural analysis of experimental steels in the TMCP condition.

<table>
<thead>
<tr>
<th>MICROSTRUCTURE</th>
<th>SERIES 1</th>
<th>SERIES 2</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>D</td>
<td>E1</td>
</tr>
<tr>
<td>α_p, α_q</td>
<td>20</td>
<td>20</td>
</tr>
<tr>
<td>α_p</td>
<td>23.75</td>
<td>27.43</td>
</tr>
<tr>
<td>α_q</td>
<td>3.29</td>
<td>2.83</td>
</tr>
<tr>
<td>ASTM GRAIN SIZE NUMBER</td>
<td>11.71</td>
<td>12.12</td>
</tr>
<tr>
<td>GRAIN SIZE (μm)</td>
<td>5.28</td>
<td>4.57</td>
</tr>
</tbody>
</table>

NOTE:

1. All nomenclature used corresponds to ISIJ classifications listed in Table 1.4 and repeated below Table 3.1a.
2. In the lower carbon Series 1 steels, no significant change in the ferritic microstructure with varying cooling rate was observed (for ≤4 °C/s). The optical microstructures evident in Steel E2 of the Series 2 steels in the TMCP condition was generally typical of that found in the Series 1 steels D, E1, F and G. Oil quenched Series 1 steels contained a mainly polygonal ferritic microstructure (α_p) but showed a small increase in the amount of quasi polygonal (α_q) ferrite and also contained pockets of bainitic ferrite (α_B).

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RESULTS

FIGURE 3.4(a) Transmission electron micrograph (x100K) showing the precipitate structure of steel E2, which is also typical of that found in steels A2 and B2, in the TMCP, solution treated and slow cooled condition (0.2 °C/s).

FIGURE 3.4(b) Transmission electron micrograph (x100K) showing the precipitate structure of Steel E2, which is typical of that found in A2 and B2 in the solution treated, slow cooled (0.2 °C/s) and aged condition (550 °C for 1 hour).
FIGURE 3.5(a) Transmission electron micrograph (x100K) showing the precipitate structure of steel E2 which is typical of that found in steels A2 and B2, in the solution treated and air cooled condition (4 °C/s).

FIGURE 3.5(b) Transmission electron micrograph (x100K) showing the precipitate structure of steel E2 which is typical of that found in steels A2 and B2, in the solution treated, air cooled (4 °C/s) and aged condition (550 °C for 1 hour).
FIGURE 3.5(c) Transmission electron micrographs showing examples of twinned martensite and lath ferrite structure found in steel A2, in the solution treated and air cooled (4 °C/s) condition.

FIGURE 3.5(d) Diffraction pattern produced by martensitic islands found in steel A2, in the solution treated and air cooled (4 °C/s) condition. Dark field image produced from spot A in diffraction pattern of field in Figure 3.5(c), micrograph 2.
FIGURE 3.6(a) Transmission electron micrograph showing the precipitate structure of steel E2, which is typical of that found in steels A2 and B2, in the solution treated and oil quenched condition (70 °C/s).

FIGURE 3.6(b) Transmission electron micrograph showing the precipitate structure of steel E2 which is typical of that found in steels A2 and B2, in the solution treated, oil quenched (70 °C/s) and aged condition (550 °C for 1 hour).
3.1.2 Precipitate Species Identification

The following series of micrographs are examples of the experimental steels after various thermal treatments. They were produced by using various techniques as discussed in Section 2.6.2.2 and were used to identify the principal precipitate species of interest. The electron micrographs in Figures 3.7(a) through to 3.7(j) show the spherical fcc Cu precipitates evident in the aged condition - 550 °C for 1 hour. The electron micrographs in Figures 3.8(a) through to 3.8(f) show the rod-like Cu precipitates present in the overaged condition - 650 °C for 9 hours. The electron photomicrographs Figures 3.9 (a) and (b) show the spherical NbCN precipitates present prior to ageing. These structures may be compared to those of Figures 3.10 (a), (b) and (c) which show the same steel in the overaged condition. These micrographs show little change in appearance or distribution of the NbCN precipitates after extensive periods of ageing.
3.7(a) Bright field electron micrograph showing fcc $\varepsilon$ Cu precipitates.

3.7(b) Diffraction Pattern of 3.7 (a)

3.7(c) Dark field corresponding to indicated spot in 3.7(b), showing $\varepsilon$ Cu precipitation

FIGURE 3.7(a) to (c)  Diffraction pattern and corresponding images (x 24.5K) used in precipitate species analysis in Steel E2 in the aged condition (550 °C for 1 hour).
FIGURE 3.7(d) to (i). Diffraction patterns and associated images produced for experimental steels A2 and B2 in the aged condition (550 °C for 1 hour).
3.8a. Bright field image (see schematic diagrams below of particle shape and size for rod like and spherical particles).

Average Length = 39.27 nm  
Standard Deviation = 12.05 nm

3.8 b. Diffraction pattern of 3.8a, showing: (111) bcc α Fe & (110) fcc Cu produced from rod like particles

Average Diameter = 21.70nm  
Standard Deviation = 8.70nm

3.8c. Dark field image produced from 110 spot in 3.8a.

3.8d. Bright field image.

3.8 e. Diffraction pattern from 3.8d, showing (001) bcc α Fe and (011) fcc Cu produced from rod shaped particles

3.8f. Dark field image from 3.8d.

FIGURE 3.8     Diffraction patterns and associated images (x 200K) produced for experimental steel E2 in the overaged condition (650 °C for 9 hours).
RESULTS

3.9a. Diffraction pattern (x 200K) showing reflection from NbCN precipitates (arrowed).

3.9b. Dark field image (x 200K) produced from 3.9a.

FIGURE 3.9  Diffraction pattern and associated image produced from experimental steel E2 in the TMCP condition.

3.10a. Bright field image (x 130K) showing NbCN precipitate particle (arrowed).

3.10b. Diffraction pattern (x 200K) showing reflections from NbCN (arrowed)

3.10c. Dark field image of NbCN (x 130K) produced from 3.10a.

FIGURE 3.10. Diffraction patterns and associated images produced for experimental steel E2 in the overaged condition (650 °C for 9 hours)
RESULTS

3.1.3. Precipitate Population Size Distributions

Precipitate population size distributions were determined for sample E2 which was normalised at 900 °C for 30 minutes and then subjected to various cooling rates from the normalising temperature (0.2 °C/s, 4 °C/s and 70 °C/s). This treatment was followed by a standard ageing treatment at 550 °C for 1 hour.

The results of this exercise using a 5nm particle diameter bin size are summarised in Table 3.2 and in Figure 3.11. A detailed example of the various calculations carried out to determine these precipitate population distributions and the volume fractions is given in Appendix 2.2, whilst definitions of the variables used are given in Appendix 2.1 - Table A2.1. The results of the precipitate distribution measurements for the other 1% Cu steels which were carried out using random fields from each steel type are given in Appendix 2.2 - Table A2.3.

TABLE 3.2 Effect of cooling rate on the volume fraction of precipitates in steel E2.

<table>
<thead>
<tr>
<th>THERMAL HISTORY</th>
<th>TOTAL No. OF PPTS. IN FOIL (Area=1μm²)</th>
<th>AVERAGE PRECIPITATE DIAMETER D (nm)</th>
<th>RELATIVE AREA $A^R$</th>
<th>FOIL THICKNESS t (nm)</th>
<th>VOLUME FRACTION f</th>
</tr>
</thead>
<tbody>
<tr>
<td>TMCP</td>
<td>221</td>
<td>13.51</td>
<td>.033831</td>
<td>159</td>
<td>.001896</td>
</tr>
<tr>
<td>SLOW COOL</td>
<td>401</td>
<td>14.20</td>
<td>.069684</td>
<td>242</td>
<td>.002774</td>
</tr>
<tr>
<td>AIR COOL</td>
<td>781</td>
<td>6.60</td>
<td>.034499</td>
<td>164</td>
<td>.000928</td>
</tr>
<tr>
<td>OIL QUENCH</td>
<td>998</td>
<td>6.38</td>
<td>.039859</td>
<td>180</td>
<td>.000951</td>
</tr>
<tr>
<td>TMCP + AGE</td>
<td>260</td>
<td>7.2</td>
<td>.092016</td>
<td>160</td>
<td>.002871</td>
</tr>
<tr>
<td>SLOW COOL + AGE</td>
<td>1182</td>
<td>8.43</td>
<td>.11188</td>
<td>227</td>
<td>.002907</td>
</tr>
<tr>
<td>AIR COOL + AGE</td>
<td>4279</td>
<td>5.85</td>
<td>.134303</td>
<td>187</td>
<td>.002981</td>
</tr>
<tr>
<td>OIL QUENCH + AGE</td>
<td>2420</td>
<td>5.73</td>
<td>.071687</td>
<td>200</td>
<td>.001406</td>
</tr>
</tbody>
</table>

NOTE: t has been calculated according to Section 2.6.2.3. For further details refer to Appendix 1.3.
FIGURE 3.11a Effect of cooling rate on the precipitate population size distributions in steel E2.

Frequency histograms.
FIGURE 3.11b Precipitate population distribution curves for steel E2.
3.2 Mechanical Properties

The experimental steels were all subjected to a variety of mechanical property tests. These included Vickers hardness testing, tensile testing and Charpy impact testing.

3.2.1 The Effect of the Cooling Rate from the Normalising Temperature on Hardness and Impact Properties

The effect of cooling rate on microstructure and on the precipitation hardening response was examined using Vickers hardness and Charpy impact testing. The results of these tests are summarised in Tables 3.3 and 3.4 and in Figures 3.13 to 3.16.

**TABLE 3.3** Vickers hardness values (HV30) for Series 1 and Series 2 steels.

<table>
<thead>
<tr>
<th>THERMAL HISTORY</th>
<th>A2</th>
<th>B2</th>
<th>E2</th>
<th>E1</th>
<th>D</th>
<th>F</th>
<th>G</th>
</tr>
</thead>
<tbody>
<tr>
<td>SLOW COOL</td>
<td>194</td>
<td>148</td>
<td>164</td>
<td>169</td>
<td>166</td>
<td>157</td>
<td>136</td>
</tr>
<tr>
<td>( \bar{x} )</td>
<td>194</td>
<td>148</td>
<td>164</td>
<td>169</td>
<td>166</td>
<td>157</td>
<td>136</td>
</tr>
<tr>
<td>( \sigma_n )</td>
<td>4.03</td>
<td>1.46</td>
<td>2.24</td>
<td>1.61</td>
<td>1.08</td>
<td>1.61</td>
<td>0.27</td>
</tr>
<tr>
<td>SLOW COOL AND AGE</td>
<td>228</td>
<td>186</td>
<td>193</td>
<td>191</td>
<td>192</td>
<td>193</td>
<td>137</td>
</tr>
<tr>
<td>( \bar{x} )</td>
<td>228</td>
<td>186</td>
<td>193</td>
<td>191</td>
<td>192</td>
<td>193</td>
<td>137</td>
</tr>
<tr>
<td>( \sigma_n )</td>
<td>4.99</td>
<td>1.88</td>
<td>2.26</td>
<td>2.0</td>
<td>0.76</td>
<td>0.78</td>
<td>0.79</td>
</tr>
<tr>
<td>AIR COOL</td>
<td>249</td>
<td>167</td>
<td>176</td>
<td>175</td>
<td>175</td>
<td>165</td>
<td>147</td>
</tr>
<tr>
<td>( \bar{x} )</td>
<td>249</td>
<td>167</td>
<td>176</td>
<td>175</td>
<td>175</td>
<td>165</td>
<td>147</td>
</tr>
<tr>
<td>( \sigma_n )</td>
<td>1.7</td>
<td>2.55</td>
<td>2.07</td>
<td>1.30</td>
<td>0.97</td>
<td>0.33</td>
<td>1.13</td>
</tr>
<tr>
<td>AIR COOL AND AGE</td>
<td>287</td>
<td>195</td>
<td>217</td>
<td>220</td>
<td>214</td>
<td>210</td>
<td>144</td>
</tr>
<tr>
<td>( \bar{x} )</td>
<td>287</td>
<td>195</td>
<td>217</td>
<td>220</td>
<td>214</td>
<td>210</td>
<td>144</td>
</tr>
<tr>
<td>( \sigma_n )</td>
<td>5.56</td>
<td>1.73</td>
<td>1.88</td>
<td>2.46</td>
<td>2.47</td>
<td>1.20</td>
<td>0.95</td>
</tr>
<tr>
<td>OIL QUENCH</td>
<td>309</td>
<td>176</td>
<td>186</td>
<td>183</td>
<td>177</td>
<td>178</td>
<td>169</td>
</tr>
<tr>
<td>( \bar{x} )</td>
<td>309</td>
<td>176</td>
<td>186</td>
<td>183</td>
<td>177</td>
<td>178</td>
<td>169</td>
</tr>
<tr>
<td>( \sigma_n )</td>
<td>9.34</td>
<td>1.40</td>
<td>0.79</td>
<td>2.81</td>
<td>0.87</td>
<td>3.74</td>
<td>0.69</td>
</tr>
<tr>
<td>OIL QUENCH AND AGE</td>
<td>310</td>
<td>206</td>
<td>243</td>
<td>231</td>
<td>228</td>
<td>225</td>
<td>160</td>
</tr>
<tr>
<td>( \bar{x} )</td>
<td>310</td>
<td>206</td>
<td>243</td>
<td>231</td>
<td>228</td>
<td>225</td>
<td>160</td>
</tr>
<tr>
<td>( \sigma_n )</td>
<td>5.37</td>
<td>4.39</td>
<td>1.64</td>
<td>2.41</td>
<td>0.85</td>
<td>3.88</td>
<td>0.25</td>
</tr>
</tbody>
</table>

**NOTE:** \( \sigma_n = \sqrt{\frac{\sum x^2 - n \bar{x}^2}{n}} \) standard deviation of the population.
FIGURE 3.12 Effect of the cooling rate from the normalising temperature on the Vickers hardness number of the higher C Series 2 Steels. (Note 1: Bars shown indicate $3\sigma_n$. Where bars are not evident this indicates that $3\sigma_n$ range is smaller than the symbol used.)
FIGURE 3.13 The effect of cooling rate on Vickers hardness of the lower carbon Series 1 steels. (Note: Bars shown indicate $3\sigma_n$. Where bars are not evident this indicates that $3\sigma_n$ range is smaller than the symbol used.)
### RESULTS

#### TABLE 3.4 Charpy impact values for Series 2 steels.

<table>
<thead>
<tr>
<th>STEEL IDENTITY</th>
<th>TMCP UNAGED</th>
<th>NORMALISED &amp; COOLED</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>70° C/s+Aged</td>
</tr>
<tr>
<td><strong>ENERGY (J) @-85° C</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A2'</td>
<td>100</td>
<td>47</td>
</tr>
<tr>
<td>A2</td>
<td>82</td>
<td>15</td>
</tr>
<tr>
<td>B2</td>
<td>110</td>
<td>37</td>
</tr>
<tr>
<td>E2</td>
<td>80</td>
<td>68</td>
</tr>
<tr>
<td><strong>FIBROSITY (%) @-85° C</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A2'</td>
<td>35</td>
<td>22</td>
</tr>
<tr>
<td>A2</td>
<td>45</td>
<td>10</td>
</tr>
<tr>
<td>B2</td>
<td>30</td>
<td>7</td>
</tr>
<tr>
<td>E2</td>
<td>25</td>
<td>22</td>
</tr>
<tr>
<td><strong>50% FATT (°C)</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A2'</td>
<td>-55</td>
<td>-20</td>
</tr>
<tr>
<td>A2</td>
<td>-70</td>
<td>+10</td>
</tr>
<tr>
<td>B2</td>
<td>-55</td>
<td>-10</td>
</tr>
<tr>
<td>E2</td>
<td>-55</td>
<td>-20</td>
</tr>
<tr>
<td><strong>UPPER SHELF TEMP (°C)</strong></td>
<td>TEMPERATURE</td>
<td>ENERGY (J)</td>
</tr>
<tr>
<td>A2'</td>
<td>-18</td>
<td>+20</td>
</tr>
<tr>
<td>A2</td>
<td>-18</td>
<td>+20</td>
</tr>
<tr>
<td>B2</td>
<td>-30</td>
<td>+40</td>
</tr>
<tr>
<td>E2</td>
<td>-20</td>
<td>+20</td>
</tr>
</tbody>
</table>

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FIGURE 3.14 The effect of cooling rate from the normalising temperature on the fibrosity of the fracture surface of Charpy samples from the Series 2 steels in the aged condition. (For equations of lines of best fit see Appendix 4.1.2).
FIGURE 3.15 The effect of cooling rate from normalising temperature on the Charpy Impact Energy of Series 2 steels in the aged condition (For equations of lines of best fit see Appendix 4.1.2).
3.2.2 The Effect of Temperature and Time on the Hardening Response

The effect of temperature and time on the precipitation hardening response was examined using Vickers hardness and tensile testing. The results of Vickers Hardness tests are listed in Appendix 3.2 and summarised in Figures 3.16 and 3.17. The results of tensile and hardness testing for both the Series 1 and Series 2 steels appear in Tables 3.5 and 3.6 and are summarised in Figures 3.18 and 3.19.
3.2.2.1 Vickers hardness testing

**RESULTS**

- **500 TO 650 °C**
- **5 TO 180 min.**
- **AIR COOL (4.0 °C/s)**

**AGEING TREATMENT**

**FIGURE 3.16** The effect of ageing temperature on the precipitation hardening response of TMCP Cu bearing experimental steels from Series 1, as measured by Vickers hardness testing (Note: Bars represent $3\sigma_n$).
FIGURE 3.17  The effect of time on the precipitation hardening response of Series 1 TMCP experimental steels.

Note: for tabulated figures including results of ageing at 650 °C for 100 hours see Appendix 3.2, Table A3.1.
3.2.2.2 Tensile testing

All tensile testing was carried out using an Instron Universal Testing Machine, Model Number: 1342. Sources of error and their effect on the measured yield and tensile strengths are given in Appendix 4.2 Table A4.1.

Tensile tests were performed for each steel selected. The effect of ageing time and temperature in both the Series 1 and 2 TMCP and TMCP and aged (for 1 hour at 550 °C) conditions for all steels examined is given in Table 3.6. This table also highlights the Vickers hardness result taken from samples subjected to the same conditions of time and temperature (prepared as described in Sections 2.5.1.1 and 2.5.1.2). These results are later used to determine a quantitative correlation between Vickers hardness and tensile strength (Section 4.3.2.4, Table 4.7 and Figures 4.6 and 4.7).

More extensive tensile testing was carried out on the Series 2 experimental steels, the results of which are shown in Figure 3.18 and 3.19 and Table 3.6.
### TABLE 3.5  
The effect of ageing on the tensile properties and hardness of Cu bearing experimental steels.

<table>
<thead>
<tr>
<th>STEEL</th>
<th>TMCP</th>
<th>550 °C</th>
<th>FOR 1</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Lower Yield</td>
<td>Tensile Strength</td>
<td>Elongat. (50mm Gauge Length)</td>
</tr>
<tr>
<td></td>
<td>(MPa)</td>
<td>(MPa)</td>
<td>(%)</td>
</tr>
<tr>
<td>Series 1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A1</td>
<td>450</td>
<td>591</td>
<td>29</td>
</tr>
<tr>
<td>B1</td>
<td>439</td>
<td>542</td>
<td>31</td>
</tr>
<tr>
<td>C1</td>
<td>450</td>
<td>641</td>
<td>25</td>
</tr>
<tr>
<td>D</td>
<td>498</td>
<td>612</td>
<td>28</td>
</tr>
<tr>
<td>E1</td>
<td>515</td>
<td>623</td>
<td>24</td>
</tr>
<tr>
<td>F</td>
<td>453</td>
<td>524</td>
<td>26</td>
</tr>
<tr>
<td>G</td>
<td>436</td>
<td>492</td>
<td>30</td>
</tr>
<tr>
<td>Series 2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A2'</td>
<td>591</td>
<td>846</td>
<td>24</td>
</tr>
<tr>
<td>A2</td>
<td>508</td>
<td>659</td>
<td>24</td>
</tr>
<tr>
<td>B2</td>
<td>458</td>
<td>590</td>
<td>23</td>
</tr>
<tr>
<td>E2</td>
<td>493</td>
<td>634</td>
<td>24</td>
</tr>
</tbody>
</table>

### TABLE 3.6  
The effect of ageing temperature on the tensile properties of Cu bearing experimental steels from Series 2.

<table>
<thead>
<tr>
<th>STEEL</th>
<th>A2'</th>
<th>A2</th>
<th>B2</th>
<th>E2</th>
</tr>
</thead>
<tbody>
<tr>
<td>TMCP</td>
<td>591</td>
<td>508</td>
<td>458</td>
<td>493</td>
</tr>
<tr>
<td>Lower Yield (MPa)</td>
<td>591</td>
<td>508</td>
<td>458</td>
<td>493</td>
</tr>
<tr>
<td>Tensile Strength (MPa)</td>
<td>846</td>
<td>659</td>
<td>590</td>
<td>634</td>
</tr>
<tr>
<td>Elongation (%)</td>
<td>24</td>
<td>24</td>
<td>23</td>
<td>24</td>
</tr>
<tr>
<td>500 °C 1 HOUR</td>
<td>680</td>
<td>630</td>
<td>525</td>
<td>590</td>
</tr>
<tr>
<td>Lower Yield (MPa)</td>
<td>680</td>
<td>630</td>
<td>525</td>
<td>590</td>
</tr>
<tr>
<td>Tensile Strength (MPa)</td>
<td>895</td>
<td>718</td>
<td>628</td>
<td>675</td>
</tr>
<tr>
<td>Elongation (%)</td>
<td>15</td>
<td>19</td>
<td>23</td>
<td>21</td>
</tr>
<tr>
<td>550 °C 1 HOUR</td>
<td>703</td>
<td>610</td>
<td>541</td>
<td>583</td>
</tr>
<tr>
<td>Lower Yield (MPa)</td>
<td>703</td>
<td>610</td>
<td>541</td>
<td>583</td>
</tr>
<tr>
<td>Tensile Strength (MPa)</td>
<td>897</td>
<td>719</td>
<td>629</td>
<td>661</td>
</tr>
<tr>
<td>Elongation (%)</td>
<td>13</td>
<td>20</td>
<td>21</td>
<td>23</td>
</tr>
<tr>
<td>600 °C 1 HOUR</td>
<td>705</td>
<td>605</td>
<td>510</td>
<td>584</td>
</tr>
<tr>
<td>Lower Yield (MPa)</td>
<td>705</td>
<td>605</td>
<td>510</td>
<td>584</td>
</tr>
<tr>
<td>Tensile Strength (MPa)</td>
<td>875</td>
<td>690</td>
<td>615</td>
<td>659</td>
</tr>
<tr>
<td>Elongation (%)</td>
<td>13</td>
<td>19</td>
<td>24</td>
<td>21</td>
</tr>
</tbody>
</table>

NOTE: All measurement errors are within -2.2 and -1.47 MPa (see Appendix 4.2, Table A4.1)
FIGURE 3.18 The effect of ageing for 1 hour on the tensile properties of the TMCP Series 2 experimental steels.
RESULTS

FIGURE 3.19 The effect of ageing for 1 hour on the change in tensile properties of the Series 2 experimental steels.
4.0 DISCUSSION

4.1 Precipitation Hardening Response.

In Cu-bearing steels such as ASTM A710 and HSLA 80, it is generally accepted that the most important strengthening mechanism is precipitation hardening by fcc Cu and coherent bcc Cu rich zones. It has been proposed by Hornbogen (118) that the phase which first precipitates is metastable and is composed of bcc copper rich clusters which are coherent with the ferrite matrix. These coherent bcc clusters transform into stable coherent fcc particles which have a KS orientation relationship (164) with the bcc ferrite. As mentioned earlier (1.7.2) Goodman, Brenner and Low (93) have found that these clusters and presumably the coherent fcc particles, grow and transform into incoherent fcc Cu precipitates when they reach a critical size, which they predict occurs when the particle diameters are about $40 \text{Å}$. This estimate corresponded well with their experimental results. Using a field-ion microscope, they found that particles as small as $8 \text{ Å}$ can be formed, but these particles only became observable by TEM when they reached a diameter greater than $50 \text{ Å}$ and became incoherent with the ferrite matrix. The resolution problem was considered to be due to the similarity of the electron scattering factors of Fe and Cu, which makes coherent particles difficult to detect by TEM. So whilst the clustering process itself cannot be followed by TEM, the presence of the clusters can be inferred from the subsequent appearance of the Cu phase. At this point it is worth noting that the minimum precipitate diameter resolvable using TEM in the current work was found to be approximately $30 \text{ Å}$.

The strength of an age hardenable alloy usually peaks when the precipitates are extremely small. According to Goodman et al. (93) the peak in Cu bearing steels corresponds to an average particle size of $24 \text{ Å}$, with a range of between 8 and $50 \text{ Å}$. As Figure 3.11 indicates, many of the Cu-rich precipitates present after thermomechanical control processing of the experimental steels were greater than $5 \text{ nm} (50\text{ Å})$ in size and are therefore likely to be incoherent with the ferrite matrix. As such, they would not be expected to contribute significantly to the alloy strength.
The maximum strengthening in these steels would be expected on ageing material in which the Cu remains in solution in the ferrite after TMCP. Precipitation of Cu can be retarded or suppressed by increasing the cooling rate after rolling but, because of the limited solubility of Cu in ferrite, complete retention of Cu in solution is not possible under normal hot rolling conditions.

4.2 Effect of Cooling Rate from Normalising Temperature on the Precipitation Hardening Response

To examine the effect of cooling rate after rolling on the mechanical properties, all of the TMCP experimental steels were normalised at 900 °C for 30 minutes and cooled to ambient temperature at rates of 0.2 °C/s, 4 °C/s and 70 °C/s. To examine the effect of these cooling rates on the microstructure, the Series 2 steels A2, B2 and E2 were examined in detail, as their chemical compositions conform more closely to the HSLA80 type alloys produced commercially. The Series 1 steels of the HSLA80 type D, E1, F and G were also examined to obtain further data, but not in as much detail as the Series 2 steels.

An extensive program of measurement of the precipitate size distribution and calculation of volume fraction was carried out in order to quantify the effect of cooling rate from the normalising temperature on the microstructure (Figure 3.11). All of the Series 2 steels, with the exception of A2', contained similar Cu concentrations and showed similar precipitate sizes and distributions for a particular cooling rate. It was therefore decided to measure only steel E2 in detail, as a representative of the other steels, because of the large amount of work involved in the manual determination of the precipitate distributions. Checks of the precipitate distribution of the other steels were carried out using random fields for each steel type.
4.2.1 Effect of Cooling Rate on Microstructure and Hardness.

Changes in hardness with cooling rate are given in Figures 3.12 and 3.13. The correlation between these changes in hardness and the changes in microstructure, which are shown in Figures 3.3 to 3.6, are discussed in the following Sections 4.2.1.1 to 4.2.1.4.

4.2.1.1 TMCP condition

The Series 2 steels in the TMCP condition generally showed a polygonal ferrite ($\alpha_p$) grain structure with a small amount of ($\alpha_q$). The most significant variation from this structure occurred in the more highly microalloyed and hence more hardenable steel A2. This steel contained more quasi-polygonal ferrite ($\alpha_q$) than E2 as well as granular bainite ($\alpha_B$). A Le Pera's etch applied to these steels (Figure 3.1) showed the presence of small amounts of martensite - austenite constituent (MA) in all three steels. The presence of MA would not generally be expected in low carbon steels under these conditions of cooling. However, the presence of significant amounts of Cu and Ni combined with the partitioning of C can produce regions of austenite which will transform only sluggishly to diffusional products. For cooling conditions associated with TMCP, diffusional transformation was at least partially suppressed, with the resulting formation of MA islands at lower temperatures.

The rolling conditions resulted in a fine grain structure, with a mean grain size ranging from 6.2 $\mu$m in E2 to 7.4 $\mu$m in A2 (Table 3.1a). Transmission electron micrographs of these steels as in Figure 3.2a, showed that all samples contained spherical Cu precipitates with a mean diameter of about 13.5 nm and a maximum precipitate size of 25 nm diameter (Figure 3.11 and Table 3.2). This was typical of the form of precipitation found in all of the experimental Cu bearing steels in the TMCP and unaged condition (Figure 3.2a).
Transmission electron micrographs of the TMCP and aged sample (Figure 3.2b) showed an increased number of fine precipitates ≤ 5nm in size, which resulted in a decrease in the mean precipitate diameter of the aged sample to 7.2 nm (Table 3.2).

4.2.1.2 Slow Cooled - 0.2 °C/s cooling rate after re-austenitising at 900 °C.

Slow cooling from 900 °C produced a relatively coarse, mixed ferrite microstructure (Figures 3.3 a to c) with average grain sizes ranging from 7.8 μm in A2 to 8.6 μm in B2 (Table 3.1a) as well as pearlite/bainite banding in all steel types (Figure 3.3d). Surprisingly, all steels contained very small amounts of bainitic ferrite, even at this very low cooling rate (Table 3.1a) presumably due to the relatively high hardenability conferred by the substitutional solution together with C enrichment of the austenite by partitioning. Transmission electron microscopy of E2 after normalising and slow cooling (Figure 3.4a) revealed a greater number of coarse precipitates per unit area than in the TMCP sample. The number of precipitates ≥ 15nm diameter per unit area in the TMCP steel was 221, compared with 401 in the slow cooled steel (Figure 3.11a). The mean precipitate size increased from 13.5 nm in the TMCP condition to about 14.2 nm in the normalised and slow cooled condition (Table 3.2), with the maximum measured size increasing from 25 in the TMCP steel to 30 nm in the slowly cooled steel (Figure 3.11a).

Ageing of the normalised samples at 550 °C for 60 minutes after slow cooling (Figure 3.4b) produced an increased number of fine precipitates ≤ 10 nm in size: 153 precipitates per unit area in the unaged condition compared with 890 per unit area in the aged condition (Figure 3.11a). This difference is emphasised by Figure 3.11b where it is evident that the frequency of precipitates in the > 3 nm to ≤5 nm and ≥5 nm to ≤10 nm size classes has increased significantly on ageing. This increase in the frequency of precipitates ≤ 10 nm is associated with a significant increase in the Vickers hardness number (eg +29HV for steel E2) (Figure 3.12 and Table 3.3). The hardness increase is surprisingly large, as it would be expected that at a cooling rate of 0.2 °C/s, insufficient Cu would have remained in solution to produce enough of the coherent Cu rich zones and
DISCUSSION

precipitates less than <5 nm in diameter (91, 93), required to produce a marked increase in hardness on subsequent ageing. However, it is apparent from the analysis of precipitate distributions (Figure 3.11) that precipitation did occur on ageing and that it was evidently sufficient to produce a substantial increment in hardness (Figures 3.12 and 3.13).

The negligible change in hardness of steel "G" (Figure 3.13) is due to the fact that this steel had a Cu content of 0.49 weight %, which is very close to the solubility limit of Cu at room temperature (Section 1.3.1). Therefore, little Cu would have been available for precipitation in the ferrite on ageing.

Those particles already present in the normalised and slow cooled samples would be expected to coarsen slightly during ageing, thus producing an increase in maximum particle size relative to the TMCP condition. It is inferred from the increase in the frequency of particles in the >3 nm to ≤5 nm size range, that some of the fine unresolved clusters or particles present prior to ageing became large enough to be visible by TEM after ageing.

4.2.1.3 Air Cooled - 4 °C/s cooling rate after re-austenitising at 900 °C

It can be seen from Figures 3.3 b and c that increasing the cooling rate from the normalising temperature to approximately 4 °C/s produces a microstructure in steels B2 and E2 which consists of fine α_p and α_q (average grain size of 6.3 μm - Table 3.1a) with some residual bainite (B), pearlite (P) and martensite - austenite (MA) islands (Table 3.1a). In contrast, the more hardenable steel A2 consisted primarily of α_B (Figures 3.3a, 3.5c and 3.5d). The use of Le Pera's etch for all 3 steels showed an increased prevalence of MA compared to the more slowly cooled condition.
Transmission electron micrographs of sample E2 in both the "normalised + air cooled" and the "normalised + air cooled + aged" conditions are shown in Figure 3.5 a and b. Both the unaged and aged samples contained spherical precipitates ≥ 10 nm in size, but the aged sample revealed a substantially greater number of finer precipitates (≤ 5 nm in size). This observation was supported by the results of the precipitate size distribution analysis for sample E2 which indicated that the average precipitate size changed from 6.6 nm diameter in the unaged sample to 5.85 nm diameter in the aged sample (Table 3.2). In both cases however, the average precipitate size was substantially finer than that present in the sample cooled at 0.2 °C/s (14.2 nm diameter in the unaged condition and 8.43 nm diameter in the aged condition). This difference in average diameter arises because fewer precipitates >10 nm in size and more precipitates ≤ 10 nm in size were formed on more rapid cooling from the normalising temperature.

The Series 2 steels A2, B2 and E2 showed an increase in hardness on ageing of 28 to 41 HV (Table 3.3 and Figure 3.12). However, in all three cases the increase on ageing was not significantly greater than the hardness increment obtained in the slow cooled steels. This result is probably attributable to the fact that the unaged structure in these steels after cooling at the faster rates generally consisted of α_q or α_p plus MA islands and the full magnitude of the increment in hardness due to Cu precipitation on ageing was masked by tempering of the bainitic and martensitic structures.

Under the same conditions of cooling, the Series 1 low C steels, with the exception of steel G, generally showed a greater increase in hardness upon ageing (Table 3.3 and Figure 3.13). The hardness increase of between 39 and 45 HV can be attributed to the increased precipitation of fine ε Cu particles (≤ 5 nm in diameter) in a ferrite matrix with a generally lower base hardness due to the lower carbon contents. The fact that the increments in hardness on ageing of the Series 1 steels are more substantial than the increases seen in the higher carbon Series 2 steels may be attributed to the fact that the ferritic microstructure in the Series 1 steels consisted mainly of α_p and α_q regardless of cooling rate (Figure 3.3e and Table 3.1b) and thus the impact of ageing on the ferritic microstructure would not have been as marked as in the higher carbon, more
hardenable Series 2 steels. Therefore, although the strength increase attributable to Cu precipitation would have generally been similar in both the Series 1 and the Series 2 steels because of the similar Cu levels, the hardness loss due to tempering of the ferritic structure would have been less severe in the Series 1 steels. Since E1 and E2 have similar compositions an estimate of the hardness increment attributable to differences in the densities of planar and linear defects (lath boundaries and recovered dislocation structures) can be made by comparing differences in hardness after ageing of the Series 1 steel, E1 and the Series 2 steel, E2. The difference is in the order of 4 Vickers hardness points.

Although only a small increase in hardness occurred due to the difference in microstructure between E1 and E2 (4 HV), after normalising and cooling at 4 °C/s a much greater increase in hardness was observed on ageing compared to the more slowly cooled steels (0.2 °C/s), indicating that the increase in cooling rate retains more of the Cu in solution in ferrite. The higher concentration of Cu in solution resulted in a greater amount of precipitation during ageing (e.g. 4279 precipitate particles per unit area on ageing of E2 in the air cooled samples, compared to 1182 per unit area in the more slowly cooled steel).

As mentioned previously, the negligible change in strength of steel "G" is due to the fact that the Cu content of this steel is very close to the solubility limit of Cu at room temperature (Section 1.3.1) and little Cu would have been available for precipitation in the ferrite on ageing.

4.2.1.4 Oil Quenched - 70 °C/s cooling rate after re-austenitising at 900 °C

A cooling rate of 70 °C/s was achieved by oil quenching from the normalising temperature. This cooling rate produced a microstructure of $\alpha_q$ and $\alpha_B$ and pockets of $\alpha^\circ_B$ in steels B2 and E2 (Figures 3.3b and c) and a fully martensitic/bainitic microstructure in A2 with a small amount of $\alpha_B$ (Figure 3.3a and Table 3.1a). In the Series 1 steels E1, D, F and G, this cooling rate
produced an equiaxed microstructure ($\alpha_p$) with an increased proportion of $\alpha_q$ compared to the lower cooling rate. These samples also contained some pockets of $\alpha_B$ (Figure 3.3e and Table 3.1b).

Precipitates formed in the "oil quenched and unaged" steels (average particle diameter = 6.38nm) were similar in size to those in the "slow cooled and air cooled" steels (average particle diameter = 6.6nm). Examination of the aged samples by TEM showed little evidence of the emergence of fine precipitates ≥3 nm and ≤5 nm during ageing, as indicated by the results of the precipitate size distribution analysis (Figure 3.11 and Table 3.2).

The fact that the number of fine precipitates (≥3 nm and ≤5 nm diameter) after ageing was smaller in the fast cooled samples (70 °C/s = 2420 precipitate particles per unit area) than in those samples cooled more slowly from the normalising temperature (4 °C/s = 4279 precipitate particles per unit area) may be explained using the following reasoning. Quenching the steel from the normalising temperature would have suppressed the precipitation of Cu, retaining most of it in solution. The subsequent ageing treatment would have enabled the formation of Cu-rich zones and fine precipitates resulting in a large increase in hardness, without many of the particles coarsening to the extent that they would be visible by TEM (≥3nm in this work, or ≥5 nm as reported in reference (93)). Thus, although it appears from the size distributions presented in Figure 3.11a that fewer fine precipitates (≥3 nm and ≤5 nm) were present in the quenched and aged sample than in the more slowly cooled samples, the marked hardness increase on ageing after the faster cooling rate (30 to 57 HV - Table 3.3, Figure 3.13) indicates that a significant increase in the density of Cu rich zones and very fine precipitates had occurred. This effect was particularly evident for the lower C Series 1 steels which, although they did not have a martensitic/bainitic type microstructure, did show a substantial increase in hardness of 47 to 51 HV. Any substantial microstructural change from ferrite to martensite would partially mask the hardness increase contributed by Cu precipitation on ageing.
In steel A2, the extent of hardening due to the precipitation of ε Cu and/or the formation of Cu-rich zones upon ageing, appeared to be insufficient to overcome the hardness loss due to the microstructural changes caused by the tempering of the martensite (Figure 3.12). For the same reason, the strength increments observed for steels E2 and B2 are smaller than what would have been expected given the increment observed for the air cooled steels. The low C Series 1 steels D, E1, F and G which did not show a martensitic/bainitic microstructure after fast cooling (Figure 3.3e), are more likely to reflect the true increment in hardness due to the precipitation of Cu.

4.2.1.5 Comparison of the TMCP and air cooled and the normalised and air cooled conditions

The microstructures of the TMCP and the TMCP and aged steel samples (generally \(\alpha_p\) with a small amount of \(\alpha_q\) and a mean grain diameter of 6.2 to 7.4 μm (Table 3.1a)), were the result of the laboratory rolling of an ingot to a 12mm x 180mm x 1710cm plate and the ageing of a 10mm cube taken from the plate. The estimated cooling rate from the finish rolling temperature (821 to 841 °C - Table 2.2a) to 500 °C was approximately 1.4 °C/s. The microstructure produced in the normalised and air cooled steel, resulted from the furnace normalising treatment, cooling and ageing of a 10mm cube. The cooling rate (from 800 °C to 500 °C) measured in the centre of the cube was 4 °C/s.

The ferritic microstructures produced in both situations were similar, although the higher cooling rate of the normalised and air cooled steel produced a greater proportion of \(\alpha_q\). However, a distinct difference was observed between the two conditions, in both the precipitate distribution and the resultant Vickers hardness increase on ageing.

The normalised and aged steels in general, had a much greater number of fine precipitates present on ageing (3730 with diameter < 5nm - Figure 3.11a) than the TMCP and aged steel plate (1851 with diameter < 5nm). Furthermore, the maximum precipitate diameter of the normalised and aged
DISCUSSION

steels was smaller (15<D<20nm - Figure 3.11a) than that present in the TMCP and aged steel (20<D<25nm - Figure 3.11a). The greater number of fine precipitates present in the normalised and aged steels were also associated with a higher fully aged hardness ($H_V = 220$ HV after ageing at 550 °C for 1 hour) compared to the TMCP and fully aged condition ($H_V = 209$ HV after ageing at 550 °C for 1 hour).

These results may be explained in terms of the differences in the thermal histories produced by the two conditions. As discussed previously (4.2.1.3 and 4.2.1.4), increasing the cooling rate from the normalising temperature retains more of the Cu in solution in the ferrite. Therefore, the slower cooling rates experienced by the TMCP steels (1.4 °C/s), compared to the normalised and air cooled steels (4 °C/s), would have allowed more time for the precipitation of Cu from solution prior to the final ageing step.

The Cu particles/zones produced during cooling from the finish rolling temperature, coarsened during the subsequent ageing treatment, resulting in an increased population of coarse precipitate particles, compared to the normalised and air cooled condition, in which precipitation on cooling would have been suppressed. This explanation is consistent with the larger maximum particle size observed in the TMCP and aged steel, compared to the normalised and aged steel. Furthermore, the precipitation prior to ageing would reduce the amount of Cu in solution in the ferrite available for precipitation during ageing.

The normalising process redissolves most of the Cu precipitate present in the TMCP condition and the higher cooling rate from the normalising temperature, suppresses the precipitation of Cu. These conditions are conducive to a larger population of fine particles and a reduced maximum particle size after ageing in the normalised steel compared to the TMCP steel.

Given the differences in particle populations between the TMCP and the normalised and air cooled steels and the absence of any significant difference in ferritic grain size (Table 3.1a) between the
two conditions, the increment in strength on ageing of the TMCP (16 HV for E1) would be expected to be less than that observed in the normalised, air cooled and aged steel (27 HV for E1).

4.2.1.6 General effects of cooling rate

From the results obtained by applying various cooling rates from the normalising temperature to the experimental steels, it is possible to estimate the proportion of strengthening attributable to Cu in its various states. Consider, for example, the lower C Series 1 steels which because of their low C content show only small differences in matrix microstructure for the various cooling rates.

Under all cooling conditions, the lowest unaged strength was obtained in the low Cu/Ni steel "G" (Cu = 0.49/ Ni = 0.42). No substantial difference in microstructure was evident between G and the other Series 1 steels. Thus, whilst recognising that a small proportion of the hardness could be due to other factors, such as dislocation density and distribution, the higher hardness of the other steels (D, E1 and F) in the oil quenched and unaged condition compared to G, can be largely attributed to the solid solution strengthening effect of 1.1 wt % Cu. The hardness difference was between 8 and 14 HV.

If it is assumed that Cu does not appreciably affect the hardenability, then the proportion of hardening due to Cu after ageing can be estimated from Figure 3.13. Steels E1 and G differ only in their Cu/Ni contents. If their hardnesses after ageing are compared, the greater increase in hardness (54 to 76 HV) shown by steel E1, may be attributed to formation of Cu-rich zones and/or the precipitation of Cu. It is also apparent from Figures 3.12 and 3.13, that the hardness of the aged steels increased with an increase in the rate of cooling from 900 °C. This result correlates well with the precipitate distributions shown in Figure 3.11a and b, which show a general increase in the number of fine precipitates (<5 nm) upon ageing as the cooling rate from the normalising temperature increases.
4.2.2 The Effect of Cooling Rate from the Normalising Temperature on the Charpy Impact Properties.

Although the effect of solutes on the impact toughness of steels is not well understood, it is known that those substitutional solutes which show significant strengthening are generally detrimental to toughness in that they increase the impact transition temperature (120, 121). Furthermore, it is recognised that precipitation can also exert an adverse effect on impact properties (120, 121, 127).

The toughness of a steel, is a measure of its ability to resist fracture at low temperature, by processes such as cleavage or intergranular fracture. Therefore, the reduction in area (or strain to fracture) is closely related to the ductile shelf energy (energy to fracture). The impact transition temperature (onset of plastic instability) on the other hand is directly related to the work hardening characteristics of a material.

The effect of cooling rate on the impact properties of aged HSLA 80 and A710 type steels is summarised in Table 3.4 and Figures 3.14 and 3.15. It is evident from Figures 3.14 and 3.15, that cooling rate has a significant effect on the toughness of the final aged product. In all cases, the Charpy energy transition and the fibrosity curves were moved to the right (Figures 3.14 and 3.15) i.e. the impact energy at any given temperature decreased, whilst the fibrous transition temperature (50 % FATT) increased. The effect of cooling rate from the normalising temperature on the absorbed energy at -85 °C and the 50% FATT was quantified through regression analysis and the results are given in Figures 4.1 and 4.2.
DISCUSSION

Figure 4.1 The effect of cooling rate from the normalising temperature on the absorbed energy at -85 °C for the Series 2 experimental steels.

Figure 4.2 The effect of cooling rate from the normalising temperature on the 50% fibrous transition temperature of the Series 2 experimental steels.
These results are consistent with the increase in the volume fraction of fine precipitates with increasing cooling rate and may be explained in terms of the basic theory of ductile fracture proposed by Henry and Plateau (171) and Gurland and Plateau (172). In general terms, this theory of ductile fracture involves the nucleation and growth of cavities and their ultimate coalescence in the final stage of catastrophic failure. Cavities may nucleate at any point of severe stress concentration such as inclusions (by interface decohesion (123)) at particles (by particle cracking (123)) or at grain boundaries (through planar slip (173)).

The factors which encourage the development of the critical volume fraction of cavities required to initiate catastrophic failure, are those which reduce the fracture strain. Thus increasing the volume fraction of stress concentrators, would reduce the strain to fracture.

As discussed previously in Section 4.2.1 the 1% Cu experimental steels, showed a distinctive step decrease in precipitate size with increasing cooling rate, which is accompanied by an increase in the volume fraction of fine precipitates (<5nm). This corresponded to a decrease in impact toughness with increasing cooling rate.

If the very fine precipitates present under these conditions resist shearing by dislocations and are still too closely spaced to allow by-pass by dislocations, then dislocation motion is only possible by cross-slip. Thus, the fine Cu particles act as strain localisers, by encouraging dislocation pile ups and increasing the stress intensification at the head of the pile up. Therefore, high cooling rates which increase the volume fraction of very fine particles would promote the development of cavities and encourage earlier catastrophic failure.

In the case of the more slowly cooled steels, the precipitate particles would become progressively larger and more widely spaced as the cooling rate decreased. In this situation they would be more easily bypassed by dislocations, which would bow out between them (Orowan bowing (87)). In this particular alloy system the rate of work hardening would not be very high, as the system is not characterised by the pronounced dislocation tangling evident in other alloy systems (77, 84, 86) and plastic deformation would
tend to be spread more evenly throughout the grains. Thus, sources of localised stress concentration would be reduced, effectively delaying final catastrophic failure.

Whilst some authors have reported that particle size is not related to ductility (174), the results in this work are consistent with findings in other alloy systems, for example Al-Li. Polmear (173) reports that aged binary Al-Li alloys suffer from low ductility and toughness, due primarily to severe strain localisation that arises because coherent particles are readily sheared by moving dislocations allowing intense local shear zones to develop which facilitate fracture.

Furthermore, the mechanism proposed is consistent with findings in similar commercial HSLA 80 type steels (25), which show that ageing of these steels past the peak strength resulted in a significant improvement in toughness properties.

It is also apparent when comparing the high Cu steel A2' (1.7% Cu) with steels A2, B2 and E2 (0.9 to 1.2 % Cu), that the Cu content has little effect on the impact toughness properties below 1.7% (Figure 4.3). This result is in agreement with the results published by Tomita et al. (31), discussed in Section 1.3.1.
FIGURE 4.3. The effect of copper content on the impact energy at -85 °C and the 50% fibrous transition temperature for the Series 2 steels.
The preceding discussion indicates that the cooling rate from the normalising temperature does have a significant effect on the microstructure, mechanical and impact properties of the Cu bearing experimental steels, with the amount of Cu retained in solution being directly dependent on the rate of cooling from the normalising temperature.

 Whilst the results of Vickers hardness testing show that an increase in hardness can be achieved by quenching prior to ageing, the impact test results indicate an increase in cooling rate is accompanied by an increase in transition temperature and a decrease in absorbed energy. These results are, at least in part, a consequence of the increase in the volume fraction of fine particles. The loss in impact toughness on quenching and tempering of these steels indicates that such processing is undesirable, as similar strength and improved impact properties can be achieved through normal air cooling after TMCP.

4.3 Determination of the Effect of Time and Temperature on Vickers Hardness and Mechanisms of Strengthening.

4.3.1 Analysis of Experimental Data

In order for precipitation of s Cu to occur upon ageing, diffusion of Cu through the ferrite is required. Therefore, the precipitation hardening response obtained from TMCP Cu bearing steels is dependent upon temperature and time. The next stage of the investigation was designed to determine the optimum temperature and time to obtain the maximum precipitation hardening of the BHP HSLA 80 experimental steels (Series 1).

The results of this work are shown Figures 3.16 and 3.17 and in Table A3.1 in Appendix 3.2. All steels, with the exception of G, showed substantial increases in hardness after ageing. Consider for example those steels aged for 60 minutes. The change in hardness on ageing at 600 °C ranged from a negligible amount in steel G (Cu/Ni = 0.49/0.42) to an average of 25 HV in the 1% Cu steels D, E1 and F. This response is consistent with the fact that steel G contained only half of the Cu and Ni content of the
other experimental steels i.e. 0.49% which is very close to the solubility limit of Cu at room temperature (Section 1.3.2), and therefore much less Cu was available for precipitation in ferrite.

In order to more clearly examine the strengthening mechanisms taking place, a series of isothermal ageing treatments were conducted. The effect of time on the precipitation hardening effect of Cu is illustrated in Figure 3.17. Time at temperature appeared to have a marked effect on hardness. For any given ageing temperature, peak hardness was reached after a given time, with longer times resulting in softening. As expected the times required to reach maximum hardness by Cu based precipitation hardening became shorter as the ageing temperature was raised.

It is a well known fact that the rate of diffusion is a function of both composition and temperature. The nature of the temperature dependence of copper diffusion can be examined more closely if an Arrhenius type rate equation for the time to reach peak strengthening (t) for various ageing temperatures (T) is applied to the experimental data, i.e. \( \frac{1}{t} = \frac{Ae^{-Q/RT}}{T} \), where A=constant, T= absolute temperature (K), R = universal gas constant = 8.314 J/mol and Q = activation energy for diffusion. If natural logarithms of the experimental values of time to reach peak temperature are plotted against the reciprocal of the absolute temperature then a straight line should result, the slope of which determines Q.
When the experimental data were examined in this fashion (Figure 4.4) the resultant line of best fit had the equation,

\[
\ln t = 18,997 \times \left( \frac{1}{T} \right) - 14.071
\]

Where \( t \) is in (s) and \( T \) is in (K). Detailed calculations are contained in Appendix 5.

If the activation energy of diffusion of Cu (Q) is calculated for this curve

\[
Q_{\text{Experimental}} = 157,941 \text{ J/mol}
\]

which is less than the value of Q for Cu\textsuperscript{64} in \( \alpha \) Fe between 600 and 750 °C found in the literature (169) where,

\[
Q_{\text{Cu\textsuperscript{64}/\alpha Fe}} = 244,382 \text{ J/mol}
\]

The discrepancy between the observed value of Q and that found in literature may be explained as follows.

It is well known that diffusion processes occur through the interiors of grains, along the grain boundaries between grains, along dislocation channels (175) and on the surfaces of metallic grains. In the specimens
used in the current work (1 cm cubes as described in Section 2.5.1.1) diffusion within the grain and along the grain boundaries and dislocation lines is of greater concern because the internal defect area is many times larger than the external surface area. It is an oversimplification to describe diffusion processes occurring in polycrystalline materials as a simple combination of diffusion through the grains, along the boundaries and dislocation lines. Diffusion along grain boundaries and dislocations tends to progress more rapidly than diffusion through the grains, but volume diffusion is more sensitive to temperature change. Thus, as the temperature is raised, the rate of diffusion through the lattice increases more rapidly than the rate of diffusion along the boundaries and dislocations. Conversely, as the temperature is lowered, the rate of diffusion along the boundaries decreases less rapidly. The nett effect is that at very high temperatures diffusion through the lattice tends to overpower the grain boundary component, but at low temperatures diffusion at the grain boundary becomes more important.

The experimental results may be explained in light of this relationship between these two mechanisms of diffusion. As mentioned earlier, diffusion along the grain boundaries which occurs at lower temperatures occurs more easily than within crystals i.e. it requires a low activation energy $Q$ i.e. $Q_{\text{grain-boundaries}} < Q_{\text{Lattice}}$. Furthermore $Q_{\text{Cu}}^{\text{Cu in aFe}}$ from the literature was determined with polycrystalline specimens at high temperatures ($\geq 650 ^\circ$C) and as such is more liable to be representative of lattice diffusion because of the overpowering effect of this mechanism at these temperatures. Therefore, it can be argued that since $Q_{\text{Experimental}}$ was determined at temperatures $< 650 ^\circ$C it would correspond to that regime in which grain boundary diffusion would be more significant, resulting in a substantially lower activation energy than the value ($Q_{\text{Cu}}^{\text{Cu in aFe}}$) reported in the literature.

However, it should be noted that the literature value for the activation energy may not be relevant as it is based on the diffusion of Cu in Fe, rather than the complex Fe-Mn-Si-Ni containing alloys investigated in the present work. Alternatively, diffusion of copper may not be the process which determines the measured activation energy.

Assuming that Cu diffusion determines the activation energy, the experimental results can be interpreted as follows. At temperatures below 650 °C, grain boundary diffusion is the most prevalent diffusion
mechanism occurring. The time (t) to reach maximum hardness by Cu based precipitation becomes shorter as the ageing temperature (T) is raised, in line with equation 4.1. For example, at 500 °C (1/T = 0.001294), peak hardness was not reached within the maximum time considered in this experimental procedure i.e. ≤ 180 minutes. Equation 4.1 predicts that at this temperature peak hardness would have been achieved in about 10.5 hours. At 550 °C peak hardness was achieved after 150 minutes at temperature, whereas for ageing at 650 °C, the peak hardness was obtained in ≤ 20 minutes. In each case, longer times after peak hardness was achieved resulted in softening. This decrease in hardness is probably due to the replacement of the Cu rich zones and fine incoherent Cu precipitates, responsible for the strength increase, with coarse incoherent Cu precipitates (>50 Å) which results in softening by overaging (93).

In all cases, the aged steel E1 displayed the highest hardness. The maximum hardness was achieved after tempering at 550 °C for 120 minutes and at 600 °C for 60 minutes. In both cases the peak hardness was 216 HV, indicating that the fully aged hardness is relatively insensitive to ageing temperature.

What is evident from these results is that for temperatures above 550 °C, softening after peak hardness occurs gradually, resulting in a plateau effect rather than a sharp drop in hardness.

It has been claimed by other authors (122) that for commercial versions of E1 (BHP's HSLA 80 type steel), a "double peak" occurs on ageing at various temperatures for 30 minutes. Furthermore, this double peak has been attributed to Nb precipitation (presumably NbCN) in the ferrite during ageing. However, no corroborative evidence for this conclusion was given. Nor was any evidence of a double peak found in the current work. As Figure 3.17 shows, generally a stable plateau occurred after the initial increase in hardness. After heat treatment for 100 hours, the hardness decreased towards that of the TMCP condition. This observation is consistent with continuous precipitation and coarsening, rather than two distinct precipitation processes.

Moreover, there is evidence which indicates that Nb does not contribute to the "secondary hardening peak". Consider, for example, steels E1, D, F and G and Figure 3.17. Steels E1, D and F all displayed the
characteristic extended hardening peak or "plateau", even though steel F contained no deliberate addition of Nb (0.008 Nb). If Nb contributes to this plateau through a "secondary hardening effect" additional to that conferred by the Cu, it would be reasonable to expect that steel F would not show the plateau. Moreover, steel G, which contained the same level of Nb as E1 and D, but which had a low Cu content (0.49 wt%), did not display any significant hardening peak. These results indicate that the strength levels observed on ageing are predominantly the result of the precipitation hardening contribution of the Cu, rather than that of the Nb.

This conclusion is further supported by observations made by electron microscopy. NbCN, which had precipitated in the austenite, was evident in those steels containing Nb (Figures 3.9 and 3.10). No change in the apparent number of Nb particles was found after ageing, although there was evidence of slight coarsening of precipitates which had formed in the austenite (Figure 3.10). NbCN precipitation in ferrite which would be necessary to produce a "secondary hardening effect" was not detected. In such a case the NbCN would display the classic Baker Nutting relationship with the ferrite (96) and no evidence was found of precipitates consistent with this orientation relationship.
4.3.2 Theoretical Analysis

The precipitation hardening response shown by the curves of Figure 3.17 for steels D, E1, F and G, involves a series of mechanisms which are difficult to differentiate. In the following section, each of the mechanisms of precipitation hardening that can potentially combine to produce these characteristic curves are outlined and the proportion of strengthening attributable to each mechanism is estimated through precipitation hardening models proposed by a number of authors. These theoretical predictions are then compared with the actual experimental results using steels D, E1, F and G as examples.

Figure 4.5a is a schematic representation of a precipitation hardening curve typical of that found in the current work. Curve 4.5b is a schematic representation of hardening trends with time associated with the individual mechanisms which are proposed to combine to produce the characteristic precipitation hardening curve of Figure 4.5a.
FIGURE 4.5  Schematic representations of various precipitation hardening mechanisms which contribute to the precipitation hardening curve typical of the Cu bearing HSLA80 type alloys. (a) Overall curve with nominal contribution to strength in the TMCP, peak aged and overaged conditions, (b) overall curve showing trends in strengthening components with ageing time.
4.3.2.1 Base strength

As discussed in Section 1.7.1.2, the work of Gladman and Dulieu in the mid 1970s (71) produced a quantitative model relating solid solution strengthening and ferrite grain size to strength (equation 1.2).

\[ \sigma_y (MPa) = K + 37(Mn\%) + 83(Si\%) + 2918(N_{\text{free}}\%) + 15ld^{-\frac{1}{2}} \]  

When applied to the experimental results of this work (Table 4.1) this formula predicts the "base" yield strengths in each steel type. The yield strength estimates for the Series 1 experimental steels range from 355 MPa in steel G to 385 MPa in steel E1.

<table>
<thead>
<tr>
<th>STEEL</th>
<th>Mn (wt%)</th>
<th>Si (wt%)</th>
<th>N_{\text{free}} (ppm)</th>
<th>d (mm)</th>
<th>\sigma_{\text{base}} (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>D</td>
<td>1.48</td>
<td>0.2</td>
<td>0</td>
<td>5.28x10^{-3}</td>
<td>368</td>
</tr>
<tr>
<td>E1</td>
<td>1.49</td>
<td>0.22</td>
<td>0</td>
<td>4.57x10^{-3}</td>
<td>385</td>
</tr>
<tr>
<td>F</td>
<td>1.51</td>
<td>0.20</td>
<td>0</td>
<td>5.43x10^{-3}</td>
<td>365</td>
</tr>
<tr>
<td>G</td>
<td>1.49</td>
<td>0.20</td>
<td>0</td>
<td>5.99x10^{-3}</td>
<td>355</td>
</tr>
</tbody>
</table>

NOTE: For calculations see Appendix 6.1.

In the case of microalloyed steels such as the experimental HSLA 80 type steels, there is additional strengthening due to hardening by the microalloying species and by the processing conditions. Thus, the predictions of yield strength by the relationship proposed by Gladman and Dulieu fall short of the experimentally observed values of yield strength in the TMCP condition (Table 3.5) which range from 436 MPa in steel G to 515 MPa in steel E1.

Additional strengthening is attributable to a number of factors of varying magnitude and hence importance. In this work only those mechanisms with significant strengthening contributions (>10 MPa) will be discussed in detail. Those mechanisms present in the unaged steel include:

- Solid solution strengthening due to Cu,
- Dislocation hardening resulting from the $\gamma$ to $\alpha$ transformation during TMCP
- Dispersion strengthening by microalloy precipitates present prior to ageing (Nb and Ti carbonitride and $\varepsilon$ Cu),

In addition, those mechanisms which contribute to strength as a result of ageing are;

- Hardening due to increasing volume fraction of incoherent $\varepsilon$ Cu precipitates and
- Precipitation hardening due to the formation of Cu rich clusters and coherent precipitates of Cu.

Each of these mechanisms is examined individually in the following sections and where possible the magnitude of their contribution to the strength of the steel is estimated and compared to experimental results.

4.3.2.2 Additional strengthening mechanisms present in the unaged steel

a. Solid solution strengthening due to Cu

Solid Solution Strengthening (SSS), often referred to in the literature as matrix strengthening, refers to the increased resistance to the movement of dislocations, through the interaction of the strain fields surrounding dislocations and solute atoms.

Whilst the magnitudes of this effect for Mn, Si, and N are considered by the equation of Gladman and Dulieu (equation 1.2), it does not contain a term which accounts for the additional strengthening effect of Cu in solution. The magnitude of this SSS effect is a function of the binding energies between solute atoms and dislocations and the solute concentration. It is of course, limited by the maximum amount of solute Cu that can be maintained in solution.
Work by Baird and Preston (75) suggests that Cu in solution raises the yield stress of ferrite by 38% for every 1% of Cu. Thus, in the case of the Series 1 experimental Steels D, E1 and F each of which contain about 1 wt% Cu, the predicted increases in yield strength range from 146 to 174 MPa and 82 MPa for the low Cu steel G (Table 4.2).

More recent quantitative work by Wada et al. (123), which concerned solution treated steels, estimated an increase of 46 MPa for every 1% Cu, this relationship gives a substantially smaller increment in strength of about 23 MPa for the low Cu steel G and 39 to 41 MPa for the 1% Cu steels D, E1 and F (Table 4.2). Both of these estimates assume incorrectly that all of the copper is retained in solution after TMCP, but only part of the Cu remains in solution, as Cu precipitates are present in the TMCP condition (Figure 3.2a).

A rough estimate of the contribution to strength attributable to SSS by Cu in the TMCP condition can be made from the experimental results. It was suggested by Hornbogen (85) that 100% precipitation of Cu has occurred after ageing a 0.9% Cu alloy for 100 hours at 600°C. Thus, whilst recognising that a small proportion of softening could be due to other factors associated with dislocation density and distribution, arising from minor differences in cooling after TMCP and annealing out of the dislocation structure during the ageing process etc., and that some minor strengthening will be produced by the overcoarsened Cu precipitates, it is not unreasonable to assume that the difference in yield stress between unaged samples and those aged for 100 hours at a similar temperature would be roughly indicative of the SSS effect attributable to the precipitable Cu. The experimental results indicate a decrease in yield strength of between 75 and 85 MPa for the 1% Cu steels and 89 MPa for the 0.5% Cu steels (Table 4.2 - equivalent to an average of 82 MPa per 1 wt% Cu in solution) after ageing for 100 hours at 650°C. This figure lies between those changes in yield strength estimated based on the work of Wada et al. (46 MPa per wt% Cu) and those estimates based on the work by Baird and Preston (170 to 186 MPa per wt% Cu)(Appendix 5.3). They are, however, closer to the estimates based on the work of Wada et al. and on this basis this estimate will be used in any further calculations requiring an estimate for SSS by Cu. The validity of this estimate is further supported by the fact that the present experimental estimate would tend to overestimate
the strength increment due to SSS by Cu because it ignores the strength decreases associated with the reduction in the dislocation density and coarsening of Cu, Nb and Ti bearing precipitates on overaging.

In Table 4.2 the % Cu in solution after TMCP has been estimated on the basis of the volume fraction of Cu measured in the steels in the TMCP condition (Appendix 6.2.1).

### TABLE 4.2. Estimate of magnitude of solid solution strengthening using the models proposed by Wada et al. (123) and Baird and Preston (75).

<table>
<thead>
<tr>
<th>STEEL</th>
<th>Total Cu content of steel (wt%)</th>
<th>Estimated Cu in solution after TMCP at room temp. (wt%)</th>
<th>Wada et al. $\Delta \sigma_{SSS}$ (MPa)</th>
<th>Baird &amp; Preston $\Delta \sigma_{SSS}$ (MPa)</th>
<th>Experimental $\sigma_{y 1}$ TMCP (MPa)</th>
<th>Experimental $\sigma_{y 2}$ 100 HOURS (MPa)</th>
<th>Experimental $\sigma_{y 1} - \sigma_{y 2}$ (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>D</td>
<td>1.00</td>
<td>0.85</td>
<td>39</td>
<td>161</td>
<td>498</td>
<td>413</td>
<td>85</td>
</tr>
<tr>
<td>E1</td>
<td>1.05</td>
<td>0.89</td>
<td>41</td>
<td>174</td>
<td>515</td>
<td>436</td>
<td>79</td>
</tr>
<tr>
<td>F</td>
<td>1.00</td>
<td>0.85</td>
<td>39</td>
<td>146</td>
<td>453</td>
<td>378</td>
<td>75</td>
</tr>
<tr>
<td>G</td>
<td>0.50</td>
<td>0.49</td>
<td>23</td>
<td>82</td>
<td>436</td>
<td>347</td>
<td>89</td>
</tr>
</tbody>
</table>

**NOTE:** $\Delta \sigma_{Wada} = 46 \text{ MPa per wt\% Cu, } \Delta \sigma_{Baird-Preston} = \left[ \text{wt\% Cu} \right] \times 0.38 \times \left( \sigma_y^{(TMCP)} \right)$

For examples of calculations see Appendix 6.2

$\sigma_{y 1}$ from Table 3.5

$\sigma_{y 2}$ from Table 4.8

**b. Dispersion strengthening by microalloy precipitates (Nb and Ti Carbonitrides and Cu) prior to ageing.**

Of the models available, the Ashby Orowan model (76, 125) is widely applied to steels because it associates the yield stress increment with randomly distributed carbonitride dispersions in ferrite.

Work carried out by Fujii, Nemoto, Suto and Monma (77) in which the precipitation hardening of Fe + 0.6, 1.4, 1.8, 2.5 and 6.0% Cu alloys was examined, resulted in the conclusion "...that strengthening by the dispersion of copper particles arises mainly from the by-pass process and that the contribution from other mechanisms are almost negligibly small" (Section 1.7.1.4). They found that "...the yield stress of these alloys at overaged states could be well explained by the simple Orowan theory". Most importantly they provided evidence for the validity of application of the Orowan theory in these steels by finding TEM evidence of the dislocation bypass process.
For the Series 1 experimental steels D, E1, F and G, the calculated maximum volume fraction of microalloy precipitates (NbCN+TiN+Cu) ranged from $6.40 \times 10^{-4}$ to $1.90 \times 10^{-3}$ (Table 4.3). Based on the Ashby Orowan model (equation 1.3), the predicted yield stress increment ($\sigma$) for these steels ranges from approximately 51 to 88 MPa.

In this work, the TEM examination of particle size distributions in the TMCP unaged steels, showed that a range of particle sizes exists, from $<5\text{nm}$ to $20\text{nm}$ (Figure 3.11a), not all of which would fall into the category of incoherent particles. However, if the work of Fujii et al. (77) is considered, the majority of these particles could potentially form part of the precipitation hardening process described by Brown (89) as Orowan bowing or Stage III (Figure 4.6).

![Diagram](image)

**FIGURE 4.6** Yield stress as a function of particle radius ($r$) at a constant volume fraction ($f$) for a precipitate hardening process [Brown(89)].
The equation for Stage III reduces to:

\[ \sigma = \frac{0.8 G b}{L} \]

where

\[ L = \left( \frac{2\pi}{3f} \right)^{\frac{1}{2}} - \left( \frac{8}{3} \right)^{\frac{1}{2}} r_o \]

which reduces to (73)

\[ L = \frac{1.77 r}{f^2} \]

\( \sigma \) = bowing stress

\( G \) = shear modulus for ferrite

\( b \) = Burgers vector for ferrite

\( r_o \) = finite radius of spherical precipitate

\( r \) = mean planar particle radius

\( L \) = the true planar spacing

\( \sigma \) = flow stress in tension

For the present case, consider steel E1, taking \( G = 8.3 \times 10^4 \text{ MPa}, b = 2.48 \times 10^{-4} \mu\text{m}, r = 6.75 \times 10^{-3} \mu\text{m} \) and \( f = 1.90 \times 10^{-3} \) (Appendix 6.3). From equation 4.3, \( \sigma = 60 \text{ MPa} \) which is less than the 88 MPa predicted by the Ashby Orowan equation 1.3. Estimates of \( \sigma \) due to dispersion strengthening for the experimental steels D, E1, F and G are summarised in Table 4.3.

### Table 4.3 Estimate of magnitude of dispersion strengthening by coarse Cu + NbCN + TiN particles prior to ageing, using the models proposed by Ashby and Orowan (125) and Brown (89)

<table>
<thead>
<tr>
<th>STEEL</th>
<th>Volume fraction of microalloy precipitate (NbCN, TiN and Cu) ( f \times 10^{-3} )</th>
<th>Ashby Orowan ( \sigma_{(\text{NbCN+Cu)}}^{\text{TMCP}} ) (MPa)</th>
<th>Brown ( \sigma_{(\text{NbCN+Cu)}}^{\text{TMCP}} ) (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>D</td>
<td>1.75</td>
<td>85</td>
<td>58</td>
</tr>
<tr>
<td>E1</td>
<td>1.90</td>
<td>88</td>
<td>60</td>
</tr>
<tr>
<td>F</td>
<td>1.72</td>
<td>84</td>
<td>57</td>
</tr>
<tr>
<td>G</td>
<td>0.64</td>
<td>51</td>
<td>35</td>
</tr>
</tbody>
</table>

**NOTE**: For calculations of \( \sigma \) see Appendix 6.3. For calculations of volume fraction of microalloy precipitate see Appendix 2.2.
Smith et al. (124) have argued that the yield stress is likely to be determined by the most effective barrier to dislocation motion. Thus, where particles constitute the most effective barrier and bypass by bowing or cutting occurs then equations 1.3 and 4.3 should predict the yield stress and not the yield increment.

If this argument is valid then it becomes evident that the available theories on dispersion strengthening by coarse precipitate particles are clearly not applicable in this instance as the measured yield stress of the Series 1 experimental steels in the TMCP and unaged condition ranges from 436 to 515 MPa (Table 3.5), which is substantially greater than that predicted by either of equations 1.3 or 4.3. If the Pythagorean addition rule first proposed by Koppenaal and Kuhlmann-Wilsdorf (167) and later reviewed by Ardell (140) is applied, this produces a theoretical estimate of between 379 MPa and 430 MPa (Table 4.9) which underestimates the experimental result by up to 87 MPa. The argument proposed by Gladman and Dulieu (76), which assumes the strengthening contributions in HSLA steels are additive, produces theoretical estimate which range between 412 and 486 MPa (from Table 4.9 - additive contributions from 'Base', 'Copper Solid Solution' and 'Dispersion' strengthening mechanisms). This estimate calculated from the addition of the individual model predictions, is closer to the experimental result, than the estimates produced individually by either equations 1.3 or 4.3 or by applying the Pythagorean rule. However, given the logic of the argument by Smith et al. (124), this result could be fortuitous and not indicative of the validity of the "additive" rule.

c. Dislocation hardening associated with cooling rate through the austenite to ferrite transformation.

Cooling directly after TMCP from the austenitic field would have introduced dislocations in the supersaturated solid solution, which would cause hardening in the alloy. However, as discussed in Section 1.7.1.6, subsequent ageing treatments would gradually eliminate the majority of these dislocations. It has been found that the contribution of these dislocations to the yield stresses is about 5 kg/mm² at most (77). On this basis the effect of these dislocations has not been considered in this work.
4.3.2.3 Additional strengthening mechanisms present in the aged steel.

As mentioned previously, it has been proposed by Hornbogen et al. (118) that the phase which first precipitates in the Fe-Cu system is metastable bcc Cu rich clusters which are coherent with the ferrite matrix. These clusters grow first into coherent bcc particles (93), then coherent fcc ε Cu particles which eventually coarsen into incoherent precipitates when they reach a critical size. Goodman, Brenner and Low (93) have found that "...more than 50 pct of the copper is still in solution when the peak strength is reached". In a 1% Cu steel such as the experimental HSLA80 steels of this work, this implies that at peak strength approximately 50% of the total Cu is present as precipitates with 10% of precipitable Cu still in solution (assuming a solubility limit of Cu in αFe of 0.4%).

During the ageing process the nucleation of clusters and solute Cu depletion of the matrix occur continuously until overageing occurs. Throughout the peak hardening process the transformation of clusters which have reached the critical size to form ε Cu precipitates continues until complete solute depletion occurs. Goodman, Brenner and Low (93) have found that the copper content of particles present in the fully aged steels (1 hour at 500 °C) was only 51% (94). Furthermore Wasserman et al. (126) and Norton (127) have shown through X ray diffraction analysis that the entire volume fraction of precipitable Cu is not out of solution until an overaged state is reached. However, based on the fact that the solubility limit of Cu in ferrite under ambient conditions is approximately 0.4 wt% (29), then at least 0.4 wt% of the Cu will remain in solution even in the overaged state.

a. Hardening due to incoherent ε Cu precipitates

There are two types of interaction which must be described depending on whether the dislocation is inside or outside the particle. Since the interaction forces are greatest when the dislocation has entered the precipitate, only this case is relevant in estimating the maximum increment in critical resolved shear stress (CRSS) due to modulus hardening.
Russell and Brown (81) have proposed that the yield stress in the overaged condition is given by the sum of the base strength and \( \tau_0 \) the strength due to the particles,

\[
\tau = \tau_0 + \frac{0.8Gb}{L} \left(1 - \frac{r^2}{L^2}\right)^{1/2}
\]

where

\[ E_1 = \text{energy per unit length of dislocation in the precipitate.} \]
\[ E_2 = \text{energy per unit length of dislocation in the matrix.} \]

Thus a plot of \( \tau vs L^{-1} \) should be linear with a slope defined by equation 4.5. From the published data of Russell and Brown (in Figure 5 of Ref. 81), the equation for the line can be calculated and expressions for the upper and lower limits of the \( \sigma_{\text{max}} \) range can be found, taking \( \sigma = 2.5\tau \). These are as follows

- upper limit: \( \sigma = \left(452.5 \times 10^3\right)L^{-1} + 205.2 \)
- lower limit: \( \sigma = \left(347.5 \times 10^3\right)L^{-1} + 183 \)

Assuming that \( L^{-1} = \frac{f^{1/2}}{1.77r} \) (equation 4.4b), \( \sigma \) can be estimated.

The calculated values of \( \sigma \) for the Series 1 experimental steels using equations 4.6 and 4.7 are summarised in Table 4.4. These estimates of the yield stress are lower than the experimental results listed in Table 3.5 for the fully aged condition.
ESTIMATES OF TOTAL YIELD STRENGTH IN THE FULLY AGED CONDITION WITH CONTRIBUTION FROM INCOHERENT Cu PRECIPITATION, BASED ON THE MODEL OF RUSSELL AND BROWN (81) (EQUATIONS 4.6 AND 4.7).

<table>
<thead>
<tr>
<th>STEEL</th>
<th>$f_{scu}$</th>
<th>Upper Limit $\sigma_{TMCP+Aged}$ (MPa)</th>
<th>Lower Limit $\sigma_{TMCP+Aged}$ (MPa)</th>
<th>Midpoint $\sigma_{TMCP+Aged}$ (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>D</td>
<td>2.22x10^{-3}</td>
<td>539</td>
<td>440</td>
<td>490</td>
</tr>
<tr>
<td>E1</td>
<td>2.41x10^{-3}</td>
<td>554</td>
<td>451</td>
<td>503</td>
</tr>
<tr>
<td>F</td>
<td>2.26x10^{-3}</td>
<td>543</td>
<td>442</td>
<td>492</td>
</tr>
<tr>
<td>G</td>
<td>1.5x10^{-4}</td>
<td>292</td>
<td>250</td>
<td>271</td>
</tr>
</tbody>
</table>

NOTE:
- For calculations see Appendix 6.4

The model of Russell and Brown clearly underestimates the experimentally determined strength of the fully aged steel. However, the difference between the experimental yield strength and the prediction made using the model may be explained by the fact that the model used to calculate the yield strength in Table 4.4 is based on dislocation cutting of the overaged Cu particles as discussed in Section 1.7.1.4 and does not take into account the effect of fine coherent Cu particles and Cu rich clusters which were also present in the fully aged experimental steel.

Fujii et al. (77) have proposed that the strengthening by dispersion of incoherent copper particles arises mainly from the by-pass process. They claim that the yield stresses of these alloys in the overaged state can be explained using the simple Orowan theory (87), in which the stress required to bypass the particles is a function of the volume fraction of precipitates present and their size (equation 1.6). Estimates of the yield stress based on the Orowan model are listed in Table 4.5.
Table 4.5  Estimates of the total yield strength in the fully aged condition with contribution from incoherent ε Cu precipitation calculated from equation 1.6 (from Fujii et al. (77)).

<table>
<thead>
<tr>
<th>STEEL</th>
<th>( f_{\text{Cu}} )</th>
<th>( l_p (\AA) )</th>
<th>( \sigma_{\text{TMCP} + \text{Aged}} ) (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>D</td>
<td>2.22x10^{-3}</td>
<td>1048</td>
<td>505</td>
</tr>
<tr>
<td>E1</td>
<td>2.41x10^{-3}</td>
<td>1002</td>
<td>528</td>
</tr>
<tr>
<td>F</td>
<td>2.26x10^{-3}</td>
<td>1038</td>
<td>510</td>
</tr>
<tr>
<td>G</td>
<td>1.50x10^{-4}</td>
<td>4194</td>
<td>126</td>
</tr>
</tbody>
</table>

NOTE: using: \( \sigma = 2.5 \tau, G = 8.3 \times 10^4, \nu = 0.29, b = 2.48 \times 10^{-10} m, \tau' = 2.73 \times 10^{-9} \AA \).

For calculations see Appendix 6.4

The Orowan model used to calculate the yield strength in Table 4.5 gives an estimate of the yield stress of the alloy in the fully aged condition. Fujii et al. (77) describe this as “the stress required to bypass the particle”, which appears to agree with the argument of Smith et al., (124) that the total yield stress is considered to be determined by the most effective barrier to dislocation motion. It is evident from a comparison of the figures for yield stress in Tables 3.5 and 4.5, that the Orowan model underestimates the final experimental yield strength by up to 45 MPa in the 1% Cu experimental steels (see Table 4.9).

An estimate of the increment in yield strength produced by incoherent ε Cu particles on ageing can also be determined by applying the Ashby Orowan model (76, 125) which is discussed in section 4.3.2.2.b in relation to the yield stress increment due to randomly distributed carbonitride and ε Cu dispersions in ferrite prior to ageing. According to the work of Fujii et al. (77) this model is applicable in these Cu bearing alloys in the overaged state (Section 4.3.2.2). When applied to the Series 1 steels D, E1, F and G the model predicts strength increments of between 45 and 47 MPa for the 1% Cu steels D, E1 and F. Estimates of the yield strength increment based on the Ashby Orowan model are listed in Table 4.6. If these estimates are compared to the experimental increment in strength on ageing summarised in Table 4.6 it is evident that for the 1% Cu steels the Ashby Orowan model provides a close estimate of the experimental result.
Table 4.6: Yield Strength increment between the unaged and fully aged experimental steels based on the Ashby Orowan model.

<table>
<thead>
<tr>
<th>STEEL</th>
<th>VOLUME FRACTION OF MICROALLOY PRECIPITATE</th>
<th>f_{\alpha Cu}</th>
<th>( l_p )</th>
<th>( \sigma_{\text{Incoherent } \alpha Cu \text{ TMCP+Aged (MPa) from equation 1.3}} )</th>
<th>( \Delta \sigma_{\text{Experimental Strength Increment (MPa) from Table 4.9}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>D</td>
<td>2.22 \times 10^{-3}</td>
<td>1048</td>
<td>45</td>
<td>52</td>
<td></td>
</tr>
<tr>
<td>E1</td>
<td>2.41 \times 10^{-3}</td>
<td>1002</td>
<td>47</td>
<td>32</td>
<td></td>
</tr>
<tr>
<td>F</td>
<td>2.26 \times 10^{-3}</td>
<td>1038</td>
<td>45</td>
<td>54</td>
<td></td>
</tr>
<tr>
<td>G</td>
<td>1.50 \times 10^{-4}</td>
<td>4194</td>
<td>12</td>
<td>-31</td>
<td></td>
</tr>
</tbody>
</table>

Note: for calculations see Appendix 6.4

b. Precipitation hardening due to coherent \( \varepsilon \text{Cu} \) and Cu rich zones or clusters

The strengthening of an alloy by coherent precipitation usually occurs either because of the interaction between the stress fields of misfitting precipitates and dislocations (coherency strengthening) or when the shearing of ordered precipitates occurs and creates antiphase boundaries along the slip plane of the precipitate (order strengthening).

The Ashby Orowan equation (1.3) discussed earlier has been applied by some authors to predict the yield stress increment associated with randomly distributed coherent precipitate dispersions in ferrite (76). However, this equation applies to dislocation bypass by bowing or cross slip of dislocations around impenetrable particles. The copper rich clusters which form in the ferrite prior to the formation of incoherent particles are coherent with the ferrite matrix and therefore they should be cut by dislocations during deformation. Hence, the Ashby Orowan equation in the form in which it appears in equation 1.3 does not apply. This view has been expressed by Smith, Dunne and Chandra (124), who argue that the Ashby Orowan equation is only applicable in cases where overaged particles occur which are sufficiently coarse and widely spaced for bowing to take place rather than particle shear.
In the case of Cu precipitation their argument appears logical in that Cu particles, particularly when they are coherent, are unlikely to form impenetrable particles, because of their relative 'softness' compared to NbCN and TiCN. Therefore, the coherent Cu particles would be most likely cut by dislocations.

This stage of the precipitation hardening process may be described by what Brown (89) calls the Friedel Cutting or Stage I of the three stages of the precipitation hardening process (Figure 4.6). This stage is characterised by a parabolic increase in yield stress which is proportional to the square root of the particle radius \((r^{1/2})\). In this case the increase in strength occurs because, as the clusters grow and multiply, a curving dislocation encounters more and more particles, effectively decreasing the particle spacing along the dislocation line.

However, difficulty arises when one attempts to quantify the effect of these Cu rich clusters on strength because, as noted earlier, it is difficult to resolve the coherent clusters by TEM because of the similarity of the electron scattering factors of Fe and Cu. Consequently, it is difficult to resolve the clusters and fine particles before they become coarser incoherent precipitates.

Russell and Brown (81) have proposed that the value of the maximum strength (or peak hardness) produced by the coherent Cu clusters is given by:

\[
\tau_{\text{max}} = 0.041 \frac{Gbf^{1/2}}{r_o}
\]

where \(r_o\) is the inner cut-off radius.

Using a value of the Schmidt factor of 2.5

\[
\sigma_{\text{max}} = 2.5[0.041 \frac{Gbf^{1/2}}{r_o}]
\]

The following data were used for the experimental Cu bearing steels of this study:

- \(G_{\text{Fe+Cu}} = 6.575 \times 10^4\text{(MNm}^{-2})\),

- \(\overline{b}_{\text{Fe+Cu}} = 2.52\text{ Å}\)
DISCUSSION

\[ r = 12 \, \text{Å} \]

which Russell and Brown indicate corresponds to the cluster size for peak strengthening,

and it is assumed that the maximum strength occurs for \( r = 2r_o \) (81) then,

\[ r_o = \frac{r}{2} = 6 \, \text{Å} \]

In addition the maximum volume fraction of Cu available for clustering was assumed to be

\[ \frac{f_{\text{Coherent}}}{\text{Cu} + \text{Cu clusters}} = \frac{f_{\text{Cu available for precipitation}}}{f_{\text{Cu precipitate observed in aged steel}}} \]

\[ = 3.3 \times 10^{-3} \]

For steel E1 equation 4.9 gives,

\[ \sigma_{\text{max}} = 163 \, \text{MPa} \]

(for estimates see Table 4.7 and for calculations see Appendix 6.5)

If this estimate of the maximum strength is compared to the fully aged experimental strength, it is evident that the model underestimates the experimental result by up to 394 MPa. As mentioned previously (Section 4.3.2.3), Goodman et al. (93) have reported that the composition of the Cu particles is not pure Cu, but rather a metastable solid solution of Fe and Cu. Therefore, the estimate of \( f_{\text{Coherent}} \) used in these calculations (Table 4.7) is likely to be significantly less than the volume fraction of particles available to contribute to the aged strength.

By substituting the experimentally determined aged strength of the steel, into equation 4.9, the model can be used to estimate the volume fraction of coherent Cu particles and Cu rich clusters which would be required to achieve the experimental strength. For steel E1, \( f_{\text{Coherent}} \) as estimated using the model, is approximately

\[ 3.7 \times 10^{-2} \] (Appendix 6.5b).

This is approximately 10 times the volume fraction calculated using experimental observations and the steel composition, implying that the average composition of the coherent s Cu particles and clusters is \( \approx 10\% \text{ Cu} \).
This analysis is based on the assumption that the shear modulus \( G \) for an Fe/Cu particle, is an average of \( G_{Cu} \) and \( G_{aFe} \), whereas in reality such a metastable solid solution would probably have a \( G \) that is much greater than either \( G_{Cu} \) or \( G_{aFe} \).

If it is assumed that the Cu bearing clusters have an average composition of 50% Cu (93), then the volume fraction of coherent Cu bearing particles would be doubled \((6.6 \times 10^{-3})\). For this volume fraction, the shear modulus for the fine particles and clusters would need to be about 163 GPa (instead of 65.75 GPa) in order to account for the observed yield strength of 557 MPa. Such a value for the shear modulus is not inconceivable because clusters or particles containing about 50% Fe would constitute a highly supersaturated metastable transition phase with a high modulus.

However, in the absence of accurate information regarding the actual composition of the coherent e Cu particles and the Cu rich clusters or alternatively a more effective imaging system which would enable an accurate volume fraction to be determined, the accuracy of the model proposed by Russell and Brown (81) cannot be tested.

The maximum hardening increment attributable to e Cu and Cu rich clusters can also be determined using a quantitative expression produced by Russell and Brown (81), from a plot of what they refer to as "the maximum increase in yield strength" as a function of the square root of the volume fraction of precipitate (Figure 4, Ref. 81). They give as the equation for the line,

\[
\sigma_{max} = 3.57 \times 10^3 \sqrt{f} - 71 \text{MNm}^{-2} \tag{4.11}
\]

substituting for \( f \) in equation 4.11 produces an estimate of the maximum hardening increment for steel E1 of 134 MPa. Estimates of hardening increments for the Series 1 experimental steels D, E1, F and G calculated from both equations 4.9 and 4.11 appear in Table 4.7.
Table 4.7 Estimate of the strength increment due to coherent $\varepsilon$ Cu and Cu rich clusters as predicted using the model proposed by Russell and Brown (81).

<table>
<thead>
<tr>
<th>STEEL</th>
<th>$f_{\text{Coherent } \varepsilon \text{Cu + Cu clusters}}$</th>
<th>Maximum Strength $\sigma_{\text{Coherent } \varepsilon \text{Cu+Cu clusters}}$ from equation 4.9 (MPa)</th>
<th>Maximum Increment in Strength on Ageing $\sigma_{\text{Coherent } \varepsilon \text{Cu+Cu clusters}}$ from equation 4.11 (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>D</td>
<td>.0031</td>
<td>156</td>
<td>126</td>
</tr>
<tr>
<td>E1</td>
<td>.0033</td>
<td>163</td>
<td>134</td>
</tr>
<tr>
<td>F</td>
<td>.0030</td>
<td>155</td>
<td>125</td>
</tr>
<tr>
<td>G</td>
<td>.0006</td>
<td>72</td>
<td>19</td>
</tr>
</tbody>
</table>

NOTE: for calculations see Appendix 6.5

Although the predictions of equation 4.11 are referred to as an "increment" in strength, the values should correspond to the total strength if the coherent precipitates dominate in determining the alloy strength. It is apparent from a comparison of the estimated strength increments summarised in Table 4.7 and the actual experimental strength increments listed in Table 4.9, that the model greatly overestimates the actual strength increment on ageing. It therefore seems more appropriate to apply the model to estimate the total strength rather than the increment and it is likely that the poor predictions relate to inaccurate values for volume fraction and shear modulus.

4.3.2.4 Correlation between Vickers hardness measurements and tensile properties.

In order to relate the theoretical calculations of yield strengths attributable to each of the various mechanisms discussed in Section 4.3.2, to the strengths obtained experimentally, it was necessary to quantify the effect of ageing on the tensile properties of the experimental steels. However, because of the limited amount of steel available it was not possible or practical to repeat for tensile testing, the range of ageing treatments carried out for Vickers hardness testing. So it was decided to look at a single temperature (550 °C) for a single ageing time (1 hour) and to correlate the resulting tensile properties with Vickers hardness values. The relationship developed enables the tensile stress for any ageing temperature to be estimated from the hardness. In this way, the theoretical predictions of yield stress could be compared with measured or derived values.
The tensile properties of the Series 1 and Series 2 steels are summarised in Tables 3.6 and 3.7. A series of regressions designed to determine the line of best fit were carried out which produced correlations with exceptionally high correlation ratios ($R^2 > 92\%$)(Figures 4.6 and 4.7).

The equations of correlation are as follows:

For TMCP steels:

\[
\begin{align*}
TS & (\text{MPa}) = 664.077 \ln(HV)-2863.178 \\
YS & (\text{MPa}) = 331 \ln(HV)-1251.720
\end{align*}
\]

\[R^2 = 0.994\] \hspace{1cm} 4.12

\[R^2 = 0.921\] \hspace{1cm} 4.13

For steels aged at 550 °C for 1 hour:

\[
\begin{align*}
TS & (\text{MPa}) = 709.348 \ln(HV)-3139.645 \\
YS & (\text{MPa}) = 544.166 \ln(HV)-2360.040
\end{align*}
\]

\[R^2 = 0.949\] \hspace{1cm} 4.14

\[R^2 = 0.967\] \hspace{1cm} 4.15

FIGURE 4.6 Correlation between Vickers hardness and strength for Series 1 and Series 2 experimental steels in the TMCP condition.

FIGURE 4.7 Correlation between Vickers hardness and strength for the Series 1 and Series 2 experimental steels in the aged condition.
These correlations where used to calculate the yield stress from the Vickers hardness test results. The tensile strengths of the experimental steels D, E1, F and G were calculated using the hardness results for various times ranging from the TMCP condition (0 minutes) to 100 hours (from Equations 4.12 to 4.15) and are summarised in Table 4.8.

<table>
<thead>
<tr>
<th>STEEL</th>
<th>TEST</th>
<th>TIME at 650 °C</th>
<th>0°C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>(Min)</td>
<td></td>
</tr>
<tr>
<td>E1</td>
<td>HV30</td>
<td>0</td>
<td>193.04</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5</td>
<td>197.21</td>
</tr>
<tr>
<td></td>
<td></td>
<td>10</td>
<td>206.64</td>
</tr>
<tr>
<td></td>
<td></td>
<td>20</td>
<td>208.90</td>
</tr>
<tr>
<td></td>
<td></td>
<td>30</td>
<td>202.78</td>
</tr>
<tr>
<td></td>
<td></td>
<td>40</td>
<td>200.09</td>
</tr>
<tr>
<td></td>
<td></td>
<td>50</td>
<td>203.64</td>
</tr>
<tr>
<td></td>
<td></td>
<td>60</td>
<td>201.35</td>
</tr>
<tr>
<td></td>
<td></td>
<td>120</td>
<td>202.57</td>
</tr>
<tr>
<td></td>
<td></td>
<td>180</td>
<td>204.40</td>
</tr>
<tr>
<td></td>
<td></td>
<td>100 hours</td>
<td>170.26</td>
</tr>
<tr>
<td>D</td>
<td>HV30</td>
<td>0</td>
<td>631.79</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5</td>
<td>608.74</td>
</tr>
<tr>
<td></td>
<td></td>
<td>10</td>
<td>641.87</td>
</tr>
<tr>
<td></td>
<td></td>
<td>20</td>
<td>649.59</td>
</tr>
<tr>
<td></td>
<td></td>
<td>30</td>
<td>628.50</td>
</tr>
<tr>
<td></td>
<td></td>
<td>40</td>
<td>619.02</td>
</tr>
<tr>
<td></td>
<td></td>
<td>50</td>
<td>631.50</td>
</tr>
<tr>
<td></td>
<td></td>
<td>60</td>
<td>623.48</td>
</tr>
<tr>
<td></td>
<td></td>
<td>120</td>
<td>627.76</td>
</tr>
<tr>
<td></td>
<td></td>
<td>180</td>
<td>634.14</td>
</tr>
<tr>
<td></td>
<td></td>
<td>100 hours</td>
<td>504.51</td>
</tr>
<tr>
<td>F</td>
<td>HV30</td>
<td>0</td>
<td>490.67</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5</td>
<td>549.67</td>
</tr>
<tr>
<td></td>
<td></td>
<td>10</td>
<td>633.90</td>
</tr>
<tr>
<td></td>
<td></td>
<td>20</td>
<td>531.98</td>
</tr>
<tr>
<td></td>
<td></td>
<td>30</td>
<td>527.89</td>
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<tr>
<td></td>
<td></td>
<td>40</td>
<td>523.94</td>
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<td></td>
<td></td>
<td>50</td>
<td>522.72</td>
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<tr>
<td></td>
<td></td>
<td>60</td>
<td>523.12</td>
</tr>
<tr>
<td></td>
<td></td>
<td>120</td>
<td>522.03</td>
</tr>
<tr>
<td></td>
<td></td>
<td>180</td>
<td>512.41</td>
</tr>
<tr>
<td></td>
<td></td>
<td>100 hours</td>
<td>412.51</td>
</tr>
<tr>
<td>G</td>
<td>HV30</td>
<td>0</td>
<td>155.57</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5</td>
<td>161.00</td>
</tr>
<tr>
<td></td>
<td></td>
<td>10</td>
<td>159.00</td>
</tr>
<tr>
<td></td>
<td></td>
<td>20</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>30</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>40</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>50</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>60</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>120</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>180</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>100 hours</td>
<td>-</td>
</tr>
</tbody>
</table>

### 4.3.2.5 Summary of theoretical estimates of contributions from various strengthening mechanisms

The unaged and peak yield strengths of the experimental steels D, E1, F and G were calculated from the Vickers hardness test results using the regression equations discussed in Section 4.3.2.4 (Equations 4.13 and 4.15 - Table 4.8). Estimates of the total strength of these same experimental steels were made using linear and Pythagorean addition of the individual contributions from the various mechanisms as calculated using the predicted strengths of the various models discussed in Sections 4.3.2.1 through to 4.3.2.3. The theoretical and experimental determinations of strength arising from this analysis are compared in Table 4.9.
TABLE 4.9  Summary table for estimates of contributions to steel strength from various mechanisms.

<table>
<thead>
<tr>
<th>STEEL MECHANISM</th>
<th>MODEL</th>
<th>D</th>
<th>E1</th>
<th>F</th>
<th>G</th>
</tr>
</thead>
<tbody>
<tr>
<td>PRIOR TO AGEING</td>
<td>Base Strength from grain size &amp; solid solution strengthening due to Mn, Si, N.</td>
<td>a. Gladman and Dulieu (71)</td>
<td>368</td>
<td>385</td>
<td>365</td>
</tr>
<tr>
<td></td>
<td>Solid Solution Strengthening due to Cu</td>
<td>b. Wada et al. (123)</td>
<td>39</td>
<td>41</td>
<td>39</td>
</tr>
<tr>
<td></td>
<td></td>
<td>c. Baird and Preston (75)</td>
<td>161</td>
<td>174</td>
<td>146</td>
</tr>
<tr>
<td></td>
<td>Dispersion Strengthening by Incoherent Microalloy Precipitates Nb, Ti</td>
<td>d. Ashby Orowan (76)</td>
<td>42</td>
<td>43</td>
<td>38</td>
</tr>
<tr>
<td></td>
<td></td>
<td>e. Brown (89)</td>
<td>29</td>
<td>29</td>
<td>26</td>
</tr>
<tr>
<td></td>
<td>Dispersion Strengthening by Incoherent Microalloy Precipitates Nb, Ti and Cu</td>
<td>f. Ashby Orowan (76)</td>
<td>85</td>
<td>88</td>
<td>84</td>
</tr>
<tr>
<td></td>
<td></td>
<td>g. Brown (89)</td>
<td>58</td>
<td>60</td>
<td>57</td>
</tr>
<tr>
<td></td>
<td>Experimental unaged strength.</td>
<td>h. Experimental tensile testing results from Table 3.5</td>
<td>498</td>
<td>515</td>
<td>453</td>
</tr>
<tr>
<td></td>
<td>Difference between experimental unaged strength estimated base strength. (%)</td>
<td>(h - a) for all steels</td>
<td>130</td>
<td>130</td>
<td>88</td>
</tr>
<tr>
<td></td>
<td>Apply Pythagorean Addition Rule (PAR)</td>
<td>a+PAR(b+g)*</td>
<td>411</td>
<td>430</td>
<td>408</td>
</tr>
<tr>
<td></td>
<td>Apply Additive Rule (AR)</td>
<td>(a+b+g)*</td>
<td>465</td>
<td>486</td>
<td>461</td>
</tr>
<tr>
<td></td>
<td>Difference between Experimental Unaged Strength and Theoretical Estimate</td>
<td>(h-PAR)</td>
<td>87</td>
<td>85</td>
<td>45</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(h-AR)</td>
<td>33</td>
<td>29</td>
<td>8</td>
</tr>
<tr>
<td>FULLY AGED</td>
<td>Equilibrium Solid Solution Strengthening by Cu</td>
<td>i. Wada et al. (123)</td>
<td>18.4</td>
<td>18.4</td>
<td>18.4</td>
</tr>
<tr>
<td></td>
<td>Strengthening due to Incoherent ε Cu (+ the base strength)</td>
<td>j. Russell and Brown (81)</td>
<td>490</td>
<td>503</td>
<td>492</td>
</tr>
<tr>
<td></td>
<td></td>
<td>k. Fujii et al. (77)</td>
<td>505</td>
<td>528</td>
<td>510</td>
</tr>
<tr>
<td></td>
<td>Strengthening increment due to Incoherent ε Cu alone</td>
<td>l. Ashby Orowan (76)</td>
<td>45</td>
<td>47</td>
<td>45</td>
</tr>
<tr>
<td></td>
<td>Strengthening increment due to Coherent Cu rich clusters</td>
<td>m. Russell and Brown (81)</td>
<td>126</td>
<td>134</td>
<td>125</td>
</tr>
<tr>
<td></td>
<td>Experimental Peak Strength</td>
<td>n. from Table 4.8</td>
<td>550</td>
<td>547</td>
<td>507</td>
</tr>
<tr>
<td></td>
<td>Experimental Strength Increment on ageing</td>
<td>52</td>
<td>32</td>
<td>54</td>
<td>-31</td>
</tr>
<tr>
<td></td>
<td>Apply Additive Rule to theoretical estimates (AR).</td>
<td>(a+e+i+l+m)*</td>
<td>616</td>
<td>642</td>
<td>610</td>
</tr>
<tr>
<td></td>
<td>Apply Pythagorean Addition Rule to theoretical estimates (PAR).</td>
<td>a+PAR(e+i+l+m)*</td>
<td>685</td>
<td>720</td>
<td>691</td>
</tr>
<tr>
<td></td>
<td>Difference between Experimental Aged Peak Strength and Theoretical Estimates</td>
<td>(AR - n)</td>
<td>66</td>
<td>95</td>
<td>103</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(PAR - n)</td>
<td>136</td>
<td>173</td>
<td>184</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Russell &amp; Brown (81)</td>
<td>96</td>
<td>119</td>
<td>140</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Fujii et al. (77) (k-n)</td>
<td>-45</td>
<td>-19</td>
<td>3</td>
</tr>
</tbody>
</table>

* Mechanisms (b), (e) and (g) are used on the basis that they appear to provide more realistic estimates (see text Section 4.3.2.2.a and b)
It must be kept in mind when comparing the experimentally measured strengths, to the estimates produced using the selected models, that several assumptions have been made which may affect the accuracy of the predictions.

i. The estimates for strengthening produced by Cu in Table 4.9, depend on the accuracy of the estimate of volume fractions of Cu in its various forms (e.g. solution, incoherent \( \varepsilon \) Cu particles and coherent \( \varepsilon \) Cu particles and clusters). These volume fractions were estimated from the particles visible in the TMCP and the TMCP and aged conditions and the chemical compositions of the experimental steels. As such they would be subject to some experimental error which could affect the agreement between the experimental results and the models.

ii. The solubility limit of Cu in ferrite has been assumed to be 0.4% from the binary (Fe-Cu) diagram, which may not be the case for this complex alloy system.

iii. It has been assumed that the composition of the \( \varepsilon \) Cu particles is almost pure Cu. However, it has been shown by Goodman Brenner and Lowe (93), that the composition of these particles can vary, with as little as 50% Cu being present in the particle for the peak hardened condition. Thus, the volume fractions of coherent \( \varepsilon \) Cu particles and Cu rich clusters are likely to be underestimated in this work, with corresponding underestimates of the strengthening by coherent particles (as discussed in Section 4.3.2.3b).

If the assumptions made in the calculations of the volume fraction of Cu in its various forms are accepted as reasonable in the context of this work then the following statements can be made.

The additive rule generally overestimates the experimental result for the aged steel by up to 103 MPa. If the Pythagorean addition rule is applied, the models examined overestimate the final strength by between 136 and 184 MPa for the high Cu steels D, E1 and F and give a very close estimate for the low Cu steel G. Whilst work by Hanson and Morris (168) has provided justification for the application of the Pythagorean addition rule for mixtures of obstacles of distinct strengths, it is evident that this rule cannot be successfully applied in this case. If the argument of Smith et al. (124) is followed and the yield stress is considered to be
determined by the most effective barrier to dislocation motion, then the models should predict the final strength and not the strength increment. In this case each of the models greatly underestimates the final aged yield strength, but as pointed out in 4.3.2.3b, the lack of agreement may be due to inappropriate values for the variables used in the equations.

The model of Fujii et al. (77) which is based on the Orowan model produces estimates closest to the experimental results. However, even in this case the experimental result for the 1% Cu steels can be underestimated by up to 45 MPa.

If the assumptions made are valid then it must be concluded that the available theories do not adequately explain the strengthening mechanism occurring in the Cu bearing steels examined. The difficulty then is to decide which mechanism is dominant in providing the strength increase evident upon ageing in these Cu bearing steels. The linear addition method produces good agreement with the measured yield strengths in the unaged TMCP condition and since it is also very widely used to estimate the strengthening contributions of the operative mechanisms in TMCP steels, it merits further analysis to gauge the relative contributions of the mechanisms relevant to the fully aged steels.

Consideration of Table 4.9, indicates that precipitation by incoherent ε Cu accounts for approximately 39% of the strengthening increment observed on ageing whilst the formation of Cu rich zones accounts for approximately 55% of the total strength increment observed on ageing. The contribution from the equilibrium level of solid solution strengthening by Cu accounts for < 6% of the strength increment (see Appendix 6.7). These inferences are consistent with the claim by Fujii et al. (77) who state: "The greatest contribution comes from the difference in the crystal structures between the precipitate and the matrix,....". Furthermore, work by Hornbogen (90) indicates that hardening is produced by a combination of mechanisms involving both the clustering process and precipitation of ε Cu. However, it should be recognised that the increment in strength observed on ageing of these Cu bearing steels, accounts for less than 12% of the aged strength of the steel. The greatest contribution to the steel strength is due to grain refinement, dislocation substructure and solid solution strengthening from Mn, Si and N following TMCP.
There are NO pp. 142-143 in original document
4.4 Tensile Properties

Having characterised the precipitation hardening response for various combinations of time and temperature by Vickers hardness testing, and correlated these results to the tensile strength measurements at a single temperature, a second trial was carried out which was designed to quantify the effects of the different ageing temperatures on the tensile properties of the experimental steels and to assess the effect of varying Cu contents on the precipitation hardening response. For this trial both the Series 1 and Series 2 steels were used to obtain a wide range of Cu contents. The results of these trials are shown in Table 3.6 and Figures 3.18 and 3.19.

All steels with the exception of G showed an increase in strength after ageing. For comparative purposes let us consider first those steels aged at 550 °C for 1 hour. The yield stress of Series 1 steels increased by between 42 and 79 MPa (Table 3.5) and for the Series 2 steels, the increase was between 83 and 112 MPa (Table 3.6). With the exception of the low Nb steel F, the tensile strengths of the Series 1 and 2 steels were generally less sensitive than the yield stress to the ageing treatment. Increases in tensile strengths ranged between 14 and 88 MPa. Elongation decreased in all cases, with the exception of the low Cu steel G, which showed no appreciable change in elongation nor any strengthening effect on ageing.

The increment in the yield stress would be expected to be greater than the increment in tensile strength for the following reason. The process of age hardening of an alloy up to maximum strength usually produces deformable particles which can be cut by dislocations. In the case of these steels, the majority of these particles or obstructions to dislocation movement would be Cu precipitates and Cu clusters. Strengthening would be produced mainly by the work done by the dislocations in either cutting through the particles, as proposed by Russell and Brown (81), or via the bypass mechanism, as claimed by Fujii et al. (77). In either case, as mentioned in Section 1.7.1.5, this alloy system does not show the pronounced tangling and looping of dislocations characteristic of other alloy systems (77, 84, 86). Some debris has been observed, which may be the result of the slip systems in the particle and the matrix not always coinciding (78), or as a result of the bypass mechanism observed by Fujii et al. (77). These dislocations accumulate as strain proceeds and can eventually give rise to a small amount of work
DISCUSSION

hardening. Furthermore, unlike some solutes which inhibit cross slip (128-131) by lowering the stacking fault energy (131), it has been reported that Ni and Cu tend to increase the stacking fault energy (132).

Therefore, if deformable particles of Cu and Cu clusters were the only substantial obstacles to dislocation motion present and the work hardening rate is not significantly increased, then the tensile strength would not be expected to be as strongly affected as the yield stress by the alloy modifications and the thermomechanical treatment.

It must be kept in mind, however, that non-deformable (and incoherent) precipitates of Nb and Ti carbonitride were also present in the matrix, as is evident from Figures 3.2 and 3.9. The effect of these non-deformable particles in producing high work hardening rates has been recognised for some time (78, 133). The increase in work hardening rate and therefore tensile strength produced by dislocation looping around these particles (87) should increase the tensile strength over that which would be expected from solid solution hardening alone.

The strength of the Series 2 steels in the TMCP condition was substantially greater than that of their Series 1 counterparts (Table 3.5 and 3.6). This result may be partly attributed to the higher C level and possibly a solid solution hardening effect due to the slightly higher Cu contents of the Series 2 steels. It does not appear to be attributable to the ferrite grain size as the Series 2 steels had slightly larger grain sizes than those of the Series 1 steels (Table 3.1a and b) (Ave Grain Size (µm): Series 1 = 4.57 to 5.99 and Series 2 = 6.2 to 7.4).

The magnitude of the increase in strength after ageing of the Series 2 steels in the TMCP and aged condition is slightly greater than that observed in the Series 1 steels and is probably due to the strengthening effect of Cu. Steel A2', in particular, showed a marked increase in strength after ageing at 550 °C for 1 hour, with the yield strength increasing by up to 112 MPa and the tensile strength by 51 MPa. This increase may be attributed to the high Cu content (1.7 wt % Cu) of this steel compared with the other experimental steels (0.9 to 1.15 wt % Cu).
The effect of various ageing temperatures on the precipitation hardening response of the Series 2 steels is summarised in Table 3.6 and Figure 3.18. Steel A2 showed the largest increase in strength after ageing, followed by A2 and E2, while B2 showed the smallest strength increment. The strength increases observed were proportional to the Cu content of each steel type.

The change in strength with increasing Cu content is shown in Figure 3.19 and is described by the equations,

\[
\Delta \sigma_{\text{yield}} (\text{MPa}) = 25.7e^{1.2(\text{wt}\%\text{Cu})} \tag{4.16}
\]

\[
\Delta \sigma_{\text{tensile}} (\text{MPa}) = 22.1e^{2.78(\text{wt}\%\text{Cu})} \tag{4.17}
\]

It is evident from this figure that strength increases exponentially with wt % Cu over the range of Cu contents studied. The results indicate that for steels with less than about 1.6 wt % Cu, the increase in yield strength after ageing is substantially larger than the increase in tensile strength. At about 1.6 wt % Cu the increment in strength after ageing is similar for both the yield and tensile stresses, whilst at 1.7 wt% Cu the increment in tensile strength is greater than that in yield.

A possible explanation for this observation is as follows. The limited solubility of Cu in ferrite means that the precipitation of Cu is difficult to suppress (see Figure 3.2). As the Cu content of the steel increases, the proportion of Cu which precipitates would also increase. Whilst no great tangling and looping of dislocations would occur in this alloy system (77, 84, 86), some debris is left after the precipitate is cut by dislocations or as a result of the bypass process. As the amount of Cu increases and the number of precipitates subsequently increases, it is not unreasonable to assume that the amount of debris from particle cutting and looping would also increase. This debris would eventually accumulate and give rise to some work hardening. If the proportion of Cu precipitated is sufficiently large, then the increase in the work hardening rate may be such that it produces a tensile strength increase equal to or greater than the increase in the yield stress produced by the fine deformable \( \varepsilon \) Cu particles precipitated in the ferrite and Cu clusters formed during ageing. It should be noted, however, that as only one steel with a Cu content > 1.1% was examined, this may well be a spurious result and not indicative of a trend. More testing of higher Cu
steels (>1.1%) would have to be carried out to effectively determine if this result is a true indication of trend.

Ageing for 1 hour produced maximum yield strengths at a precipitation hardening temperature of 500 °C for the BHP HSLA 80 (steel E2) and at 550 °C for the other commercial steels. This result corresponds well with the hardness results given in Figure 3.17. Yield strengths remained relatively stable as the ageing temperature increased above 500 °C, with small changes ranging from 0 to 27 MPa.
4.5 Summary

4.5.1 Effect of Cooling Rate From Normalising Temperature

In order to examine the retention of Cu in solution directly after TMCP and hence the precipitation of Cu during the subsequent ageing process, the effect of cooling rate from the normalising temperature was examined.

Generally, as the cooling rate from the normalising temperature was increased, the proportion of the austenite which transforms to bainite and martensite increased and the average precipitate particle diameter in the aged condition decreased (Table 4.10). In addition, the hardness rose due to an increase in the dislocation density. However, this increment was minor and of the order of 4 Vickers hardness points for the fastest cooling rate investigated. The amount of Cu which precipitated as fine ε Cu after ageing also increased as the cooling rate increased (Table 4.10).

The Charpy impact energy at any given temperature was found to decrease with increasing cooling rate, eg for the BHP experimental steel E2 the absorbed energy decreased with increasing cooling rate according to the relationship

\[
\text{Charpy Impact Energy at -85 °C (J) = -15.105 ln (Cooling Rate (°C/s)) +107.27}
\]

The Charpy impact transition temperature also increased, eg for the BHP experimental steel E2 impact transition temperature increased with increasing cooling rate according to the relationship

\[
50\% \text{ FATT (°C) = 8.5029 ln (Cooling Rate (°C/s)) - 49.78}
\]
TABLE 4.10  Summary of the effect of cooling rate from the normalising temperature on the size and distribution of copper rich particles, the Vickers hardness and the impact properties of the experimental steels.

<table>
<thead>
<tr>
<th>Cooling Rate (°C/s)</th>
<th>Normalised at 900 °C cooled and UNAGED</th>
<th>Normalised at 900 °C cooled and AGED at 550°C for 1 hour</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.2</td>
<td>4</td>
</tr>
<tr>
<td>Average Particle Diameter (nm)</td>
<td>14.2</td>
<td>6.6</td>
</tr>
<tr>
<td>Number of Fine ε Cu Particles ≤ 10nm Diameter per unit area</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Number of particles &gt;10nm Diameter per unit area</td>
<td>248</td>
<td>67</td>
</tr>
<tr>
<td>Average ΔHV on ageing Series 1 (not including G)</td>
<td>28</td>
<td>43</td>
</tr>
<tr>
<td>Series 2</td>
<td>34</td>
<td>36</td>
</tr>
<tr>
<td>Average Absorbed Energy at -85 °C (J)</td>
<td>134</td>
<td>66</td>
</tr>
<tr>
<td>Average 50%FATT (°C)</td>
<td>-92</td>
<td>-48</td>
</tr>
</tbody>
</table>

These results support the proposal that the amount of Cu retained in solution during cooling from the solution temperature is directly dependent on the rate of cooling. However, the results of the mechanical property and impact testing for the highest cooling rate examined (70 °C/s) indicate that little advantage to the overall mechanical property performance can be gained from the quenching and ageing of these steels, and that the optimum strength/impact benefit can be achieved through normal air cooling prior to ageing.

Approximate estimates of the magnitude of strengthening attributable to Cu in its various states in an unaged 1.0 % Cu bearing steel were derived from these results. The increment in hardness which may be attributable to the solid solution hardening effect of Cu in the unaged condition is between 8 and 14 HV, whilst the increment which may be ascribed to precipitation hardening is between 54 and 76 HV.
4.5.2 Effect of Time and Temperature on the Ageing Response of TMCP Steel.

In order for precipitation of Cu to occur upon ageing, diffusion of Cu through the ferrite is required and therefore the precipitation hardening response obtained from these Cu bearing steels is dependent upon time and temperature. The manner in which the process operator can influence the precipitation of Cu during the post TMCP ageing treatment was examined by looking at the effect of time and temperature on the mechanical properties. Time at temperature has a marked effect on hardness. For any given ageing temperature, peak hardness was reached after a given time with longer times resulting in softening. As expected the time to reach peak hardness through the precipitation of copper and the formation of Cu clusters became shorter as the ageing temperature was raised.

For ageing temperatures (T) between 500 and 650 °C the time to reach peak hardness (t) is described by the equation:

\[
\ln t(s) = 18,997 - \frac{1}{T(K)} - 14.071
\]

The maximum hardness increment (26HV) was obtained after ageing at 550 °C for 120 minutes and at 600 °C for 60 minutes, indicating that the fully aged hardness is relatively insensitive to ageing temperature. In a commercial situation where furnace time and energy consumption are costly variables, a preferable option might be 60 minutes at 550 °C, as half the furnace residence time taken to achieve peak strength, produces over 96% of the maximum achievable hardness.

Increasing the temperature and reducing the time is a viable option for commercial processing but it should not be taken to extremes. For example, whilst 20 minutes at 650 °C produces 69% of the maximum achievable hardening increment, it would be difficult in a commercial situation to achieve 650 °C evenly throughout the plate/pattern in the short residence time. Obtaining an even temperature profile throughout the plate is a critical consideration in order to minimise mechanical property variation.
The experimental results indicate that softening after peak hardness occurs very slowly, producing a plateau effect rather than a sharp drop in strength with time. Whilst claims have been made in the literature that a double peak occurs during the ageing of commercial versions of BHP's HSLA80 type steel and that this phenomenon is attributable to Nb precipitation, no evidence to support this claim was found in this current work. Moreover, the results of comparative experimentation and TEM analysis provide evidence which indicates that Nb does not contribute to a secondary hardening peak and that the strength levels observed are entirely attributable to precipitation hardening by Cu, rather than to any effect of the Nb.

4.5.3 Theoretical Analysis of Experimental Results

Strengthening in the experimental Cu bearing HSLA steels is attributable to a number of factors of varying magnitude and hence importance. A number of models were examined in order to determine theoretically which mechanism provided the most significant contribution to strength. If the assumptions made in the calculation of the volume fractions of Cu in each of its various forms are reasonable, then it can be said that, precipitation of incoherent \(\varepsilon\) Cu accounted for approximately 39% of the total strength increase observed upon ageing, whilst the formation of Cu rich zones or clusters gave the highest contribution to the strength accounting for up to 55% of the strength increment observed on ageing. The equilibrium level of solid solution strengthening by Cu accounted for less than 6% of the strength increment.

Whilst the proposal by Smith et al. (124) that the yield stress is determined by the most effective barrier to dislocation motion is appealing, when this principle is applied to the theoretical estimates produced by the models, then it would appear that

1. all of the models greatly underestimate the final yield strength, and
2. this proposal is not applicable in the case of the Cu bearing HSLA steels examined in this work.

However, in the absence of any accurate determination of the composition of fine coherent particles and Cu rich zones or clusters the accuracy of the Russell and Brown model (81) and other models cannot be
ascertained. Based on the observations of Goodman et al. (93), it may be assumed that the volume fractions of coherent ε Cu particles and Cu rich zones calculated from the experimental observations and the chemical compositions of the steels, underestimate the actual volume fractions. If the model of Russell and Brown (81) is applied to estimate the $f_{\text{Coherent}}^{\text{Cu+Cu}}$ clusters which would be required to produce the observed strength of the aged steel, it was determined that the volume fraction required to produce the observed strength was approximately 10 times greater than the volume fraction determined in this work. This implies that the ε Cu particles and Cu rich clusters present are metastable solid solutions of Cu and α Fe, which have an average Cu content of approximately 10%. Alternatively, the required volume fraction could be somewhat smaller if the shear modulus were higher than the value assumed.

It was found that when the Pythagorean addition rule was applied to the theoretical estimates of the individual contributions to yield strength of the aged steel, it greatly overestimated the experimental result (by between -136 and 184 MPa for the 1% Cu steels D, E1 and F). Linear addition, whilst closer to the experimental results, generally overestimated the experimental result by up to 103 MPa for the 1% Cu steels.

If the models are examined on their individual ability to estimate the contribution by a particular mechanism, it is found that the model of Fujii et al. (77) which is based on the Orowan model produces estimates closest to the experimental results for the 1% Cu steels. However, even in this case the model can underestimate the experimental result by up to 45 MPa.

A correlation between Vickers hardness and tensile properties for the Cu bearing experimental steels was established which gave;

for TMCP steels;

\[
\begin{align*}
\text{TS} &= 664 \ln (\text{HV}) - 2863 \\
\text{YS} &= 331 \ln (\text{HV}) - 1251.7
\end{align*}
\]
DISCUSSION

for steel aged at 550°C for 1 hour

\[ \text{TS} = 709.3 \ln (HV) - 3140 \]
\[ \text{YS} = 544.2 \ln (HV) - 2360 \]

with high correlation ratios (>92%).

4.5.4 Tensile Properties

Having characterised the precipitation hardening response for various combinations of time and
temperature by Vickers hardness testing and having correlated these results to the tensile strength
measurements at a single temperature, it was necessary to establish the effect of,

- the different ageing temperatures on the tensile properties of the experimental steels and
- varying Cu contents on the precipitation hardening response.

All steels with the exception of the low Cu steel G, showed an increase in strength on ageing, in accordance
with the results of the Vickers hardness testing carried out previously.

With the exception of the low Nb steel F, the tensile strengths of the Series 1 and 2 steels were generally
less sensitive than the yield stress to the ageing treatment. It is proposed that this difference in increment
upon ageing between yield and tensile strengths is due to the fact that the only substantial obstructions to
dislocation motion are deformable \( \varepsilon \) Cu particles and Cu rich zones. No significant tangling and looping of
dislocations have been found to occur in this alloy system (77, 85, 86), and thus the work hardening rate is
not greatly increased and therefore the tensile strength would not be as dramatically affected by the alloy
modifications and the thermomechanical treatment as the yield stress.

It was found that the magnitude of the increase in strength on ageing is proportional to the amount of Cu
contained in the steel and is described by the following equations.
\[
\Delta YS = 25.7e^{1.2(\text{wt}\% \text{Cu})} \\
\Delta TS = 2.21e^{78(\text{wt}\% \text{Cu})}
\]

There appears to be a relationship between the Cu content of a steel and the difference in incremental strength increase between yield and tensile. It was found that for steels with less than about 1.6\% Cu the increase in yield strengths after ageing is substantially larger than the increase in tensile strength whilst at approximately 1.6 wt\% Cu and above the increment in strength after ageing is similar in both yield and tensile. However, more testing of steels with > 1.1\% Cu is required to confirm this conclusion.

It is proposed that this increase in tensile increment at Cu >1.6 wt\% may be associated with an increase in the dislocation concentration and distribution and hence work hardening rate which in turn was related to an increase in the proportion of non deformable (incoherent) Cu particles associated with the increased Cu content.

This is an interesting and useful trend to understand from the perspective of commercial alloy design where steels are generally designed on the basis of achieving a minimum yield strength requirement rather than a tensile strength requirement. In designing a similar steel the relationship can be used to optimise the Cu microalloy level in order to achieve a certain design yield strength. Keeping in mind of course that there is a certain minimum level of Cu below which no strength increment is achieved (0.8\% according to Takahashi et al.(29)) and above which it is reported that further additions have little additional effect on strength (34).
5.0 CONCLUSIONS

The precipitation hardening response of a series of Cu bearing HSLA steels typical of the commercial grades represented by the ASTM specification A710 and the military specification MIL-S-16216 (also known as HSLA 80) was examined. This type of steel depends on the proper control of thermomechanical and thermal treatment to precipitate copper in the ferrite matrix, thus increasing the strength of the steel. During the commercial production of these steels there are two stages in their thermal history at which the process operator can influence the way in which Cu precipitates and hence the yield and tensile strength of these steels. The first of these stages is directly after TMCP during the cooling of the steel plate from the rolling temperature and the second stage is during the subsequent ageing treatment. The first stage was examined in the laboratory by studying the effect of cooling rate, following a normalising treatment, on the mechanical properties and the second was examined using a series of isothermal ageing treatments. The following conclusions were drawn regarding the precipitation hardening response of the Cu bearing steels investigated.

5.1. Effect of Cooling Rate From Normalising Temperature

Generally, as the cooling rate from the normalising temperature was increased:

- the proportion of the austenite which transforms to bainite and martensite increased.
- the volume fraction of small particle sizes increased in the aged condition.
- the average precipitate particle diameter in the aged condition decreased
- the hardness increment due to an increase in the dislocation density rose. However, this increment was minor and of the order of 4 Vickers hardness points for the fastest cooling rate investigated.
- the amount of Cu which precipitates as fine Cu after ageing increased.
- the increment in hardness increased.
- the Charpy impact energy decreased.
- the Charpy impact transition temperature increased.
The results indicate that:

- Ageing after TMCP and slow cooling after normalising, resulted in a step shift in the particle size distribution curve to lower sizes.

- The amount of Cu retained in solution during cooling from the solution temperature is directly dependent on the rate of cooling.

- Little advantage to the overall mechanical property performance can be gained from the quenching and ageing of these steels, as any increase in hardness obtained is accompanied by a concomitant decrease in impact toughness properties. Potentially the best strength/impact benefit can be achieved through normal air cooling.

- The increment in hardness which may be attributed to the solid solution hardening effect of Cu in the unaged condition is between 8 and 14 HV.

- The increment in hardness which may be ascribed to precipitation hardening in the normalised and aged steel is between 54 and 76 HV. This increment on ageing, is greater than that which occurs in the TMCP and aged condition, due to the greater population of fine particles (<5nm diameter) present in the normalised and aged steel as a result of the faster cooling rate from the normalising temperature.

5.2 Effect of Time and Temperature on the Ageing Response of TMCP Steel.

- For any given ageing temperature, peak hardness was reached after a given time with longer times resulting in softening. As expected, the time to reach peak hardness through the precipitation of copper and the formation of Cu clusters became shorter as the ageing temperature was raised. For ageing temperatures (T) between 500 and 650 °C the time to reach peak hardness (t) is described by the equation:

\[
\ln t(s) = 18,997 \frac{1}{T(K)} - 14.071
\]
• The activation energy associated with the age hardening process was measured to be 157,941 J/mol, which is lower than the literature value for bulk diffusion 244,382 J/mol, but is consistent with a strong contribution by grain boundary and dislocation pipeline diffusion.

• The maximum hardness increment was obtained after ageing at 550 °C for 120 minutes and 600 °C for 60 minutes (26HV). The fact that the same peak strength was achieved for two different ageing temperatures indicates that the fully aged hardness of these steels is relatively insensitive to ageing temperature.

• The experimental results indicate that softening after peak hardness occurs very slowly, producing a plateau effect rather than a sharp drop in strength with time. Therefore the incoherent Cu particles remain effective in limiting dislocation motion either by shear or bowing.

• The results of comparative experimentation and TEM analysis provide evidence which indicates that Nb does not contribute a secondary hardening peak and that the strength levels observed are attributable to precipitation hardening by Cu, rather than to Nb.

5.3 Theoretical Analysis of Experimental Results

5.3.1 Application of Models to Experimental Results

A number of models were examined in order to determine theoretically which mechanism provided the most significant contribution to strength. If it is assumed that the most effective barrier to dislocation motion will ultimately determine the yield stress then it was found that:

• when using the experimentally determined and calculated volume fractions of the various kinds of precipitates, all of the models greatly underestimate the final yield strength of the Cu bearing HSLA steels examined in this work.
CONCLUSION

- the model of Fujii et al. (77) which is based on the Orowan model produces estimates closest to the experimental results. However, even in this case the experimental result for the 1% Cu steels is generally underestimated by up to 45 MPa.

A shortcoming of the analysis was the assumption that the precipitates which were presumed to constitute the most effective barriers to dislocation motion were nearly pure copper as there is evidence in the literature that this is in fact not the case (93). If the model of Russell and Brown (81) is applied to determine the volume fraction of precipitates and clusters which would be required to achieve the actual experimental strength and this value is compared to the volume fraction determined from experimental observation and chemical compositions of the experimental steels, it was determined that:

- the coherent ε Cu particles and the Cu rich clusters most likely to be an Fe rich metastable solid solution and therefore their volume fraction is likely to be underestimated.
- the average Cu content of the particles and clusters was approximately 10%.
- alternatively if the copper content is assumed to be approximately 50% as proposed by Goodman et al. (93), the shear modulus of the coherent ε Cu particles and the Cu rich clusters would need to be approximately 163 GPa in order to account for the observed yield strength.

If the observed strength is considered to be associated with the contributions of a series of discrete strengthening methods, the Pythagorean addition rule and the linear addition rule were used to predict the observed strengths. It was found that:

- the Pythagorean addition rule when applied to the theoretical estimates of the individual contributions to yield strength of the aged steel, overestimated the experimental results by between 136 and 184 MPa for the 1% Cu steels D, E1 and F.
- the linear addition rule overestimated the experimental results (by between 66 and 103 MPa for the 1% Cu steels D, E1 and F and 82 MPa for the low Cu steel G).

Based on the proportions of strengthening attributed to each mechanism, as estimated from linear addition of the strengthening increments, it was determined that;
CONCLUSION

- precipitation strengthening by incoherent \( \varepsilon \) Cu accounts for approximately 39% of the total strength increase observed upon ageing.
- the formation of Cu rich clusters provided the largest contribution to strength, accounting for up to 55% of the strength increment observed on ageing.
- the equilibrium level of solid solution strengthening by Cu accounted for less than 6% of the strength increment.
- the increment in strength on ageing was only a small proportion of the base strength due to grain refinement, dislocation structure and solid solution strengthening following TMCP (6 to 12%).

5.3.2 Correlation Between Vickers Hardness and Tensile Properties

Correlations between Vickers hardness and tensile properties for the Cu bearing experimental steels were established which gave;

- for the TMCP condition;
  
  \[
  \begin{align*}
  TS (\text{MPa}) &= 664 \ln (HV) - 2863 \\
  YS (\text{MPa}) &= 331 \ln (HV) - 1251.7 
  \end{align*}
  \]

- for the TMCP and aged condition (550\(^{\circ}\)C for 1 hour)
  
  \[
  \begin{align*}
  TS (\text{MPa}) &= 709.3 \ln (HV) - 3140 \\
  YS (\text{MPa}) &= 544.2 \ln (HV) - 2360 
  \end{align*}
  \]

The correlation ratios were higher than 92%.
5.4 Tensile Properties

- All steels, with the exception of the low Cu steel G, showed an increase in strength on ageing, confirming that a copper level of > 0.49% is necessary to strengthen hot rolled copper bearing steels through precipitation hardening.
- With the exception of the low Nb steel F, the tensile strengths of the Series 1 and 2 steels were generally less sensitive than the yield stress to the ageing treatment.
- The magnitude of the increase in strength on ageing is proportional to the amount of Cu contained in the steel and is described by the following equations.

\[ \Delta YS = 25.7e^{1.2(\text{wt}\%\text{Cu})} \]
\[ \Delta TS = 2.21e^{2.78(\text{wt}\%\text{Cu})} \]

- For steels with less than about 1.6% Cu the increase in yield strength after ageing was substantially larger than the increase in tensile strength, whilst at approximately 1.6 wt% Cu and above the increments in yield and tensile strengths were similar. It is proposed that the greater tensile increment for Cu ≥1.6 wt% is associated with an increase in the dislocation concentration and distribution and hence work hardening rate which arises from the increase in the proportion of non deformable (incoherent) Cu particles resulting from the increased Cu content.
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APPENDIX 1  ELECTRON METALLOGRAPHIC TECHNIQUES

1.1  Camera Constant Calibration

![Ring pattern from gold standard used to calculate Camera Constant $\lambda L$.](image)

**FIGURE A1.1.** Ring pattern from gold standard used to calculate Camera Constant $\lambda L$.

**TABLE A1.1** Calculation of the Camera Constant $\lambda L$ from the diffraction ring pattern produced by a gold standard.

<table>
<thead>
<tr>
<th>RING NUMBER</th>
<th>D HORIZONTAL (mm)</th>
<th>D VERTICAL (mm)</th>
<th>AVERAGE RADIUS R (mm)</th>
<th>INDICES (hkl)</th>
<th>d SPACING (A)</th>
<th>$\lambda L$ $\lambda L = Rd$ (mm A)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>15.42</td>
<td>15.69</td>
<td>7.78</td>
<td>111</td>
<td>2.355</td>
<td>18.322</td>
</tr>
<tr>
<td>2</td>
<td>17.66</td>
<td>18.08</td>
<td>8.94</td>
<td>200</td>
<td>2.039</td>
<td>18.229</td>
</tr>
<tr>
<td>3</td>
<td>24.90</td>
<td>25.37</td>
<td>12.57</td>
<td>220</td>
<td>1.442</td>
<td>18.126</td>
</tr>
<tr>
<td>4</td>
<td>29.25</td>
<td>29.66</td>
<td>14.73</td>
<td>222</td>
<td>1.230</td>
<td>18.118</td>
</tr>
<tr>
<td>5</td>
<td>30.37</td>
<td>30.97</td>
<td>15.34</td>
<td>331</td>
<td>1.177</td>
<td>18.055</td>
</tr>
<tr>
<td>6</td>
<td>39.40</td>
<td>39.90</td>
<td>19.83</td>
<td></td>
<td>0.9358</td>
<td>18.323</td>
</tr>
</tbody>
</table>

AVERAGE $\lambda L$ 18.196
1.2 Indexing of a Typical Electron Diffraction Pattern

FIGURE A1.2 Diffraction pattern produced from fine spherical particle in steel E2 in the TMCP and aged condition.

FIGURE A1.3. Schematic representation of diffraction pattern reproduced in Figure A1.2 from fine spherical particle in steel E2 in the TMCP and aged condition.
### APPENDICES

**TABLE A1.2** Indexing the pattern in Figures A1.2 and A1.3, using $\lambda L = 13.98 \text{ mm}^2$.

<table>
<thead>
<tr>
<th>SPOT ID</th>
<th>DIAMETER (mm)</th>
<th>$r = D/2 (\text{mm})$</th>
<th>$d = \lambda L/r$</th>
<th>INDEX Tentative</th>
<th>CHARACTERISTIC UNIT CELL SIZE $a_0 = \sqrt[3]{(h^2+k^2+l^2)}$</th>
<th>ID. Tentative</th>
<th>$d$ for Tentative ID</th>
<th>$a$ for Tentative ID</th>
<th>RECALC $\lambda L \lambda L = rd$</th>
</tr>
</thead>
<tbody>
<tr>
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<td>$\alpha$ Fe</td>
<td>2.03</td>
<td>2.861</td>
<td>13.99</td>
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</table>

*Zone Axis <110>$\alpha$Fe*

|  |  |  |  |  |  |  |  |  |  |
|---|---|---|---|---|---|---|---|---|
| D | 22 | 11 | 1.271 | 022 | 3.595 | fcc Cu | 1.278 | 3.615 | - |
| E | 15.5 | 7.75 | 1.804 | 002 | 3.6 | fcc Cu | 1.808 | 3.615 | - |

*Zone Axis <100>fcc Cu*

**CHECK:**

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<th>ACTUAL</th>
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1.3 Foil Thickness - As Determined by the Contamination Spot Method.

Examples of contamination spots used to calculate the foil thickness are shown in Figures A1.4 a through to e. Contamination spots were produced at various distances radially from the perforation in the foil, this enabled the thickness of the foil profile to be determined. The resulting average foil thicknesses obtained from these measurements are summarised in Table A1.3.

FIGURE A1.4 Contamination spots used to calculate the foil thickness for Table A1.3.
TABLE A1.3  Contamination spot foil thickness determination results (in foils of E2).

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<tr>
<th>Thermal History</th>
<th>Average Foil thickness (nm)</th>
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<tr>
<td></td>
<td>( \bar{t} = 158.99 )</td>
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<td>TMCP 1.4 °C/s</td>
<td></td>
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<td></td>
</tr>
<tr>
<td>SLOW COOL .2 °C/s</td>
<td>( \bar{t} = 241.77 )</td>
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<td>UNAGED</td>
<td></td>
</tr>
<tr>
<td>AIR COOL 4 °C/s</td>
<td>( \bar{t} = 164.26 )</td>
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<tr>
<td>UNAGED</td>
<td></td>
</tr>
<tr>
<td>OIL QUENCH 70 °C/s</td>
<td>( \bar{t} = 179.79 )</td>
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<tr>
<td>UNAGED</td>
<td></td>
</tr>
<tr>
<td>TMCP 1.4 °C/s &amp; AGED</td>
<td>( \bar{t} = 160.43 )</td>
</tr>
<tr>
<td>SLOW COOL .2 °C/s &amp; AGED</td>
<td>( \bar{t} = 226.57 )</td>
</tr>
<tr>
<td>AIR COOL 4 °C/s &amp; AGED</td>
<td>( \bar{t} = 186.73 )</td>
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<tr>
<td>OIL QUENCH 70 °C/s &amp; AGED</td>
<td>( \bar{t} = 200.19 )</td>
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APPENDIX 2  DETERMINATION OF PRECIPITATE POPULATION SIZE DISTRIBUTION

2.1 Calculation of Volume Fraction of Particles in TEM Foils

2.1.1 Definitions

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<th>Variable</th>
<th>Definition</th>
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<tr>
<td>$F_s$</td>
<td>Standard Field Size = 1μm$^2$</td>
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<tr>
<td>$F_a$ (nm$^2$)</td>
<td>Test field area</td>
</tr>
<tr>
<td>$P$</td>
<td>Number of particles in test area</td>
</tr>
<tr>
<td>$P_a$</td>
<td>Number of particles per unit area ie. $P_a = P \times \frac{F_s}{F_a}$</td>
</tr>
<tr>
<td>$P_i$</td>
<td>Number of particles of $i^{th}$ size $= \sum_j P$ $j = 1$ to $N$</td>
</tr>
<tr>
<td>$P^T$</td>
<td>Total number of particles of all sizes examined $= \sum_j P_i$ $i = i$, $j = 1$ to $N$</td>
</tr>
<tr>
<td>$D_a$ (nm)</td>
<td>Particle diameter</td>
</tr>
<tr>
<td>$N$</td>
<td>Number of applications of test area</td>
</tr>
<tr>
<td>$F_a^T$</td>
<td>Total test field area ie $F_a^T = \sum_j F_s$ where $j = 1$ to $N$</td>
</tr>
<tr>
<td>$A$ (nm$^2$)</td>
<td>The area of a spherical particle as it appears through the eyepiece $A = \pi r^2$ $= \pi \left( \frac{D}{2} \right)^2$</td>
</tr>
<tr>
<td>$A_i^T$</td>
<td>The total area covered by particles of $i^{th}$ size $= \sum_{i,j} A_i P_j$ $i = i$, $j = 1$ to $N$</td>
</tr>
<tr>
<td>$A^T$</td>
<td>The total area of all the particle sizes examined</td>
</tr>
<tr>
<td>$A^r$</td>
<td>Relative area $= \frac{A^T}{F_a^T}$</td>
</tr>
<tr>
<td>$f$</td>
<td>Volume fraction $= -2 \ln(1 - A) \left[ \frac{D}{D + 3f} \right]$</td>
</tr>
</tbody>
</table>
2.2 Example of Calculations for Volume Fraction - Produced for Steel E2 in the TMCP Condition.

i. for particle diameter = 5nm
   \[ A = \pi r^2 = \pi (2.5)^2 = 19.63 \text{ nm}^2 \]

ii. The total area of ith sized particle with area \( A_i \)
   \[ A_i^T = \sum_{i,j} A_i P_j \]
   \[ = A_i P_i^T \]
   For \( i = 1 \) and \( D = 5 \text{nm} \) and \( P_i^T = 19 \) from Table A2.2 and Figure 3.12a
   \[ A_i^T = 19.63 \times 19 \]
   \[ = 372.97 \text{nm}^2 \]

repeating this procedure for all precipitate sizes produces,

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<th>Size Class ( i )</th>
<th>Precipitate Diameter (nm)</th>
<th>( A_i^T )</th>
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<td>1</td>
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<td>2199.12</td>
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<tr>
<td>5</td>
<td>25</td>
<td>981.74</td>
</tr>
</tbody>
</table>

\[ \sum_i A_i^T = A_T \]
where \( i = 1 \) to 5

iii. Relative Area of particles is
   \[ A^R = \frac{A^T}{F_a^T} \]
   substitute \( F_a^T = 1 \mu m^2 \) (ie 1,000,000 nm\(^2\)) from Table A2.2
   \[ = \frac{33,830.23}{1,000,000} \]
   \[ = .033830 \]

iv. Substituting into Equation 2.3 using
   \( D = \) Average precipitate diameter = 13.51 from Table 3.3 and
   \( t = \) Foil thickness = 179.87 from Table 3.2,
gives the volume fraction of particles which is
   \[ f = \left[-2\ln\left(1 - A^R\right)\right] \frac{D}{(D + t)} \]
   \[ = \left[-2\ln(1-.033830)\right][13.51/(13.51 + 3 \times 159)] \]
   \[ = 1.896 \times 10^{-3} \]
This procedure was carried out for steel E2 in each condition and the results are summarised in Table A2.2.

**TABLE A2.2** Calculations of volume fraction produced for steel E2.

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<th>A_i^T (nm^2)</th>
<th>A_i^T (nm^2)</th>
<th>Fa^T (nm^2)</th>
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TABLE A2.2 Continued  Calculations of volume fraction produced for steel E2.

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<th>THERMAL HISTORY</th>
<th>D (nm)</th>
<th>P&lt;sup&gt;T&lt;/sup&gt;</th>
<th>A&lt;sub&gt;i&lt;/sub&gt; (nm&lt;sup&gt;2&lt;/sup&gt;)</th>
<th>A&lt;sub&gt;i&lt;/sub&gt;&lt;sup&gt;T&lt;/sup&gt; (nm&lt;sup&gt;2&lt;/sup&gt;)</th>
<th>Fa&lt;sup&gt;T&lt;/sup&gt; (nm&lt;sup&gt;2&lt;/sup&gt;)</th>
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TABLE A2.3  Volume fractions calculated for Series 1 experimental steels from random field observations (Sections 2.6.2.4 and 3.1.4).

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</tbody>
</table>
APPENDICES

APPENDIX 3  PRECIPITATION HARDENING RESPONSE

3.1 Cooling Curves From 900 °C.

FIGURE A3.1 Cooling Curve for static oil quench from 900 °C to 300 °C (Cooling rate from 800 to 500 °C = 70 °C/s).

FIGURE A3.2 Cooling Curve for static furnace cooling from 900 °C to 300 °C (Cooling rate from 800 to 500 °C = 0.2 °C/s).
FIGURE A3.3  Cooling Curve for air cool from 900 °C to 300 °C (Cooling rate from 800 to 500 °C = 4 °C/s).
### TABLE A3.1 The effect of ageing temperature on the precipitation hardening response of Cu bearing experimental steels from Series 1.

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<th>TIME (min)</th>
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</table>

The table above shows the number of hours worked for different hours (120, 180, 100) by different individuals (D, E, F, G) and the corresponding values for a particular measure (2.93, 0.90, 2.63).
4.1 Charpy Impact Testing

4.1.1 Standard Testpiece Machining and Testing Details

Charpy test pieces were machined according to AS1544.2-1989 to a standard 10mm x 10mm x 55mm test piece (Figure A4.1) and tested according to AS1544.2-1989 standard practices and procedures at various temperatures to determine the transition curve.

Regression analysis was performed on the Charpy testing results for each steel type and lines of best fit were calculated for each cooling rate. The results are summarised in Tables A4.1 and A4.2.
**APPENDICES**

**TABLE A4.1** Regression equations for the charpy impact energy curves produced for Series 2 experimental steels A2’, A2, B2 and E2 in the normalised and aged condition (Figure 3.15).

<table>
<thead>
<tr>
<th>STEEL</th>
<th>COOLING RATE (°C/s)</th>
<th>EQUATION FOR LINE OF BEST FIT FOR ABSORBED ENERGY (J)</th>
<th>R²</th>
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<tbody>
<tr>
<td>A2’</td>
<td>TMCP</td>
<td>E = 0.0002(T)^3 - 0.0367(T)^2 + 0.1204T + 222.11</td>
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<tr>
<td></td>
<td>0.2</td>
<td>E = 0.0006(T)^3 + 0.0562(T)^2 + 1.8128T + 289.33</td>
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<td>4</td>
<td>E = 6E-05(T)^3 + 0.005(T)^2 + 1.618T + 190.35</td>
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<td>E = -9E-05(T)^3 - 0.007(T)^2 + 1.6945T + 187.71</td>
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<tr>
<td>A2</td>
<td>TMCP</td>
<td>E = 0.0001(T)^3 + 0.0061(T)^2 + 0.978T + 187.19</td>
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<tr>
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<td>E = 6E-05(T)^3 - 0.0009(T)^2 + 1.0153T + 227.76</td>
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<td>E = 0.0003(T)^3 - 0.0288(T)^2 + 0.8843T + 194.87</td>
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</tr>
<tr>
<td>B2</td>
<td>TMCP</td>
<td>E = -9E-06(T)^3 + 0.021(T)^2 + 1.1912T + 96.414</td>
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<td>E = -0.0006(T)^3 - 0.0941(T)^2 - 2.3284T + 253.13</td>
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<td>E = 0.0003(T)^3 + 0.056(T)^2 + 3.5721T + 191.91</td>
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<td>E = -0.0002(T)^3 - 0.0101(T)^2 + 1.5161T + 114.74</td>
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<td>E2</td>
<td>TMCP</td>
<td>E = -0.0001(T)^3 - 0.0131(T)^2 + 0.5085T + 141.75</td>
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<td>0.2</td>
<td>E = -0.0139(T)^2 + 1.1578T + 192.61</td>
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<td>4</td>
<td>E = 0.0036(T)^3 + 1.453T + 142.87</td>
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<td>70</td>
<td>E = 0.0045(T)^3 + 1.5218T + 165.89</td>
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**TABLE A4.1** Regression equations for the Charpy impact fibrosity curves produced for Series 2 experimental steels A2’, A2, B2 and E2 in the normalised and aged condition (Figure 3.16).

<table>
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<tr>
<th>STEEL</th>
<th>COOLING RATE (°C/s)</th>
<th>EQUATION FOR LINE OF BEST FIT FOR FIBROSLTY (%) FOR THE TEMPERATURE RANGE 20 °C TO -100 °C</th>
<th>R²</th>
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<tbody>
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<td>A2’</td>
<td>TMCP</td>
<td>F = 0.0002(T)^3 + 0.0073(T)^2 + 0.0317T + 99.149</td>
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<td>0.2</td>
<td>F = 0.0196(T)^2 -1.3201T + 81.297</td>
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<td>4</td>
<td>F = 7E-05(T)^3 + 0.0074(T)^2 + 1.0567T + 91.475</td>
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<tr>
<td></td>
<td>70</td>
<td>F = 8E-06(T)^3 + 0.0562(T)^2 + 1.1172T + 77.625</td>
<td>0.9328</td>
</tr>
<tr>
<td>A2</td>
<td>TMCP</td>
<td>F = -0.0003(T)^3 - 0.048(T)^2 - 1.174T + 98.28</td>
<td>0.9609</td>
</tr>
<tr>
<td></td>
<td>0.2</td>
<td>F = -5E-05(T)^3 - 0.0136(T)^2 - 0.2199T + 99.958</td>
<td>0.9995</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>F = -1E-04(T)^3 - 0.0104(T)^2 + 0.6125T + 95.976</td>
<td>0.9928</td>
</tr>
<tr>
<td></td>
<td>70</td>
<td>F = -2E-05(T)^3 + 0.0017(T)^2 + 0.6916T + 42.131</td>
<td>0.9824</td>
</tr>
<tr>
<td>B2</td>
<td>TMCP</td>
<td>F = -0.0008(T)^3 - 0.0918(T)^2 + 1.8352T + 98.668</td>
<td>0.9687</td>
</tr>
<tr>
<td></td>
<td>0.2</td>
<td>F = -0.0003(T)^3 - 0.0504(T)^2 - 1.8279T + 81.877</td>
<td>0.9999</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>F = -0.0002(T)^3 - 0.0219(T)^2 + 0.5322T + 92.953</td>
<td>0.9692</td>
</tr>
<tr>
<td></td>
<td>70</td>
<td>F = -3E-05(T)^3 + 0.0022(T)^2 + 0.9758T + 59.171</td>
<td>0.9663</td>
</tr>
<tr>
<td>E2</td>
<td>TMCP</td>
<td>F = -0.0006(T)^3 - 0.0706(T)^2 - 1.3397T + 98.797</td>
<td>0.9386</td>
</tr>
<tr>
<td></td>
<td>0.2</td>
<td>F = -0.0096(T)^3 - 0.0734T + 108.65</td>
<td>0.9669</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>F = 0.0048(T)^2 + 0.9976T + 68.024</td>
<td>0.9876</td>
</tr>
<tr>
<td></td>
<td>70</td>
<td>F = 0.004(T)^3 + 1.01T + 79.775</td>
<td>0.9836</td>
</tr>
</tbody>
</table>
4.2 Tensile Testing

Tensiles were machined and tested according to AS1391 - 1974. The dimensions of the tensile test pieces produced are given in Figure A4.2.

FIGURE A4.2 Circular test piece dimensions according to AS1391 - 1974.
TABLE A4.1 Estimate of the testing errors for a circular cross section tensile test piece (see Figure A4.2) tested on the Instron 1342.

<table>
<thead>
<tr>
<th>Error</th>
<th>Source</th>
<th>Uncertainty in test piece diameter.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:</td>
<td></td>
<td>Micrometer reads to .01mm. Therefore assume +0.01mm error.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Diameter of test piece = 10.0mm</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Radius of test piece = 5.0mm</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Error % = (0.01mm/5mm) x 100</td>
</tr>
<tr>
<td></td>
<td></td>
<td>= +0.2%</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Error</th>
<th>Source</th>
<th>After recalibration, in the stress range 450 to 675 MPa which corresponds to the load range 35 to 55 kN.</th>
</tr>
</thead>
<tbody>
<tr>
<td>2:</td>
<td></td>
<td>Error % = 0 to -0.1%</td>
</tr>
</tbody>
</table>

Total Error: Example:

Sample A2
Yield Strength = 493 MPa
Error = -1.47 MPa to +0.99 MPa
Tensile Strength = 634 MPa
Error = -1.9 MPa to +1.27 MPa
APPENDICES

APPENDIX 5  TEMPERATURE DEPENDENCE OF DIFFUSION OF Cu IN FERRITE

TABLE A5.1  Time to peak hardness at various ageing temperatures

<table>
<thead>
<tr>
<th>TEMPERATURE T (°C)</th>
<th>TEMPERATURE T (°K)</th>
<th>TIME TO PEAK HARDNESS t (s)</th>
<th>ln t</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>D</td>
<td>E1</td>
</tr>
<tr>
<td>500</td>
<td>773</td>
<td>&gt;10,800</td>
<td>&gt;10,800</td>
</tr>
<tr>
<td>550</td>
<td>823</td>
<td>9,000</td>
<td>9,000</td>
</tr>
<tr>
<td>600</td>
<td>873</td>
<td>2,100</td>
<td>2,100</td>
</tr>
<tr>
<td>650</td>
<td>923</td>
<td>600</td>
<td>900</td>
</tr>
</tbody>
</table>

NOTE:  Data taken from Table A3.1 and Figure 3.17

If we consider an Arrhenius equation for the time to reach peak strengthening, ie

\[
\text{Rate} = Ae^{-\frac{Q}{RT}}
\]

\[
\frac{x}{t} = Ae^{-\frac{Q}{RT}}
\]

per unit distance ie x = 1

\[
\frac{1}{t} = Ae^{-\frac{Q}{RT}}
\]

\[
\ln t = \ln A - \frac{Q}{RT}
\]

and apply it to the experimental data, then a plot of 1/T vs ln t should result in a straight line (Figure 4.3), the slope of which can be used to determine Q, ie:

\[
\ln t = \frac{Q}{RT} \ln A
\]

Using D as an example determine the equation for the line.
\[
\text{slope} = \frac{Q}{R} = \frac{\ln t_2 - \ln t_1}{\ln t_2 - \ln t_1}
\]

i. Continued.

\[
\ln 600 - \ln 9,000 = \frac{1}{923} - \frac{1}{823}
\]

\[
= 20,571
\]

\[
\therefore \quad \ln t = \frac{1}{20,571 - \ln A} \quad \text{A5.3}
\]

Determine ln A

\[
\ln A = 20,571 \times \frac{1}{T} - \ln t
\]

A5.4

at \(T = 873 \, ^\circ\text{K}, \, t = 2100\, \text{s}\)

Substitution For \(T\) and \(t\) into equation A5.4

\[
\ln A = 20,571 \times (\frac{1}{873}) - \ln 2100
\]

= 15.91

\[
\therefore \quad \text{the equation for line A is,}
\]

\[
\ln t = \frac{1}{20,571 - 15.91} \quad \text{A5.5}
\]

If this procedure is repeated for all the data the average line of best fit for all the data points is

\[
\ln t = \frac{1}{18,997} - 14.071 \quad \text{A5.6}
\]

iii. Calculation of Q for diffusion of Cu in Ferrite.

from equation A5.6

\[
\frac{Q}{R} = 18,997
\]

\[
Q = 18,997 \times R
\]

\[
= 18,997 \times 8.314 \, \text{J/mol}
\]

\[
= 157,941 \, \text{J/mol}
\]

compare with Q for Cu\(^{64}\) (determined for temperatures 650 to 750 \(^\circ\text{C}\)) in \(\alpha\) Fe from literature (169)
\[ Q = 58.380 \text{ kcal/mol} \]
\[ = 58.380 \times 4186.05 \text{ J/mol} \]
\[ = 244,382 \text{ J/mol} \]

iv Calculate time to peak hardness at 500 °C

\[
\ln t = \frac{1}{T} - 14.071
\]
\[
= \frac{1}{773} - 14.071
\]
\[
t = e^{\frac{18.997}{773} - 14.071}
\]
\[= 36,485 \text{ seconds} \]
\[= 10.5 \text{ hours} \]
APPENDIX 6 APPLICATION OF MODELS TO EXPERIMENTAL DATA

6.1 Base Strength Due to Grain Size and Solid Solution Strengthening by Mn, Si & N

Estimate of the magnitude of the base strength using the model of Gladman and Dulieu (71). Using Steel E1 as an example.

i. Calculate the free Nitrogen ($N_{\text{free}}$)

Using chemical analysis data from Table 2.1

$$N_{\text{free}} = [N_{\text{total}} - 3.4197 \times \text{Ti} - 1.9263 \times \text{Al}]$$

$$< 0$$

∴ no free N available

ii. Substitute for variables in Gladman and Dulieu model (equation 1.2), using grain sizes (d) from Table 3.1b and chemical analysis data from Table 2.1.

$$\sigma_{\text{base}} \, (\text{MPa}) = K + 37(\%\text{Mn}) + 83(\%\text{Si}) + 2918(\% \, N_{\text{free}}) + 15.1d^{-1/2}$$

$$= 88 + 37(1.49) + 83(0.22) + 2918(0) + \frac{15.1}{\sqrt{4.57 \times 10^{-3}}}$$

$$= 385 \, \text{MPa}$$
6.2 Solid Solution Strengthening

6.2.1 Estimate of magnitude of solid solution strengthening using the models proposed by Wada et al. (123) and Baird and Preston (75).

Using steel E1 as an example.

i. Determine the proportion of Cu still in solution in the TMCP condition from point count analysis (Appendix 2).

\[
\frac{f_{\text{solute}}}{} = \frac{f_{\text{Cu}}}{} - \frac{f_{\text{Cu}}}{\text{precipitate}}
\]

A6.1

a. Determine \( f_{\text{Cu}} \) for 100g of steel

\[
f_{\text{Cu}} \text{ Total} = \frac{\text{wt}\%\text{Cu}}{\rho_{\text{Cu}}} + \frac{\text{wt}\%\alpha\text{Fe}}{\rho_{\alpha\text{Fe}}} = \frac{1.05}{8.933} + \frac{98.95}{7.85} = 9.24 \times 10^{-3}
\]

b. Determine what proportion of \( f_{\text{precipitate}} \) is actually made up of Cu precipitates

Assumption 1: The precipitates which are actually visible in the TMCP sample are a combination of NbTi(CN) and Cu. Therefore the actual volume fraction of precipitates \( f_{\text{precipitate}} \) is made up of;
Assumption 2: Upon cooling from above 1200 °C, the species which first precipitates will be TiN. If the Ti precipitate completely removes the free N available, Nb will then precipitate as a carbide. Depending on the existing conditions the NbC will form onto the existing TiN, thus producing a complex precipitate NbTi (CN). Even though a complex precipitate forms it is valid to use the density of NbCN and TiN in any calculation as long as the relative proportion of the microalloy in question is accounted for in the calculation.

How much TiN precipitates first? - Calculated using chemical analysis data from Table 2.1.

\[
\begin{align*}
\text{wt\% Ti} &= 0.013 \\
\text{wt\% N} &= 0.0022 \\
\text{wt\% Nb} &= 0.027 \\
\text{atomic weight Ti / atomic weight N} &= \frac{47.88}{14.01} \\
&= 3.4176 \\
\therefore \text{Ti which precipitates as TiN} &= 3.4176 \times N \\
&= 3.4176 \times (0.0022) \\
&= 7.5 \times 10^{-3} \\
\therefore \text{wt\% TiN} &= 7.5 \times 10^{-3} + 0.0022 \\
&= 9.7 \times 10^{-3}
\end{align*}
\]

\[
\begin{align*}
\text{atomic weight C / atomic weight Nb} &= \frac{12.011}{92.91}
\end{align*}
\]
APPENDICES

\[ \text{Carbon which precipitates as NbC} = 0.027 \times 0.129 = 3.048 \times 10^{-3} \]

\[ \therefore \text{wt\% NbC} = 0.027 + 3.048 \times 10^{-3} = 0.030 \]

Assume all of the Nb then precipitates on top of existing TiN as some form of NbC, then a reasonable estimate of the additional weight % is:

\[ \text{Total weight \% (NbTi (CN)) precipitate} = \text{wt\%TiN} + \text{wt\% NbC} = 9.7 \times 10^{-3} + 0.030 = 0.0397 \]

Determine \( f_{\text{NbC}} + f_{\text{TiN}} \) as follows;

Using \( \rho_{\text{TiN}} = 5.43 \frac{g}{cm^3}, \rho_{\text{NbC}} = 7.57 \frac{g}{cm^3}, \rho_{\alpha\text{Fe}} = 7.85 \frac{g}{cm^3} \) for 100g of steel

\[ f_{\text{ppt}} = \frac{\text{wt\%Pt} \rho_{\text{Pt}}}{\text{wt\%Pt} \rho_{\text{Pt}} + \text{wt\%} \alpha\text{Fe} \rho_{\alpha\text{Fe}}} \]

\[ f_{\text{NbCN}} = \frac{0.030}{7.57} \frac{1}{7.57 + 99.97} \frac{1}{7.85} = 3.16 \times 10^{-4} \]

\[ f_{\text{TiN}} = \frac{0.0097}{5.43} \frac{1}{5.43 + 99.99} \frac{1}{7.85} = 1.40 \times 10^{-4} \]
Substitute for \( f_{\text{NbC}} \), \( f_{\text{TVN}} \) and \( f_{\text{Precipitate}} \) (from Table 3.2 and Appendix A2.2) into equation A6.2

\[
\begin{align*}
\frac{f_{\text{Cu precipitate}}}{\text{TMCP}} &= \frac{f_{\text{Precipitate}}}{\text{TMCP}} - (f_{\text{NbC}} + f_{\text{TVN}}) \\
&= 0.00189 - (3.16 \times 10^{-4} + 1.4 \times 10^{-4}) \\
&= 1.44 \times 10^{-3}
\end{align*}
\]

ii. Determine the volume fraction of Cu responsible for solid solution strengthening in the TMCP condition.

Substitute for \( f_{\text{Cu TOTAL}} \) and \( f_{\text{Cu Precipitate}} \) in equation 1.

\[
\begin{align*}
\frac{f_{\text{Soluble Cu}}}{{\text{Cu TMCP}}} &= 0.00924 - 0.00144 \\
&= 0.0078
\end{align*}
\]

Convert this to wt%

\[
\begin{align*}
\frac{\text{wt}\%_{\text{Cu}}}{\rho_{\text{Cu}}} &= \frac{\text{wt}\%_{\text{Cu}} + \text{wt}\%_{\alpha_{\text{Fe}}}}{\rho_{\text{Cu}} + \rho_{\alpha_{\text{Fe}}}} \\
\frac{\text{wt}\%_{\text{Cu}}}{\rho_{\text{Cu}}} \cdot f_{\text{Soluble Cu}} + \frac{\text{wt}\%_{\alpha_{\text{Fe}}}}{\rho_{\alpha_{\text{Fe}}}} f_{\text{Soluble Cu}} &= \frac{\text{wt}\%_{\text{Cu}}}{\rho_{\text{Cu}}} \\
\frac{\text{wt}\%_{\text{Cu}}}{\rho_{\text{Cu}}} f_{\text{Soluble Cu}} + \frac{\text{wt}\%_{\alpha_{\text{Fe}}}}{\rho_{\alpha_{\text{Fe}}}} f_{\text{Soluble Cu}} &= \frac{\text{wt}\%_{\alpha_{\text{Fe}}}}{\rho_{\alpha_{\text{Fe}}}} f_{\text{Soluble Cu}} \\
\frac{\text{wt}\%_{\text{Cu}}}{\rho_{\text{Cu}}} - \frac{\text{wt}\%_{\text{Cu}}}{\rho_{\text{Cu}}} f_{\text{Soluble Cu}} + \frac{1}{\rho_{\text{Cu}}} &= \frac{\text{wt}\%_{\alpha_{\text{Fe}}}}{\rho_{\alpha_{\text{Fe}}}} f_{\text{Soluble Cu}}
\end{align*}
\]
wt% Cu = \frac{\text{wt\% Fe}}{\rho_{\text{Fe}}} \cdot \frac{f_{\text{Soluble Cu}}}{\rho_{\text{Cu}}} \cdot \frac{99.99}{7.8 \times 10^{-3}} \cdot \frac{785}{8.933} \cdot \frac{8.933}{8.933} = 0.889

iii. Calculate $\sigma_{\text{SSS}}$

From the model of Wada et al. (123)

$\sigma_{\text{SSS}}^{Wada} = 46 \times 0.889$

= 40.88 MPa

from the model of Baird and Preston (76) and using the yield stress for E1 from Table 3.5

$\sigma_{\text{SSS}}^{Baird+Preston} = 0.889 \times 0.38 \times 515$

= 174 MPa

6.2.2 Estimate the magnitude of strengthening attributable to Solid Solution strengthening by Cu after ageing (ie at equilibrium) using the model proposed by Wada et al. (123)

Cu in solution at equilibrium in all steels would be 0.4 wt\% ($f = 3.51 \times 10^{-3}$).

$\sigma_{\text{SSS}}^{Equilibrium\ Wada} = 46 \times 0.4$

= 18.4 MPa
6.3 Dispersion Strengthening

Estimate the magnitude of dispersion strengthening by coarse Cu + Nb + Ti prior to ageing. Using steel E1 as an example.

Assumption 1: The precipitates we actually see in the TMCP condition are a combination of NbTiCN and Cu then,

\[ f_{\text{Precipitate}} = f_{\text{NbTiCN}} + f_{\text{Cu}} \]

i. Using \( f_{\text{Precipitate}} = .00189 \) and \( D = 13.51\text{nm} = .01351\mu\text{m} \) (from \( f \) and \( D \) in Table 3.2)

Calculate \( \sigma \) using Ashby - Orowan equation (1.3)

\[
\sigma_{\text{NbTiCN+Cu}} = \frac{5.9\sqrt{0.00189}}{\left(0.1351\right)^{\frac{2}{3}}\frac{2.5 \times 10^{-4}}{2.5 \times 10^{-4}}} 
\]

\[ = 88.2 \text{ MPa} \]

ii. Using \( f_{\text{Precipitate}} = .00189 \) and \( D = 13.51\text{nm} = .01351\mu\text{m} \) (from \( f \) and \( D \) in Table 3.2) and

\( G_{\alpha\gamma} = 8.3 \times 10^4 \text{ MNm}^{-2} \) and \( b_{\alpha\gamma} = 2.48 \times 10^{-4} \mu\text{m} \) calculate \( \sigma \) using Brown model

(equations 4.3 and 4.4),

\[
L = \frac{1.77r}{f^{\frac{1}{2}}} 
\]

\[
= \frac{1.77(0.00675)}{\sqrt{0.00189}} \quad \text{from } r = \frac{D}{2} 
\]

\[ = 0.2746\mu\text{m} \]

\[
\sigma_{\text{NbTiCN+Cu}} = \frac{0.8Gb}{L} 
\]

\[
= \frac{0.8(8.3 \times 10^4)(2.48 \times 10^{-4})}{0.2746} 
\]

\[ = 59.97 \text{ MPa} \]
iii. Calculate $\sigma_{NbTiCN}$

$$f_{NbTiCN} = f_{NbCN} + f_{TiN}$$
$$= 3.16 \times 10^{-4} + 1.4 \times 10^{-4}$$
$$= 4.56 \times 10^{-4}$$

$$L = \frac{1.77r}{f/2}$$
$$= \frac{1.77(0.00675)}{\sqrt{4.65 \times 10^{-4}}}$$
$$= 0.5595 \mu m$$

$$\sigma_{NbTiCN} = \frac{0.8Gb}{L}$$
$$= \frac{(0.8)(8.3 \times 10^4)(2.48 \times 10^4)}{0.5595}$$
$$= 29.42 \text{ MPa}$$
6.4 Hardening by Incoherent $\varepsilon$ Cu Precipitation.

Estimate of the yield strength attributable to precipitation by incoherent $\varepsilon$ Cu. Using steel E1 as an example.

**Assumption 1:** The precipitates we actually see in the TMCP and aged condition are a combination of NbCN, TiN and various forms of Cu.

i. Calculate the volume fraction of incoherent $\varepsilon$ Cu (using $f_{\text{Incoherent}}^\varepsilon$ Cu $= f$ from Table 3.2 and $f_{\text{AMCN}}$ and $f_{\text{AM}}$ from Appendix 6.3).

\[ f_{\text{Incoherent}}^\varepsilon \text{Cu}_{\text{TMCP+Aged}} = f_{\text{Precipitate}}^\varepsilon \text{Cu}_{\text{TMCP+Aged}} - f_{\text{NbCN}} - f_{\text{TiN}} \]

\[ = 0.00287 - 3.16 \times 10^{-4} - 1.4 \times 10^{-4} \]

\[ = 2.44 \times 10^{-3} \]

ii. Estimate yield strength of the aged steel with the strength increment on ageing attributable to incoherent $\varepsilon$ Cu using the model of Russell and Brown (81).

Substituting for $r = D/2$ from Table 3.2 into equation 4.4.

\[ L^{-1} = \frac{f_{\text{Incoherent}}^\varepsilon \text{Cu}_{\text{TMCP+Aged}} \sqrt{2}}{1.77r} \]

\[ D = 7.2 \text{nm} \]

\[ r = 7.2/2 = 3.6 \text{nm} \]

\[ = 36 \text{Å} \]

\[ = 7.71 \times 10^{-4} \mu\text{m}^{-3} \]
Substitute for \( L^{-1} \) into equations 4.6 and 4.7.

\[
\sigma_{\text{Incoherent}}^{\text{eCu\ TMCP+Aged\ Upper\ Limit}} = 452.5 \times 10^3 (L^{-1}) + 205.2
\]
\[
= 452.5 \times 10^3 (7.71 \times 10^{-4}) + 205.2
\]
\[
= 554 \text{ MPa}
\]

\[
\sigma_{\text{Incoherent}}^{\text{eCu\ TMCP+Aged\ Lower\ Limit}} = 347.5 \times 10^3 (L^{-1}) + 183
\]
\[
= 452.5 \times 10^3 (7.71 \times 10^{-4}) + 205.2
\]
\[
= 450 \text{ MPa}
\]

iii. Estimate the yield strength of the aged steel with strength increment on ageing attributable to incoherent \( \varepsilon \) Cu using the model of Fujii et al. (77).

Using
\[
G = 8.3 \times 10^4 \text{ MNm}^{-2}
\]
\[
\nu = 0.29
\]
\[
b = 2.48 \text{ \AA}
\]
\[
d (\text{TMCP & Age}) = 7.2 \text{ nm}
\]
\[
r' = d/2 = 36 \text{ \AA}
\]

Substitute \( f_{\text{Incoherent\ eCu\ TMCP+Aged}} \) for \( f \) and \( r' \) into the equation for \( l_p \)

\[
l_p = \left[ \frac{2\pi}{3f} - 2\sqrt{\frac{2}{3}} r' \right]
\]
\[
= \left[ \frac{2\pi}{3 \times 2.4 \times 10^{-3}} - 2\sqrt{\frac{2}{3}} \right]
\]
\[
= 1002 \text{ \AA}
\]
substitute for $l_p$, $G$, $b$, and $\nu$ into equation 1.8

$$
\tau_{\text{Incoherent eCu TMCP+Aged}} = \frac{Gb}{4\pi} \times \frac{1}{l_p} \left(1 + \frac{1}{1 - \nu}\right) \ln \left(\frac{l_p}{2b}\right)
$$

$$
= \frac{(83000)(2.48)}{4p} \times \frac{1}{1002} \left(1 + \frac{1}{1 - 0.29}\right) \ln \left(\frac{1002}{2 \times 2.48}\right)
$$

$$
= 211.2 \text{ MPa}
$$

using

$$
\sigma_{\text{Incoherent eCu TMCP+Aged}} = 2.5\tau
$$

$$
= 2.5 \times 211.2
$$

$$
= 528 \text{ MPa}
$$
iv. Estimate yield strength increment attributable to incoherent ε Cu using the Ashby Orowan model (77).

\[
\Delta \sigma_{\text{Incoherent} \varepsilon \text{Cu}} = \frac{5.9 \sqrt{f}}{D \left( \frac{2}{3} \right)^{\frac{1}{2}}} \ln \left( \frac{D \left( \frac{2}{3} \right)^{\frac{1}{2}}}{2.5 \times 10^{-4}} \right)
\]

\[
= \frac{5.9 \sqrt{2.4 \times 10^{-3}}}{0.036 \left( \frac{2}{3} \right)^{\frac{1}{2}}} \ln \left( \frac{0.036 \left( \frac{2}{3} \right)^{\frac{1}{2}}}{2.5 \times 10^{-4}} \right)
\]

\[
= 47.02 \text{ MPa}
\]
6.5 Strengthening Due to Coherent $\varepsilon$ Cu and Cu Rich Clusters

Estimate the strengthening due to coherent $\varepsilon$ Cu and Cu rich clusters as predicted using the model of Russell and Brown (81). Using Steel E1 as an example.

i. The maximum volume fraction of precipitate available for clustering is assumed to be:

$$f_{Coherent} = f_{Precipitable} - f_{Incoherent}$$  \[A6.5.1\]

wt\% Cu in Steel E1 $= 1.05\%$

Solubility limit of Cu in $\alpha$Fe $= 0.4\%$

Therefore the approximate amount of Cu available for precipitation $= (1.05 - 0.4)\%$ $= 0.65\%$

Expressed as a volume fraction - for 100g of steel.

$$f_{Precipitable} = \frac{wt\%Cu}{\rho_{Cu}} \frac{wt\%Cu}{\rho_{Cu} + wt\%\alpha Fe/\rho_{\alpha Fe}}$$

$$= \frac{0.65}{8.933} + 99.35/7.85$$

$$= 5.72 \times 10^{-3}$$

from previous calculations(Appendix 6.2 and 6.4 ) we know

$$f_{Incoherent} = 2.4 \times 10^{-3}$$

Substitute into equation A6.5.1.

$$f_{Coherent} = 0.005716 - 2.4 \times 10^{-3}$$

$$= 3.32 \times 10^{-3}$$
However, if as according to Goodman et al. (93), the composition of the Cu particles is approximately 51% Cu, then this estimate of $f_{Coherent}^{Cu+Cu\text{Clusters}}$ would greatly underestimate the volume fraction of particles available to contribute to the final strength.

ii. Determine the peak strength of the aged steel from equation 4.9 i.e $\sigma_{Coherent}^{Cu+Cu\text{Clusters}}$

iiia. Using $\overline{G}_{aFe+Cu} = 6.57 \times 10^4$ MNm$^{-2}$ (average of $G_{aFe}$ and $G_{Cu}$)

$$\overline{b}_{aFe+Cu} = 2.52 \AA$$

(average of $b_{aFe}$ and $b_{Cu}$)

and assuming that

$$r_o = r/2$$

$$= 6 \AA$$

substitute into equation 1.8.

$$\tau = \sqrt{\frac{0.041 \cdot \overline{G} b f^{1/2}}{r_o}}$$

\[ A6.5.2 \]

$$\sigma_{Coherent}^{Cu+Cu\text{Clusters}} = 2.5 \tau$$

$$= 2.5 \cdot 0.041 \cdot \frac{G b f_{Coherent}^{1/2}}{r_o}$$

$$= 2.5 \cdot 0.041 \cdot \frac{(6.575 \times 10^4)(2.52)(3.32 \times 10^{-3})^{1/2}}{(6)}$$

$$= 163 \text{ MPa}$$

If as mentioned previously this $f_{Coherent}^{Cu+Cu\text{Clusters}}$ has been underestimated due to the composition of the particles potentially being $\approx 51\%$ Cu (based on the work of Goodman et al. (93)), then equation A6.5.2 can be used to estimate the volume fraction of particles required to achieve the experimental aged strength $f^{1}_{Coherent}^{Cu+Cu\text{Clusters}}$. 
\[ f_{\text{Coherent } \epsilon \text{Cu+Cu Clusters}}^1 = \left( \left( \frac{\sigma_{\text{Coherent } \epsilon \text{Cu+Cu Clusters}}}{(2.5)(0.041)(G_b)} \right) \right)^{1/2} \]

\[ = \left( \frac{547 \times 6}{(2.5)(0.041)(6.575 \times 10^4 \times 2.52)} \right)^{1/2} \]

\[ = 0.0373 \]

\[ = 3.7 \times 10^{-2} \]

iib. Determine the increment in \( \sigma \) due to \( \epsilon \) Cu + coherent Cu rich zones from equation 4.11.

Substituting for \( f_{\text{Coherent } \epsilon \text{Cu+Cu Clusters}} \) calculated from experimental observations and chemical composition of the steel into equation 4.11

\[ \sigma_{\text{Coherent } \epsilon \text{Cu+Cu Clusters}} = 3.57 \times 10^3 f^{1/2} - 71 \text{MPa}^{-2} \]

\[ = 3.57 \times 10^3 \times 0.0033^{1/2} - 71 \text{MPa}^{-2} \]

\[ = 134 \text{ MPa} \]
6.6 Pythagorean Addition

6.6.1 Estimate of the Total Strength of the Experimental Steels When Composed of Mixtures of Obstacles of Distinct Strengths.

Assume

\[ \sigma_{\text{TOTAL}} = \sigma_{\text{BASE}} + \sigma_{\text{SECOND PHASE OBSTACLES}} \]

a. Calculate \( \sigma_{\text{SECOND PHASE OBSTACLES}} \)

Apply Pythagorean addition rule (PAR) first proposed by Kopenaal and Kuhlmann - Wilsdorf (167), of the form,

\[ (\tau_c)^2 = (\tau_{a1})^2 X_1 + (\tau_{a2})^2 X_2 \]

A6.6-1

where \( \tau = \) increment in the strength of the material

\[ X_1 = \frac{n_{s1}}{n_s} \]

\[ X_2 = 1 - X_1 = \frac{n_{s2}}{n_s} \]

\( n_{s1} \) and \( n_{s2} \) = the number/volume fraction of obstacles per unit area of types 1 and 2.

In this work, the steel has contributions to its strength from

i. Matrix Strengthening \( (\sigma_{\text{base}} = \sigma_i) \)

ii. Microalloy precipitates present in the unaged steel \( (\sigma_{\text{NbTiCN+Cu}} = \sigma_{\text{ii}}) \)

\( (\sigma_{\text{NbTiCN}} = \sigma_{\text{ii}}) \)

iii SSS by Cu \( (\sigma_{\text{SSS}} = \sigma_{\text{iii}}) \)

in the unaged condition and from

iv. Incoherent \( \varepsilon \) Cu \( (\sigma_{\text{Incoherent } \varepsilon \text{Cu}} = \sigma_{\text{iv}}) \)

\( (\sigma_{\text{TMCP+Aged}} = \sigma_{\text{iv}}) \)
APPENDICES

v. Coherent ε Cu and Cu clusters

\[
\sigma_{\text{Coherent}} = \sigma_v
\]

vi. Equilibrium level of Solid Solution Strengthening by Cu ie. from 0.4 wt% which remains in solution

\[
\sigma_{\text{ESS Equilibrium}} = \sigma_{\text{vi}}
\]

in the aged condition.

therefore for the steel in the fully aged condition the form of equation A6.6 -1 which applies to the contributions to the strength increment achieved on ageing is;

\[
(\sigma_{\text{PAR}})^2 = (\sigma_{\text{lb}})^2 X_{\text{lb}} + (\sigma_{\text{iv}})^2 X_{\text{iv}} + (\sigma_{\text{v}})^2 X_{\text{v}} + (\sigma_{\text{vi}})^2 X_{\text{vi}}
\]

A6.6.2

.: The total strength of the fully aged steel would be given by

\[
\sigma_{\text{TOTAL}} = \sigma_{\text{PAR}} + \sigma_i
\]

For steel E1 using data from Tables 4.4, 4.7, 4.9 and Appendices 6.2 and 6.3;

<table>
<thead>
<tr>
<th>n</th>
<th>Strength Increment</th>
<th>(\sigma_{\text{PAR}}) (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>i. Base</td>
<td>99.993</td>
<td>385</td>
</tr>
<tr>
<td>ii. NbTiCN+Cu</td>
<td>4.57 x 10^{-4}</td>
<td>29</td>
</tr>
<tr>
<td>iv. Incoherent ε Cu</td>
<td>2.41 x 10^{-3}</td>
<td>47</td>
</tr>
<tr>
<td>v. Coherent ε Cu and Cu clusters</td>
<td>3.30 x 10^{-3}</td>
<td>134</td>
</tr>
<tr>
<td>vi. Cu available for Solid Solution Strengthening at Equilibrium</td>
<td>.00035</td>
<td>18.4</td>
</tr>
</tbody>
</table>

\[
n = n_{\text{lb}} + n_{\text{iv}} + n_{\text{v}} + n_{\text{vi}}
\]

\[
= (0.45 + 2.41 + 3.30 + 3.52) \times 10^{-3}
\]

\[
= 6.52 \times 10^{-3}
\]
\[ X_{ii} = \frac{n_{ii}}{n} = \frac{4.57 \times 10^{-4}}{6.52 \times 10^{-3}} = 0.0699 \]

\[ X_{iv} = \frac{n_{iv}}{n} = \frac{2.41 \times 10^{-3}}{6.52 \times 10^{-3}} = 0.3699 \]

\[ X_v = \frac{n_v}{n} = \frac{3.30 \times 10^{-3}}{6.52 \times 10^{-3}} = 0.5059 \]

\[ X_{vi} = \frac{n_{vi}}{n} = \frac{3.50 \times 10^{-3}}{6.52 \times 10^{-3}} = 0.0541 \]

Hence

\[ \sigma_{TOTAL} = 385 + \sqrt{(29)^2 (0.0699) + (47)^2 (0.3699) + (134)^2 (0.5059) + (18.4)^2 (0.0541)} \]

\[ = 720 \text{ MPa} \]

Generally the Pythagorean addition rule accounts for the contribution to the CRSS of distinct obstacles of two or more strengths. It ignores how to account for the flow stress of the matrix and when applied to modelling it is generally assumed that it is zero. However in this work it is not appropriate to ignore the contribution from matrix strengthening, hence when a term for this base strength is included in the Pythagorean equation it overwhelms the estimates of contribution from the other mechanisms. It was decided therefore that a truer estimate of the final strength would be achieved if the base strength of the matrix were added to the estimate of the increment on ageing produced by the various mechanisms and calculated using Pythagorean addition.
Estimate of Contributions to Strength From Individual Mechanisms

(Calculated from linear addition of strength increments attributable to each mechanism)

| i. Theoretical Fully Aged Yield Strength (MPa) | $\sigma_{\text{Fully Aged}}$ | D | E1 | F |
| ii. Theoretical TMCP Yield Strength (MPa) | $\sigma_{\text{TMCP}}$ | 465 | 486 | 461 |
| iii. Theoretical increment in Yield Strength (MPa) | $\Delta \sigma$ | 151 | 156 | 149 |
| Volume Fractions of Cu in Various Forms | | | | |
| $f_{\text{Cu Incoherent}}$ | $n_1$ | .0022 | .0024 | .0022 |
| $f_{\text{Cu Coherent + Cu rich zones}}$ | $n_2$ | .0031 | .0033 | .0030 |
| $f_{\text{Cu in Solution at Equilibrium}}$ | $n_3$ | .00035 | .00035 | .00035 |
| $n$ | $5.65 \times 10^{-3}$ | $6.05 \times 10^{-3}$ | $5.55 \times 10^{-3}$ |
| $\varepsilon \text{ Cu Incoherent}$ | $X_1$ | 0.389 | 0.396 | 0.396 |
| $\varepsilon \text{ Cu Coherent + Cu rich zones}$ | $X_2$ | 0.548 | 0.545 | 0.541 |
| $\varepsilon \text{ Cu in Solution at Equilibrium}$ | $X_3$ | 0.062 | 0.058 | 0.063 |
| Proportion of Strengthening Increment (MPa) | $\Delta \sigma_i \times X_i$ | | | |
| $\varepsilon \text{ Cu Incoherent}$ | $\Delta \sigma_1$ | 58.7 | 61.8 | 59.0 |
| $\varepsilon \text{ Cu Coherent + Cu rich zones}$ | $\Delta \sigma_2$ | 82.7 | 85.02 | 80.6 |
| $\varepsilon \text{ Cu in Solution at Equilibrium}$ | $\Delta \sigma_3$ | 9.4 | 9.4 | 9.4 |
| Proportion of Strengthening Increment as a % of the Total Strength Increment | $\frac{\Delta \sigma_i \times 100}{\Delta \sigma}$ | | | |
| $\varepsilon \text{ Cu Incoherent}$ | | 38.9 | 39.6 | 39.6 |
| $\varepsilon \text{ Cu Coherent + Cu rich zones}$ | | 54.8 | 54.5 | 54.1 |
| $\varepsilon \text{ Cu in Solution at Equilibrium}$ | | 6.2 | 5.8 | 6.3 |
PUBLICATIONS


