THE INFLUENCE OF THERMOMECHANICAL PROCESSING ON THE ANNEALING RESPONSE OF 3CR12 STEEL

by

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A thesis submitted to the Faculty of Engineering, University of Cape Town, in fulfilment of the degree of Master of Science in Engineering.

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February 1998
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Published by the University of Cape Town (UCT) in terms of the non-exclusive license granted to UCT by the author.
Without the assistance of many people, this dissertation in its entirety would not have been possible. I am therefore particularly grateful to:

♦ Rob Knutsen, my supervisor, for his help and guidance throughout this project.
♦ Glen Newins, Nick Dreze, Mike Dietz and Reggie Hendricks for the machining of test apparatus and specimens.
♦ Dave Dean for the electronic advice and assistance, and Mira Topic for assistance in the laboratory.
♦ Bernard Greeves and James Petersen for the developing and printing of slides and photographs.
♦ John Tarboton and Jurg Zaayman (Columbus Stainless) for their interesting and ever-helpful knowledge of 3CR12.
♦ Trevor Sewell (Electron Microscope Unit, UCT) for his assistance with Image Analysis.
♦ Sid Mayer (Capital Equipment Corp.), David Tinker (Eagle Technology) and Alan Duckham for their assistance with software and hardware.
♦ Boart Longyear Research Centre for financial assistance.
♦ James, Joe, Ryan, Brad, Woolster, Janet and Lungi; thanks for being there.

♦ Mom and Dad; as usual, IOU. Thank you for everything.

"Quid pro quo"
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SYNOPSIS

An investigation was performed on alloys of a 12wt% Cr steel (3CR12) that had undergone different thermomechanical processing routes prior to the annealing step of production. The aim of this research was to identify any changes in the annealing response of 3CR12 steel due to the different thermomechanical processing routes to which the alloys had been subjected.

Three alloys of 3CR12 were subjected to various cooling treatments immediately following hot rolling. This was accomplished by water quenching, air cooling and insulatory cooling of the hot-rolled plates. Characterisation of the alloys in the hot-rolled and annealed conditions included optical and electron microscopy, macro- and microhardness tests, tensile tests and impact energy tests, dilatometry, differential thermal analysis and volume fraction analysis.

Alloys in the as-rolled state exhibited an increase in martensite content related to an increase in the cooling rate following hot rolling. The increase in martensite content influenced the alloys' mechanical properties by raising their bulk hardness, UTS and yield strength. This was coupled with a decrease in the elongation and impact toughness of the alloys. Furthermore, the Ac₁ was found to increase with higher cooling rates following hot rolling. Variations in the as-rolled microstructures influenced the alloys' subsequent annealing response, with there being a greater and more immediate response to the annealing treatment by alloys subjected to higher cooling rates after hot rolling. The fully annealed alloys showed little variation in their microstructures or mechanical properties, despite clear variations in their as-rolled microstructures.
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1. INTRODUCTION

The commercial production of 3CR12 steel includes a hot rolling step, following which, the steel is wound around a mandrel to form a coil where it is allowed to cool. Thereafter the steel may be subjected to an annealing treatment to both soften the material for further processing, and to control further microstructural development.

Owing to the coil’s large size, different locations in its cross section will experience different cooling rates (as shown by the figure below). An unwanted spin-off of these different cooling rates is the variation in the steel’s microstructure and consequently, variations in the mechanical properties along the length of the unwound steel sheet.

Advances in knowledge of the metallurgy of 3CR12 have led to improved production practices, enabling steelmakers to curtail these variations in mechanical properties to within acceptable limits. Nevertheless, there will always be a small variation in the steel’s microstructure as a result of these different cooling rates inside the coil. This variation in microstructural properties could possibly influence the response of the steel to any subsequent annealing treatments. Therefore, the response of variations of the microstructure of 3CR12 steel to annealing treatments is of great commercial significance.

![Figure 1.1: The cooling rates experienced by different locations in a 1.3m wide coil](image-url)
The primary objective of this research is to evaluate changes in the microstructure of 3CR12 steel as a result of different cooling rates during the thermomechanical processing of the steel, i.e. a complete characterisation of the alloys in their as-rolled condition prior to annealing. This knowledge will assist in the characterisation of the steel's microstructure and mechanical properties following the annealing treatment, and more importantly, will aid in the ultimate objective of this research, explaining any differences in the responses of differently cooled conditions of 3CR12 to annealing treatments.
2. LITERATURE REVIEW

2.1 THE EVOLUTION OF 3CR12

2.1.1 THE ROLE OF 12WT% CR STEELS

Unlike stainless steels, the identity of 12wt% Cr steels’ founder is not subject to much conjecture. Harry Brearly\(^1\), whilst working on the production of a gun barrel steel in Sheffield, England, accidentally discovered (albeit a dismal gun barrel steel) a hardenable yet corrosion resistant steel. The steel reported by Brearly in 1913 was the first true 12wt% Cr alloy\(^2\).

Early 12wt% Cr steels, such as the martensitic AISI 410, suffered from poor weldability and consequently their use in sheet and plate form was limited as steel in this form generally required welding. In the early 1970s a new generation of 12wt% Cr steels, typified by the ferritic AISI 409, was developed with improved weldability and formability\(^1\). Unfortunately AISI 409 exhibited a low toughness due to grain growth in the heat affected zone (HAZ)\(^3,4\) and so its weldability was also not ideal\(^1,4\). Furthermore, it was found to have insufficient strength for certain structural applications and exhibited a high ductile-to-brittle transition temperature (DBTT)\(^5\).

Nevertheless, ferritic stainless steels continued to be of great interest to researchers due to their corrosion resistance and favourable production costs - particularly in chromium-producing countries such as South Africa\(^4\). Ball and Hoffman\(^4\) concluded that any successful ‘redesign’ of a ferritic steel, viz. AISI 409, would have to incorporate a stable fine-grained microstructure with reduced amounts of the interstitial elements, nitrogen and carbon.

Using compositions based on AISI 409, the chemical composition of a new steel was developed using the Kaltenhauser Ferrite Factor Relationship\(^4,5,6,7\). The steel was developed at the Southern Cross Steel laboratories, a division of Middelburg Steel and Alloys (now Columbus Stainless) and was provisionally designated SX 3 CR 12 \(^4\).
Work showed that the steel exhibited good mechanical properties, good corrosion resistance and most importantly, an adequate weldability. Poor weldability, the problem that had beleaguered 12wt% Cr steels since Brearly, had finally been overcome. "... a sad case of metallurgical neglect" was how Maxwell et al. chronicled the 65 years prior to SX 3 CR 12.

SX 3 CR 12 was patented (South African patent no. 78/1684) in 1978 under the name "3CR12", an acronym for chromium containing corrosion resistant 12wt% chromium steel. Following the successful acceptance of 3CR12 into the marketplace at least four other 3CR12 look-alikes have been launched by other steel makers. The steel makers jointly predicted capturing approximately 10% of the stainless steel market before the end of the millennium.

### 2.1.2 THE DEVELOPMENT OF 3CR12

Originally two varieties of 3CR12 were produced by Middelburg Steel and Alloys (MS&A). The major difference between the two varieties was in the nickel content. A version with 1.2wt% Ni was marketed for very high strength applications whilst the 0.6wt% variety was used for more general applications.

In the mid-1980s work began at MS&A on characterising property variations over the length of annealed coils. It had been found that 10% to 15% of the coils produced displayed variable properties over their length, or were difficult to soften following annealing. This required an expensive and time consuming re-annealing step. The term 'self-annealed' (cf. autotempering) was proposed to explain these variable properties. It was theorised that as the coil cooled after the annealing treatment, heat retained in the coil tempered the martensite. With the benefit of hindsight, this can be seen as an unlikely explanation, since the $M_T$ of the 3CR12 was approximately $300^\circ C$, consequently the kinetics of any tempering would be too slow at such temperatures.

In the late-1980s with the 'self-annealed' concept in mind, an attempt at solving the variable properties problem was made. It involved covering the hot-rolled coil with an insulatory material that would reduce heat loss from the coil after annealing,
thereby increasing the tempering time and yielding more uniform properties throughout the coil’s length. Despite what is now known to have been flawed reasoning, this procedure was successful. Nevertheless, it was realised that a scientific understanding of the concept was required^9.

Pistorius and van Rooyen^10 refuted the ‘self-annealed’ theory by means of continuous cooling transformation (CCT) diagrams. They demonstrated that slower cooling rates caused austenite to decompose into proportionately more ferrite than martensite, which explains why the procedure involving an insulative cover was successful. They also showed that the alloying elements, titanium and nickel, could be dispensed with, which would lead to a reduction in cost and surface defects^9,10. The decision to produce 3CR12 with lower levels of nickel and titanium, known as 3CR12L, was made in 1989^9.

<table>
<thead>
<tr>
<th></th>
<th>AISI 409</th>
<th>SX 3 CR 12</th>
<th>3CR12Ti</th>
<th>3CR12L</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>0.08 max</td>
<td>0.025</td>
<td>0.025</td>
<td>0.025</td>
</tr>
<tr>
<td>Si</td>
<td>1.0 max</td>
<td>0.4</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>Mn</td>
<td>1.0 max</td>
<td>0.9</td>
<td>1.2</td>
<td>1.0</td>
</tr>
<tr>
<td>Cr</td>
<td>10.5-11.75</td>
<td>11.5</td>
<td>11.5</td>
<td>11.5</td>
</tr>
<tr>
<td>Ni</td>
<td>0.5 max</td>
<td>0.6</td>
<td>0.6 or 1.2</td>
<td>0.1</td>
</tr>
<tr>
<td>N</td>
<td>-</td>
<td>0.02</td>
<td>0.02</td>
<td>0.02</td>
</tr>
<tr>
<td>Ti</td>
<td>6 x C min</td>
<td>0.2</td>
<td>0.3</td>
<td>0</td>
</tr>
</tbody>
</table>

Table 2.1: Compositional evolution of 3CR12

The evolution of 3CR12’s composition is illustrated in Table 2.1. Several other forms of 3CR12 are presently being produced by Columbus Stainless, each conforming to different international specifications, such as AISI 410s or DIN 1.4003 in prEN 10088. Batch and line annealable forms of 3CR12 are produced.

2.2 3CR12’S ALLOYING ELEMENTS

Several 3CR12 alloys are dealt with in this thesis and since no individual element’s effects can be isolated, a broad discussion of the influences of each major alloying element has been included.
2.2.1 AUSTENITE AND FERRITE FORMERS

The Kaltenhauser Ferrite Factor Relationship\(^6\), used in the development of 3CR12 (section 2.1.1), is in fact a modified form of a relationship first proposed by Thielemann\(^{11}\). Thielemann recognised that alloying elements had different effects on the phase equilibria of steels. The alloying elements were able to be classed into two broad groups as follows:

- **Austenite Formers** - expand the austenite field across the phase diagram, whilst restricting the ferrite field (see Figure 2.1).
- **Ferrite Formers** - expand the ferrite field across the phase diagram, whilst restricting the austenite field\(^{12}\).

![Figure 2.1: The effect of equal additions of carbon and nitrogen (austenite formers) on austenite and ferrite fields\(^6\)](image)

At this stage attention must be drawn to the terms *formers* and *stabilisers*, as the author has found that many workers do not draw a distinction between these terms and may use them interchangeably. Usage of the terms *ferritisers* and *austenitisers* in earlier papers complicates the issue further, leading to the decision to refrain from using these terms completely. As may be deduced from the above paragraph, alloying elements which are referred to as *formers* will expand a certain phase across the phase diagram. Alloying elements which promote the retention of a phase on cooling or deformation, are known as *stabilisers*. Addition of these elements will expand the phase field *down* to lower temperatures\(^{13}\).
Despite the knowledge that alloying elements could be separated into two distinct groups, viz. austenite and ferrite formers, it was soon realised that the ability to rank the relative strengths of different austenite and ferrite formers would prove to be even more significant. Zener\textsuperscript{14} in 1940 proposed the first equation which allowed alloying elements to be classed thermodynamically:

\[
\log \frac{C_i}{C_a} = \frac{\Delta H}{RT}
\]

\(C_i\) and \(C_a\) are the fractional concentrations of an element in the austenite and ferrite phases respectively, \(\Delta H\) is the change in enthalpy (see equation below), \(R\) is the molar gas constant and \(T\) is the absolute temperature.

Now using the relationship,

\[
\Delta H = H_\gamma - H_\alpha
\]

in which \(H_\gamma\) or \(H_\alpha\) is the increase in enthalpy caused by the addition of one unit of an alloying element to austenite or ferrite respectively, the following situation (shown graphically by Figure 2.2) will then arise.

\(\diamond\) For ferrite formers, \(H_\alpha < H_\gamma\), thus \(\Delta H > 0\).

\(\diamond\) For austenite formers, \(H_\alpha > H_\gamma\), thus \(\Delta H < 0\)\textsuperscript{12}.

\[\text{Figure 2.2(a): } H_\alpha > H_\gamma, \text{ thus } \gamma \text{ favoured} \quad \text{(b): } H_\alpha < H_\gamma, \text{ thus } \alpha \text{ favoured}^{12}\]
These equations thereby permitted the quantitative comparison of austenite and ferrite formers, since their relative strengths could be calculated as shown by Figure 2.3.

\[ F(\alpha) = -40 \cdot (%C + %N) - 2 \cdot %Mn - 4 \cdot %Ni + %Cr + 6 \cdot %Si + 8 \cdot %Ti + 4 \cdot %Mo + 2 \cdot %Al \]

From this relationship one can predict whether the resultant microstructure of a steel will be predominantly ferritic or martensitic.

- Ferrite Formers (Cr, Ti, Si, Mo, Al) have positive values in the above relationship, and thus the higher \( F(\alpha) \) is, the more ferritic the resultant microstructure is expected to be.
Austenite Formers (C, Mn, Ni, N) have negative values, consequently the lower the value of $F(\alpha)$, the more austenitic (and thus martensitic) the resulting microstructure is expected to be.

Typical values for 3CR12 were claimed to range between 8 and $12^{\text{15}}$.

Other methods have been used in an attempt to predict the phase of a steel due to the alloying elements. Schaeffler$^{16}$ published empirically determined equations for chromium and nickel equivalents in austenitic welds. Like the Kaltenhauser Ferrite Factor Relationship, Schaeffler's expressions attempted to account for the 'potency' of the minor alloying elements. These expressions are used in conjunction with a Schaeffler Diagram (Figure 2.4) which enables the user to predict the phase formed at room temperature following rapid cooling from a solution treated condition.

Figure 2.4: A Schaeffler Diagram$^{19}$

Knutsen$^{17}$ illustrated how other workers modified Schaeffler's equivalency factors into the form used today. It must again be emphasised that the majority of the expressions are related to the weld metal's composition, which due to the rapid cooling rates do not represent equilibrium structures$^{17}$. Nevertheless, as noted by Knutsen, they are still considered useful in determining the approximate phase
constitution of Cr-Ni steels. The following modifications of Schaeffler’s equivalency factors are now generally accepted:\textsuperscript{18,19}:

\[
nickel\ equivalence = \%Ni + \%Co + 0.5\cdot\%Mo + 0.3\cdot\%Cu + 30\cdot\%C + 25\cdot\%N
\]

\[
chromium\ equivalent = \%Cr + 2\cdot\%Si + 1.5\cdot\%Mo + 5\cdot\%V + 5.5\cdot\%Al + 1.75\cdot\%Nb + 1.5\cdot\%Ti + 0.75\cdot\%W
\]

The development of these equivalents led Kaltenhauser and Lefevre\textsuperscript{20} to modify the Kaltenhauser Ferrite Factor Relationship along similar lines. One may notice from Figure 2.5, that this ‘modification’ simply entailed splitting \( F(\alpha) \) into austenite formers and calling it the nickel equivalent, whilst labelling the remaining coefficients (the ferrite formers) as the chromium equivalent. They also created a diagram similar to the Schaeffler Diagram, with the equivalency relationships mentioned earlier constituting the graph’s axes, as shown by Figure 2.5. These relationships (particularly the Kaltenhauser Ferrite Factor Relationship) have been employed in many papers dealing with 3CR12\textsuperscript{1,3,4,5,7}. Hewitt performed the first large-scale study of the Kaltenhauser Ferrite Factor, nickel equivalent and chromium equivalent relationships, by comparing predicted results against empirical data\textsuperscript{9}. From this work it was concluded that the relationships studied were not very accurate in their predictions (as illustrated by Figure 2.6 overleaf) and that they were of little use to industry.

\textbf{Figure 2.5:} Graph illustrating the modified Kaltenhauser equivalents for 12wt\% Cr steels\textsuperscript{3}
2.2.3 IMPORTANT ALLOYING ELEMENTS OF 3CR12

Unless otherwise stated, the influences of alloying elements were taken from work dealing with 3CR12 or 12wt% steels of a similar composition to that of 3CR12.

2.2.3.1 CARBON

This interstitial element, as shown in Figure 2.3, is the most powerful austenite former and stabiliser. Consequently, increasing amounts of carbon in solid solution will increase the amount of martensite formed, due to carbon increasing austenite's stability\textsuperscript{21,22}, and consequently the alloy's hardenability\textsuperscript{23} (the ability of a steel to form martensite, even at slow cooling rates). By increasing the austenite stability, carbon also inhibits the growth of δ-ferrite\textsuperscript{21}, which is responsible for much of 3CR12's anisotropic properties, such as delamination, which has been found to persist even following annealing treatments\textsuperscript{24}. Furthermore, this causes an increase in the hardness of the martensite itself\textsuperscript{2,21,25,26}. Similarly, for carbon contents between 0.008wt% and 0.029wt%, there is an increase in bulk hardness with an increase in carbon content\textsuperscript{22}.

Conversely, this increase in hardness leads to a decrease in toughness of the martensite\textsuperscript{23} and the HAZ\textsuperscript{21}, due to the carbon segregating to austenite. Therefore, stabilisers such as titanium (recall titanium stabilised 3CR12Ti in Table 2.1) and
niobium, which form the carbides TiC and NbC, were employed. The presence of NbC and TiC serves the dual purpose of lowering the soluble content of carbon in austenite, and as these precipitates are formed in preference to Cr$_{23}$C$_6$, they also restrict formation of the detrimental Cr$_{23}$C$_6$. The carbide content will increase with an increase in carbon content. An increase in the carbon content will also impair corrosion resistance and decrease weldability. Further work endorsing the effect of carbon on steels' hardenability was undertaken by Grange et al., who found that the as-quenched hardness of carbon and low-alloy steels depended solely on the carbon content. This was not a surprising finding, since it is well known that the hardenability (and thus hardness) of a steel depends implicitly on the stability of the austenite phase, and consequently, the austenite phase's composition.

Of particular significance to this thesis was that Kosikiniemi et al. suggested that carbon was the main element that controlled tempering kinetics. In a series of 12wt% Cr alloys, steels with carbon $\geq 0.014$wt% required prolonged annealing before becoming completely softened.

### 2.2.3.2 NITROGEN

Nitrogen, like carbon, is an interstitial element (exhibits high diffusivity) and a powerful austenite former and stabiliser. Therefore, these two elements have similar effects on 12wt% Cr steels in terms of toughness and strength (Figure 2.7 overleaf). Again, like carbon, nitrogen segregates to the austenite phase and therefore the nitrogen content has to be kept very low in order to keep the martensite tough. Early steelmaking could not keep the nitrogen and carbon contents sufficiently low and therefore, as mentioned earlier, stabilisers such as titanium and niobium were employed. Nowadays, modern steelmaking permits the reduction of the nitrogen and carbon contents to below 0.03wt%, thereby rendering stabilisation unnecessary. Irvine et al. concluded that every property of a 12wt% Cr steel was affected adversely with high carbon and nitrogen contents.
A low nitrogen content (<0.01wt%) will permit a high toughness in 3CR12, and will cause a reduction in the detrimental Ti(C,N), thereby allowing the formation of more sulphides (TiS). A rise in the nitrogen content was found to increase the steels' strength but also lower the steel's toughness. Nitrogen additions also lead to a finer martensitic structure due to nitrogen stabilising the austenite. Orava et al. found that nitrogen had no effect on the martensite hardness of a non-stabilised 12wt% Cr steel. This challenges the work of Irvine et al. who found that nitrogen increased the hardness of martensite in a low carbon 12wt% Cr steel.

Work by Attamert and King on duplex stainless steels has shown that nitrogen has a low solubility in ferrite (this is intuitive since earlier it was said that nitrogen segregates to austenite), thereby causing the ferrite to become supersaturated with nitrogen. Upon cooling, chromium-rich nitrides precipitate in the ferrite, leading to chromium depletion around the precipitates which leads to localised corrosion (generally at grain boundaries) known as sensitisation. This generally occurs in the HAZ of a weld but can be overcome by the addition of the stabilisers titanium or niobium. This situation is analogous to the precipitation of Cr$_{23}$C$_7$. 

Figure 2.7: The effect of nitrogen on 12Cr-Mo-V steels with a varying carbon content
Zaayman found that low carbon and nitrogen contents led to a decrease in the DBTT of the HAZ, due to the restriction of \( \delta \)-ferrite's growth by increasing the austenite stability. However, higher concentrations had a detrimental effect as the HAZ became harder and the DBTT increased\(^{21}\). Similar increases in the DBTT, due to nitrogen additions, were found by other workers\(^{32,33}\).

### 2.2.3.3 TITANIUM

Titanium can be added to 12wt\% Cr steels to prevent austenite, and thus martensite formation, due to martensite's poor toughness\(^3\). Titanium takes the carbon and nitrogen out of solution (and martensite)\(^{34}\) to form Ti(C,N), which restrict grain growth in the HAZ by 'pinning' the grain boundaries\(^3\). The removal of titanium was found to increase toughness, as TiC acts as sites for cleavage fracture\(^3\). Titanium also stabilises the steel against intergranular corrosion (refer to explanation in the previous section), and an increase in titanium increases the steel's general corrosion resistance\(^5\). Moderate titanium levels (0.3wt\% to 0.4wt\%) were found to ensure the formation of TiS and not the more detrimental MnS inclusions\(^{15,30}\). This is due to TiS being thermodynamically more stable than MnS, and therefore forming in preference to MnS\(^{15,30}\). It can therefore be seen that titanium is not tied up exclusively in carbonitrides\(^30\).

![Figure 2.8: Iso-hardness plots for 3CR12 with varying levels of titanium\(^5\)](image-url)
Hoffman\textsuperscript{5} showed that titanium (0.16wt\% to 0.39wt\% Ti) assisted in the tempering response of 3CR12 following hot rolling, i.e. an increase in titanium was found to quicken the softening response\textsuperscript{5}. This is illustrated in Figure 2.8. Conversely, for a low carbon 11.5wt\% Cr alloy, Prozzi \textit{et al.}\textsuperscript{34} found that titanium slowed the softening response during tempering. Prozzi's explanation was that titanium retarded the recovery stage of the softening (Figure 2.9). Irvine \textit{et al.}\textsuperscript{25} also observed a retardation of tempering in a 12wt\% Cr, 1wt\% Ni steel following a 0.5wt\% addition of titanium.

![Figure 2.9: The effect of titanium (and vanadium) on the annealing response of 3CR12 according to Prozzi\textsuperscript{34} (P = Holloman-Jaffe Parameter)](image)

2.2.3.4 CHROMIUM

Chromium is well known for its good corrosion resistance (Figure 2.10 overleaf) and pitting resistance\textsuperscript{31}. A minimum of 11wt\% Cr is needed for there to be a reasonable oxidation resistance\textsuperscript{25}, whilst a minimum of 12wt\% Cr is needed for the 'stainlessness' condition\textsuperscript{35}. Chromium was also found to cause some solid solution hardening and depression of the $M_s$\textsuperscript{25}. Depression of the $M_s$ will result in a reduction in the amount of autotempering, thereby allowing the interstitial carbon to further harden the martensite\textsuperscript{25}. Autotempering is the tempering of a steel whilst it is cooling down following a heat treatment (this is analogous to the 'self-annealed' theory proposed for 3CR12 in section 2.1.2).

None of the reviewed references commented on chromium's effect on the tempering response.
2.2.3.5 NICKEL

In terms of transformation temperatures, nickel has been found to depress the $M_s$, $A_1$ and $A_3$ of 3CR12, whilst increasing the $A_4$ and $A_5$, as shown by Figure 2.11 (for the relative positions of these transformation temperatures on the iron-chromium phase diagram, see Figure 5.3, p. 81). Work by Ball\textsuperscript{4,36} shows that nickel increases the martensite hardness and content. The latter is not surprising since nickel is a fairly strong austenite former (Figure 2.3), whilst the former is explained by solid solution hardening and depression of the $M_s$ temperature which results in less autotempering\textsuperscript{25}. Nickel also decreases carbon's solubility in the matrix, leading to supersaturation and the formation of Cr$_7$C$_3$ and Cr$_2$C precipitates\textsuperscript{25}. Although nickel is the third most powerful austenite former, its high cost (8 US$/kg)\textsuperscript{37} prevents its use on a larger scale.

Ball\textsuperscript{36} also found that nickel increased the driving force for austenite nucleation and fine scale intergranular nucleation. Zaayman\textsuperscript{21} found that small additions of nickel improved the impact properties of the HAZ, but only in combination with comparatively low amounts of carbon or nitrogen. Zaayman's explanation for this was that being an austenite former, nickel restricted $\delta$-ferrite grain growth by increasing the austenite stability, while at the same time not depressing the $M_s$ too greatly\textsuperscript{27}. Work by Irvine \textit{et al.}\textsuperscript{25} showed that nickel retarded the final stages of softening of a steel whilst undergoing tempering.
2.2.3.6 MANGANESE

Manganese (like nickel) increases the hardenability of 12wt% Cr steels in addition to decreasing the carbide content\textsuperscript{23}. It was also found to decrease the DBTT and increase the martensite content of the HAZ\textsuperscript{21}.

Irvine \textit{et al.}\textsuperscript{25} commented that manganese had similar effects to nickel in terms of retarding tempering. However, because it was a weaker austenite former (hence its influence was far less marked), there was less justification to use it as an alloying element in order to alter the steel’s hardenability, tempering resistance etc.

2.2.3.7 NIOBIUM

Niobium (like titanium) is a strong ferrite former. Consequently, only small amounts of niobium may be added without detrimentally affecting the steel’s strength. It appears to have a similar function to titanium, in that it reacts with carbon and nitrogen to form stable carbides and nitrides respectively\textsuperscript{23}. This lowers the soluble content of carbon and nitrogen\textsuperscript{23}, which in turn lowers the martensitic hardness (as explained in section 2.2.3.1). The carbides and nitrides also stabilise the ferrite and prevent intergranular corrosion\textsuperscript{27}. A high content (0.3wt\%) of niobium leads to the formation of Nb(C,N) which ‘pin’ the δ-ferrite grain boundaries and consequently prevent excessive grain growth\textsuperscript{23,38}. Nb(C,N) were also found to be beneficial to the impact properties of the HAZ\textsuperscript{21}. 

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure211.png}
\caption{The influence of nickel additions to the transformation temperatures of 3CR12\textsuperscript{7}}
\end{figure}
Irvine et al.\textsuperscript{25} found that increases in the niobium content would increase the tempering resistance of a 12wt\% Cr steel.

### 2.2.3.8 MOLYBDENUM

Molybdenum imparts good pitting and corrosion resistance to 12wt\% Cr steels\textsuperscript{31,39}. It was also found to increase the DBTT of 12wt\% Cr steels as shown by Figure 2.12\textsuperscript{27}.

![Figure 2.12: The influence of molybdenum on the DBTT of chromium-containing steels\textsuperscript{27}](image)

Molybdenum has also been found to stabilise the M\textsubscript{2}X precipitate (it becomes Mo\textsubscript{2}C after high additions of molybdenum) by refining its size, thereby leading to a finer dispersion which results in an increase in hardness\textsuperscript{25}.

### 2.2.3.9 VANADIUM

Vanadium was found to increase the hardness of 12wt\% Cr steels. This is most likely because of its stabilisation of the M\textsubscript{2}X precipitate. Prozzi et al.\textsuperscript{34} found that during tempering treatments of 3CR12 with vanadium additions, a 'pinning' mechanism was occurring, retarding recrystallisation and ferrite grain growth. This resulted in a slower tempering response as illustrated by Figure 2.9.
2.3 ANNEALING OF 3CR12

2.3.1 BACKGROUND TO PRECIPITATE FORMATION

Martensite is a supersaturated solid solution of carbon in iron with a body centred tetragonal (bct) structure. The supersaturation of interstitial carbon atoms results in a metastable structure with much internal stress. There is therefore a strong driving force to decompose to a more thermodynamically stable (and softer) structure of ferrite and carbides. This can be achieved by the precipitation of interstitial elements, as due to their smaller size, they exhibit a higher diffusivity than substitutional elements.

2.3.1.1 PRECIPITATE STABILITY

Owing to the many nitride- and carbide-forming alloying elements that constitute a 12wt% Cr steel, a variety of precipitates can form in the steel upon annealing. The enthalpies of formation shown in Figure 2.13 illustrates the relative stabilities of some of the precipitates found in 3CR12. An interesting point is that the carbides and nitrides of titanium and niobium are thermodynamically more stable than those of chromium and iron. This justifies the usage of titanium and niobium as stabilisers.

Figure 2.13: Enthalpies of formation, $\Delta H_f$, of carbides and nitrides relative to Fe$_3$C.
A further notable point shown in Figure 2.13 is that the differences in the enthalpies of formation between the chromium carbides are not clearly contrasted. This deliberate vagueness may be attributed to the different experimental techniques used by different investigators. This has led to serious disagreements in published energies of formation for chromium carbides.

For a thermodynamic comparison of chromium carbides, an accurate comparison of the energies of formation of chromium carbides is required. Anthonysamy et al. performed the first investigation that determined the energies of formation of all the chromium carbides, using the same technique, over the temperature range 700°C to 900°C.

<table>
<thead>
<tr>
<th>Carbide</th>
<th>ΔH (kJ mol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr₂₃C₆</td>
<td>-264 ± 5</td>
</tr>
<tr>
<td>Cr₇C₃</td>
<td>-104.1 ± 5</td>
</tr>
<tr>
<td>Cr₃C₂</td>
<td>-63.1 ± 2.4</td>
</tr>
</tbody>
</table>

**Table 2.2:** Average energies of formation of chromium carbides between 700°C and 900°C

The work of Anthonysamy et al., presented in Table 2.2, shows that between 700°C and 900°C, the most stable form of chromium carbide is Cr₂₃C₆, with the least stable form being Cr₃C₂. Hence, according to theory, Cr₂₃C₆ is most likely to precipitate between 700°C and 900°C. This finding is indirectly supported by the work of Thomson and Bhadeshia who showed that M₂₃C₆ was the most stable carbide throughout the temperature range of 400°C to 800°C in a 12wt% Cr steel. Therefore, it is reasonable to deduce that Cr₂₃C₆ is the most stable chromium carbide that will develop between 700°C and 800°C in a 12wt% Cr steel.

Nevertheless, experimentally it appears that the form of carbide that develops during heat treatments between 700°C and 800°C is still a contentious issue amongst researchers. Prozzi et al. found that tempering a 11.5wt% Cr steel at 600°C and 750°C, yielded precipitates (determined by electron diffraction) of the form M₂₃C₆, thereby concurring with theory. However, Mecozzi et al. found that tempering treatments at 680°C yielded only (Fe,Cr)₃C precipitates and made no mention of the
presence of $M_{23}C_6$ precipitates. The existence of this conflict is openly acknowledged by Thomson and Bhadeshia\textsuperscript{43}, who agree that the initial phase found following heat treatments at 700°C may be Fe\textsubscript{3}C, even though $M_{23}C_6$ is expected to be more stable at these temperatures. They suggested that this may be due to the precipitates growing by means of \textit{paraequilibrium transformation}\textsuperscript{44}.

A \textit{paraequilibrium transformation} is when a local equilibrium is not maintained at the phase boundary due to the substitutional elements not segregating to a specific phase. Only the interstitial carbon diffuses across the phase boundary\textsuperscript{45}. This elemental partitioning taking place during a \textit{paraequilibrium transformation} is illustrated in Figure 2.14.

\textbf{2.3.1.2 PRECIPITATE FORMATION}

Irvine \textit{et al}.\textsuperscript{25} gives a good account of the precipitation in a 12wt\% Cr-0.1wt\% C steel upon tempering at progressively higher temperatures, which further corroborates the relationships shown in Figure 2.13.

At 300°C, precipitation of Fe\textsubscript{3}C or cementite (precipitated between martensitic plates) occurs which leads to a slight drop in hardness due to the carbon being removed from solution. As the temperature is increased further, more elements are able to diffuse and subsequently, other alloy carbides form. This is explained by the other elements' diffusion coefficients ($D$) increasing with temperature according to the Arrhenius-type equation\textsuperscript{46}. 

in which $D_o$ is a material constant, $Q$ is the activation enthalpy (energy of formation), $T$ is the absolute temperature and $R$ is the molar gas constant.

At higher temperatures the Fe$_3$C redissolves during the formation of other fine matrix precipitates. These precipitates are mainly $M_7C_3$ (Cr$_7$C$_3$) and some $M_2X$. Cr$_7$C$_3$ is formed by the separate nucleation of Fe$_3$C transforming *in-situ* to Cr$_7$C$_3$.$^{25}$ The $M_2X$ is most likely based on Cr$_2$C, although with high additions of nitrogen, the $M_2X$ could very likely be in the form Cr$_2$N, and this could form preferentially to Cr$_7$C$_3$. $M_2X$ could be stabilised preferentially with the use of molybdenum or vanadium additions.$^{47}$ Vanadium carbides are however more stable than molybdenum carbides, which are more readily dissolved at lower temperature.$^{27}$ This can be readily verified by referring to Figure 2.13. As explained in section 2.2.3.1, an increase in carbon will result in an increase in the carbides present, which includes the Cr$_7$C$_3$ and Cr$_2$C precipitates.$^{25}$ At higher tempering temperatures ($500^\circ$C +), larger carbides of the form $M_{23}C_6$ develop on the martensite laths and prior austenite and ferrite grain boundaries.$^{23}$

**Figure 2.15**: Alloy contents as a function of temperature in carbides of a 12wt% Cr steel.$^{43}$
If the tempering temperature is increased further, the $\text{M}_{23}\text{C}_6$ coarsens at the expense of the $\text{M}_7\text{C}_3$ and $\text{M}_2\text{X}$ precipitates. The $\text{Cr}_7\text{C}_3$ precipitates change from coherent to incoherent and finally spheroidise.

Carbon removal due to the $\text{Cr}_7\text{C}_3$ precipitates' coarsening causes pronounced softening. Work by Wang and Chen has also shown that an increase in carbide size will cause a reduction in the toughness of a 0.1 wt% carbon steel. For a 12 wt% Cr steel, the equilibrium solution temperature of the carbides was found to be 950°C, although the time at temperature was found to play a significant role.

Thus, the general concensus is that precipitation in a 12 wt% Cr steel occurs in the sequence:

$$\text{M}_7\text{C}_3 \rightarrow \text{M}_7\text{C}_3 \rightarrow \text{M}_{23}\text{C}_6$$

### 2.3.1.3 SECONDARY HARDENING

The formation of the alloy carbides may be accompanied by a marked increase in strength. This phenomenon is known as secondary hardening and is seen in 12 wt% Cr steels with additions of molybdenum, vanadium, titanium, nickel, manganese and carbon, all in varying degrees. Secondary hardening can also appear in 3CR12 as evidenced by Figure 2.16. The secondary hardening process occurs when the coarser $\text{Fe}_3\text{C}$ precipitate is replaced by finer alloy precipitates (as discussed in section 2.3.1.2) and the precipitates reach a critical dispersion parameter. Simultaneously the steel attains its maximum strength. Thereafter the alloy carbide coarsens and so the steel's strength declines.

This phenomenon is often represented in the form of a time-temperature parameter (Holloman-Jaffe Parameter) vs. hardness graph, which will feature extensively in later chapters. The reasons for tempering curves (illustrating secondary hardening) being represented in this format were given by Holloman and Jaffe as follows:

- Conventional tempering response curves (hardness as a function of tempering temperature for a single time) were of limited use, as tempering times varied in
practical. Thus a method of converting tempering curves from one time to another would be advantageous.

- In determining the tempering treatment for a given metal, it would be advantageous to temper the metal at a higher temperature for a shorter period of time.

- In order to avoid tempered martensite embrittlement (refer to the following section), it would be more convenient to be able to determine in advance what tempering times are required for a certain hardness when annealing at a higher temperature.

Holloman and Jaffe formulated a parameter\(^50\) \((P)\) known as the Holloman-Jaffe Parameter, which is both time and temperature dependant. It is represented by the equation:

\[
P = T \cdot (C + \log t)
\]

in which \(T\) is the absolute temperature and \(t\) is the tempering time in seconds. The constant, \(C\), was found to have a value of approximately 20 for alloy steels\(^1\), and earlier work on 12wt% Cr steels used this value\(^25,27\). However, Prozzi \textit{et al.}\(^34\) showed that a value of 12 (from work by Rickett \textit{et al.}\(^51\)) was better suited for 3CR12.

2.3.2 MARTENSITE’S RESPONSE TO ANNEALING

2.3.2.1 TEMPERED MARTENSITE EMBRITTLEMENT

A problem resulting from the annealing/tempering of martensite is that of tempered martensite embrittlement (TME)\(^18,52,53\). TME (also known as “350°C embrittlement”, “500°F embrittlement” or “one-step embrittlement”)\(^53,54\) is the uncharacteristic drop in toughness of a steel due to a tempering treatment. This phenomenon occurs in some alloy steels as a result of tempering at approximately 350°C and can be detected by a sharp decrease in impact energy and/or an increase in the DBTT\(^53\). The failure mode was also found to change from ductile to brittle\(^52\). It has been widely accepted that TME is associated with impurity segregation at prior austenite grain boundaries or ferrite-carbide interfaces, and the replacement of the \(\varepsilon\)-carbide (hcp structure)\(^55\) with
Several theories have been proposed to explain TME\textsuperscript{52,56}, but according to Ghosh \textit{et al.}\textsuperscript{53}, a clear theory has yet to be found.

TME is not expected to develop in 3CR12 as the Ac\textsubscript{1} (and hence annealing temperatures) of 3CR12 are considerably higher (± 400°C higher) than the temperature range in which TME occurs. Secondly, \varepsilon-carbide is found to develop only in steels with carbon contents of 0.3wt\% or higher\textsuperscript{18} - 3CR12 is a low carbon steel of approximately 0.02wt\% carbon.

\subsection*{2.3.2.2 ANNEALING/TEMPERING RESPONSE}

Observations of the effects of individual elements on the annealing response of 12wt\% Cr steels or 3CR12 have already been discussed in section 2.2.3. Clearly steels alloyed with elements that promote a more rapid transformation of martensite to ferrite and carbides will exhibit a low tempering resistance, i.e. these alloys will soften more quickly.

An interesting finding noted by Kosikiniemi \textit{et al.}\textsuperscript{22} was that a 12wt\% Cr steel with higher rolling temperatures softened considerably slower than the same steel with a lower rolling temperature when undergoing similar annealing treatments. No attempt was made by the authors to explain this finding. A possible explanation for their observation may be found in the work of Andrews\textsuperscript{57}, who showed that austenite's chemical composition remains unchanged during cooling, and that the M\textsubscript{s} depends on the chemical composition of austenite. Similar observations were made by Alvarez \textit{et al.}\textsuperscript{28}, who found that a steel's hardenability (and thus M\textsubscript{s}) does not necessarily depend on the steel's nominal composition, but rather the austenite composition at a given heating temperature (i.e. the austenite composition changes at different soaking temperatures). The finding of Alvarez \textit{et al.} is fairly logical if one takes account of the Arrhenius-type equation\textsuperscript{46} - with increasing temperature, there is an increase in elements' diffusion coefficients.

Therefore, if austenite phases of different compositions (due to different soaking temperatures) were cooled until eventually transforming to martensite, there is a real possibility that the resulting martensite composition may vary, due to differences in
the initial austenite composition from which it developed (recall that the austenite compositions remain unchanged throughout cooling). Upon annealing, these different compositions of martensite may temper at different rates. Put more succinctly, the austenite composition (and possibly the martensite composition) is determined by the average soaking temperature.

A strong model was proposed by workers\textsuperscript{58} attempting to model the tempering characteristics of 3CR12. It was observed that during annealing there was a clear trend in terms of tempering resistance or tempering response. The softer the steel prior to annealing, the slower the tempering response would be. Conversely, the harder the steel, the more rapid the tempering response would be, i.e. the steel would soften faster. These observations are shown in Figure 2.16.

Their explanation, based exclusively on physical mechanisms, deduced that the harder 3CR12 (which had experienced higher cooling rates following hot rolling, and consequently had more martensite present in the microstructure) had a more highly strained martensite with a higher dislocation density. This provided a greater driving force (than in the softer 3CR12) for the decomposition of martensite to ferrite and carbides. Likewise, the ferrite phase in the harder 3CR12 was also more highly strained than its slower cooled counterpart phase, and as a consequence was more likely to undergo recrystallisation.

![Figure 2.16: Graph showing how 3CR12 with a higher initial hardness softens quicker than 3CR12 with a lower initial hardness\textsuperscript{58}](image-url)
Apart from the tempering curves shown in Figure 2.16, there was unfortunately no further evidence to support this deduction. Ideally this work could have been supported by electron microscopy which would have produced a qualitative comparison of the density and nature of the dislocations, thereby vindicating their explanation.

Dislocation density can however be compared quantitatively as shown by Dolzenkov\textsuperscript{59}. Dolzenkov's work on a low carbon steel confirmed that an increase in the coercive force of a material was indirect evidence of the increase in dislocation density of a steel. This was based on earlier work by Gertsriken \textit{et al.}\textsuperscript{60}, who showed that the coercive force of a material was proportional to the square root of the average dislocation density.

Although a graph of time vs. hardness is the most commonly-used form of presenting the tempering characteristics of a steel, it has been shown (section 2.3.1.3) that there are other means\textsuperscript{50} of displaying the results. Nevertheless, these methods always rely on data from hardness tests. Performing hardness tests is time-consuming and expensive, as many data points are required to give a continuous indication of the tempering characteristics of a steel. Work by Cheng \textit{et al.}\textsuperscript{61} has shown that dilatometry could be used as a relatively inexpensive means of evaluating the tempering response of an iron-nitrogen martensite in steel.

Dilatometry involves the study of the change in length (and therefore volume) of a material as a function of temperature. As phase transformations involve the reordering of atoms into different crystal structures, and these changes in crystal structures are generally accompanied by a change in volume, it stands to reason that dilatometry can be used to detect phase transformations.

It has been mentioned earlier that 3CR12 is a dual phase steel of ferrite and martensite and section 2.3.1 describes in detail why there is a large driving force for martensite to decompose into ferrite and carbides\textsuperscript{34}. Therefore, if 3CR12 is annealed, the martensite will decompose into a mixture of ferrite and carbides (the carbides are discussed in greater detail in section 2.3.1.2). The decomposition of the martensite is a phase
transformation and consequently will be detectable by a dilatometer. Furthermore, the rate of change in length is related to the transformation kinetics. If there is a sudden change in length a massive transformation will be occurring, whereas if there is a relatively small change in length, the transformation kinetics are very slow.

This method is very powerful as it does not require continual operator input and furthermore, gives a continuous indication of the tempering response of a steel, compared to the discrete intervals yielded by hardness tests.

2.3.3 DYNAMIC SOFTENING MECHANISMS

By 1970 it had been established that there were two distinct mechanisms that reduced dislocation density during hot working, viz. dynamic recovery and dynamic recrystallisation.

2.3.3.1 DYNAMIC RECRYSTALLISATION

Recrystallisation normally occurs in alloys with a low stacking fault energy (SFE) and involves the massive elimination of dislocations by the motion of a high angle grain boundary. Dynamic recrystallisation is generally preceded by dynamic recovery (which reduces dislocation density by annihilation and the formation of subgrains) and the subsequent transformation of subgrains into high angle grain boundaries. Consequently, dynamic recrystallisation plays a major role in the softening of a steel and the formation of a steel's grain structure.

Dynamic recrystallisation occurs when a critical strain is reached due to there being inadequate recovery (whereas McQueen et al. states that dynamic recovery operates independently of strain). The dislocated structure must also be sufficiently dense, such that new grains can nucleate. This critical strain increases as the steel grain size increases and will accelerate the rate of softening. The new grain growth will cause a refinement of the grain size and a subsequent improvement in the steel's ductility. Nucleation of new grains then takes place along grain boundaries due to the higher dislocation densities present. When the nucleation sites at the original grain boundary are exhausted and these grains have reached their full size, a
‘necklace’ of newly nucleated grains appears around the original grain. The recrystallisation then continues by means of a 'cascade' of successive layers moving inwards until the new grains impinge upon each other at the centre of the original grain\textsuperscript{62,64}.

2.3.3.2 SECOND PHASE PARTICLES AND RECRYSTALLISATION

Although the formation of recrystallised grains should lead to the development of dislocation free grains (section 2.3.3.1), Tua et al.\textsuperscript{65} observed a higher-than-expected dislocation density in recrystallised grains. It was suggested that the creation of these dislocations may have been due to the movement of the recrystallisation interface as it moved over carbide particles.

Gladman\textsuperscript{66} classified the effects of second phase particles into three groups:

- Coarse particles such as spherical Fe\textsubscript{3}C (1 - 2\textmu m Ø) cause a general acceleration in recrystallisation. This can be attributed to favoured nucleation on the carbide itself and implies that the critical nucleus size is smaller than that of the carbide\textsuperscript{66}.
- Intermediate-size particles (20 - 30nm Ø) were found to have little effect on the recrystallisation kinetics, possibly because the particle was too small to provide an effective nucleation site\textsuperscript{66}.
- Fine particles (2 - 3nm Ø) were found to retard recrystallisation kinetics. These particles were also found to retard recovery, by inhibiting the formation of low angle grain boundaries\textsuperscript{62,66} by means of a 'pinning' mechanism, thereby preventing grain boundary migration\textsuperscript{66}.

2.4 HEAT TRANSFER

The necessity of including a subject not too readily associated with Materials Engineering will become apparent in later chapters. Owing to the author’s initial unfamiliarity with the subject, and for the subsequent calculations and discussion to be clear, a review of heat transfer theory is necessary.
2.4.1 BACKGROUND

Defined simply, heat transfer is the transfer of energy (heat) as a result of a difference in temperature. Knowledge of heat transfer permits the accurate prediction of a material's temperature as a function of time under certain specified conditions. As there are many inaccuracies associated with thermocouple usage in industry, this approach offers great potential. There are three physical mechanisms or modes that constitute heat transfer, viz. conduction, convection and thermal radiation. In a typical furnace all three of these modes of transfer may occur to varying degrees.

2.4.1.1 CONDUCTION

If a temperature gradient exists in a body, heat will flow from a high temperature to a low temperature region. This mode of heat transfer will only take place within a medium, or between different media that are in direct physical contact. It is the only mode of heat transfer in solids. The basic law of conduction, known as Fourier's Law, states:

\[ q = -kA \frac{\partial T}{\partial x} \]

in which \( q \) is the rate of heat transfer, \( k \) is a constant known as the thermal conductivity, \( A \) is the surface area and \( \partial T/\partial x \) is the temperature gradient.

Conduction may be subdivided into steady-state (temperature gradient and thus heat flow does not vary with time) and unsteady-state (temperature gradient and thus heat flow does vary with time) conditions. Clearly, a metal sample when placed in a furnace (already at a higher equilibrium temperature) experiences unsteady-state conduction, as the sample's temperature will increase with time. However, one must also account for the temperature gradients that exist within the metal sample (otherwise there would be no heat flow out to the sample's surface). The mathematics now becomes overly complex, and a simpler solution (even if slightly less accurate) is needed. The solution is known as the lumped-heat-capacity method.
The lumped-heat-capacity method assumes a material has zero internal thermal resistance, or conversely, infinite thermal conductivity. Therefore, no temperature gradients will exist within the sample and the sample's temperature will be uniform throughout. The mathematics required now becomes simpler. Provided certain criteria are fulfilled (criteria beyond the scope of this review), this method will yield results with an acceptable accuracy\textsuperscript{67,68}.

Employing this method, for a cube of side $a$, its temperature $T$, at time $t$ becomes:

$$\frac{T - T_\infty}{T_i - T_\infty} = \exp^{-(6h / a p c)t}$$

in which $T_i$ and $T_\infty$ are the start and finish temperatures, $p$ and $c$ are the density and specific heat of the metal, and $h$ is the heat transfer coefficient\textsuperscript{68}.

### 2.4.1.2 CONVECTION

If there was no fluid (in this case, air) movement whatsoever, all heat transfer would be due to conduction. However, if there is any fluid movement, convection heat transfer occurs. Convection, which is the most important form of heat transfer between a solid and a fluid, can be subdivided into free convection and forced convection. Free (or natural) convection arises when density gradients formed by heat transfer cause fluid flow when acted upon by gravity. This form of convection occurs in a conventional furnace. Forced convection arises when an external force blowing across a surface results in fluid flow. The fluid flow in both cases causes changes in the temperature gradient, and thus heat transfer rates as explained by Newton's Law of Cooling:\textsuperscript{67,68}

$$q = h \cdot A \cdot (T_w - T_\infty)$$

in which the heat transfer coefficient, $h$, is determined by the fluid flow's properties (which is beyond the scope of this review).
2.4.1.3 THERMAL RADIATION

Heat transfer due to radiation is determined by the emitting body's temperature and encompasses wavelengths between $10^{-7}$ m and $10^{-4}$ m. This form of heat transfer does not require a carrying medium and can therefore occur in a vacuum. If the heated sample absorbs heat, yet reflects none, it is known as a blackbody. In most cases, however, the materials' emissivity ($\varepsilon$) or 'greyness' must be accounted for, as most materials are not perfect blackbodies. Furthermore, radiation only travels in straight lines, and so a shape or 'view' factor must also be incorporated so as to account for heat loss in this manner. Thus, thermal radiation can be accounted mathematically by:

$$q = F_e \cdot F_G \cdot \sigma \cdot A \cdot (T_i - T_e)^4$$

in which $F_e$ is the emissivity factor, $F_G$ is the shape factor, and $\sigma$ is the Stefan-Boltzmann constant.$^{67,68}$

2.4.2 HEAT TRANSFER APPLICATIONS

Remarkably few papers have dealt with the utilisation of heat transfer for annealing applications. Using the lumped-heat-capacity theory described in section 2.4.1.1, Smith and van Warmelo$^{58}$ developed an empirical model which accurately predicted the temperature of 3CR12 plates whilst undergoing roller hearth annealing.

![Figure 2.17: Comparison of empirical and theoretical data for 8mm plate in roller hearth annealing furnace$^{58}$](image)
By combining this empirical model with the 3CR12's tempering curves, they developed a model which could predict the final hardness of hot-rolled 3CR12 plates during annealing. The model's predictive capabilities also permitted modification of the annealing parameters for commercial production of 3CR12. This resulted in an increase in line speeds and a significant drop in the unacceptable material produced.58

Figure 2.18: Example of output from Smith and van Warmelo's model for a plate quenched from 900°C 58
3. EXPERIMENTAL TECHNIQUES

3.1 EXPERIMENTAL ALLOYS

3.1.1 ALLOY COMPOSITION

Three different compositions or heats of 3CR12 were produced by Columbus Stainless in 1996/1997 for this research. The nominal compositions (in wt%) of the 3CR12 alloys studied are shown in Table 3.1 below:

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<thead>
<tr>
<th></th>
<th>Alloy A</th>
<th>Alloy B</th>
<th>Alloy C</th>
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</tbody>
</table>

Table 3.1: Nominal Compositions of 3CR12 alloys

3.1.2 ALLOY PRODUCTION

Following casting, the cast ingots of each heat were subjected to a homogenisation treatment comprising a two hour soak at 1230°C. The function of the homogenisation treatment was to remove dendrite growth, resulting from the ingots’ casting, and to form an equi-axed grain structure. The ingots were hot-rolled following their removal from the homogenisation furnace. Each ingot was rolled to a final gauge of
approximately 10mm, by means of a 25% reduction in gauge per rolling pass. The last pass temperatures of each heat (measured with a pyrometer) were approximately 1030°C. Directly following hot rolling, the plates were cooled in one of three different media, viz. water, air or fibrefrax*. The function of the air and fibrefrax cooling was to emulate the cooling rates that would be experienced in different locations of a commercially produced coil of hot-rolled 3CR12. The insulatory nature of the fibrefrax enabled plates cooled in it to experience the slowest cooling rate. Water quenching was performed in order to expand the experimental matrix.

![Figure 3.1: Graphic illustrating the laboratory production route of the alloys](image)

### 3.2 METALLOGRAPHY

#### 3.2.1 OPTICAL MICROSCOPY

Optical microscopy was performed with a Reichert MeF3-A light microscope. Specimen preparation involved mounting specimens in a thermoplastic resin and grinding them to a 4000 grit finish. The ground specimens were then polished with a SiO₂ suspension to a surface finish of +/- 0.01μm Rₐ prior to etching. Nine etchants used in previous studies of 3CR12 were evaluated by the author in an earlier report[^69]. The two etchants found to be most effective in revealing phase contrasts of the 3CR12 alloys of interest, were selected for use in this thesis. These etchants were:

[^69]: A furnace wool, produced by Cumar Resistant Materials.
Experimental Techniques

Etchant A:
3g $K_2S_2O_5$ (potassium metabisulphite)
1.5g $NH_2SO_3H$ (sulphamic acid)
0.75g $NH_4F.HF$ (ammonium biflouride/ammonium hydrogen diflouride)
100ml distilled water
(specimen dip-etched for approximately 3 seconds)

Etchant B:
100ml of 1:5vol/vol HCl
2g $NH_4F.HF$ (ammonium biflouride/ammonium hydrogen diflouride)
1g $K_2S_2O_5$ (potassium metabisulphite)
(specimen dip-etched for approximately 10 seconds)

Specimens etched in Etchant A were generally studied using Bright Field, as a clear phase contrast could be seen without the need for a distinction in relief. Nomarski Interference Contrast was used when specimens etched in Etchant B were studied, as only relief contrast was provided by this etchant. Transverse sections of the specimens were studied, as the ‘pancake-like’ wrought microstructure is clearer when viewed from this position.

3.2.1.1 VOLUME FRACTION ANALYSIS (VFA)

X-ray diffraction analysis (XRD) is arguably the most effective means of determining the martensite content of steels\textsuperscript{70}. Compared to the conventional means of VFA by optical microscope, XRD is less time consuming and more accurate. The claim that VFA is less accurate stems from work\textsuperscript{71} showing that strain-induced martensitic laths were too small to be resolved individually by using an optical microscope. Consequently VFA would indicate the presence of greater quantities of martensite than actually present. Unfortunately, XRD cannot discern between ferrite and martensite in 3CR12 (owing to similarities in their crystal structures)\textsuperscript{72}, thus VFA employing optical microscopy was the only technique that could be used to determine the martensite content. Volume Fraction Analysis was performed on the 3CR12 alloys using a Joyce-Loebel image analyser based in the Electron Microscope Unit at the University of Cape Town. A minimum of 29 micrographs at 100x magnification
of each specimen were processed and analysed by the image analyser. Figure 3.2 illustrates how an ordinary micrograph (Figure 3.2a) is processed by the image analyser into an image (Figure 3.2b) consisting of regions of black (martensite) and white (ferrite), which can then be analysed.

3.2.2 SCANNING ELECTRON MICROSCOPY (SEM)

Scanning electron microscopy was performed with a Cambridge S200 SEM equipped with a Tracor Northern TN5400 energy dispersive x-ray microanalyser. Specimens were sputter-coated with an Au-Pd coating prior to their examination by the SEM in the secondary electron mode at an acceleration voltage of 20kV.

3.3 MECHANICAL TESTING

3.3.1 TENSILE TESTING

Tensile tests were performed using a computer-controlled Zwick 1484 Universal Tensile Tester equipped with a digital extensometer. Tests were performed at room temperature with a strain rate of $10^{-3}$ s$^{-1}$. The specimens' dimensions complied with ASTM E8M for substandard size round tensile specimens. The specimens' gauge length was 25mm with a diameter of 5mm. The tensile axis was in the rolling
direction. Owing to the large size of the experimental matrix, only two samples of each condition were tested.

3.3.2 IMPACT TESTING

Charpy impact tests were performed with an Avery Impact Tester on samples in the hot-rolled and annealed conditions. All tests were performed at room temperature with an initial energy of 294J. The specimens’ dimensions complied with ASTM E23 for substandard size specimens. Notches were made in the T-L orientation and a minimum of three samples were tested for each condition of the alloys.

![Rolling Direction](image)

Figure 3.3: Charpy V-Notch specimen orientation and dimensions (in mm)

3.3.3 MACRO- AND MICROHARDNESS TESTS

Microhardness tests were performed under a load of 10gf with a Matsuzawa MXT-α7 Microhardness Tester using a Vickers Indentor. Macrohardness tests were performed under a 30kgf load with an Eseway SPVR.2.M Hardness Tester, also using a Vickers Indentor. All macro- and microhardness tests were performed at room temperature on samples mounted in a thermoplastic resin. A minimum of five tests were performed on each sample to gain macro- and microhardness values.

3.4 DIFFERENTIAL THERMAL ANALYSIS (DTA)

Differential thermal analysis was performed with a computer-controlled Netzsch DTA. The 3CR12 specimens were heated to 1000°C at a rate of 10°C.min⁻¹ in a nitrogen/argon atmosphere. Al₂O₃ was used as the reference sample.
3.5 DILATOMETRY

3.5.1 BACKGROUND

Dilatometry was performed with a low thermal mass dilatometer that had originally been constructed in the Materials Engineering Department at the University of Cape Town. The dilatometer's temperature was measured by means of a K-Type thermocouple. Extension was measured by an analogue Linear Variable Differential Transducer (LVDT). Data had originally been captured from the LVDT and thermocouple by means of a chart recorder. This method was not ideal owing to obvious inaccuracies and inefficiencies associated with the output being in the form of a single hard copy. A previous worker had attempted to partially capture data from the dilatometer by using a computer, but this approach was not entirely successful. Therefore, a new approach using only a computer to capture and process data was required.

Another limitation of the dilatometer was that its maximum achievable cooling rate was approximately 2°C.min⁻¹. This cooling rate was not satisfactory for the creation of continuous cooling transformation (CCT) diagrams, which require a range of cooling rates that can exceed 50°C.min⁻¹. Therefore, some form of forced cooling of the specimen was required.

It was further observed that the analogue LVDT was prone to 'drifting' over long periods of time, thereby yielding erroneous results. 'Drifting' (an inherent problem in analogue LVDTs) is an unpredictable shift in one direction only (i.e. positive or negative) of an LVDT's output. 'Drifting' would not affect the determination of transformation temperatures during continuous heating or cooling, as temperatures (measured by thermocouple) would be unaffected. 'Drifting' would, however, seriously affect the output of isothermal annealing tests when attempting to measure with the LVDT, the change in length over long periods of time. This problem could not be resolved using the existing equipment.
3.5.2 UPGRADING OF DILATOMETER

TestPoint™ v.3 programming language by Capital Equipment Corporation was used by the author to create a data acquisition program for use on the dilatometer. The resulting Windows-based program, DilaData (refer to Appendix A for a program listing), enables an operator to control the sampling frequency, and whether or not the data is to be saved to file (text format). If saved to file, the data can be manipulated with the use of a spreadsheet. During a test, the elapsed time, extension and temperature, are presented real-time on digital displays and also in the form of two graphs, extension vs. temperature and time vs. extension. Analysis of these graphs for developing trends etc. is possible during a test. In a calibration test, temperatures measured by DilaData in the range 10°C to 1000°C were accurate to within 2°C.

A vacuum-tight cooling line was installed in the dilatometer. The cooling line allowed an inert gas such as helium or argon to be pumped into one end of the specimen chamber and exhausted via an outlet on the opposite end. This modi-
fication increased the cooling rate of the dilatometer from $2^\circ\text{C}.\text{min}^{-1}$ to over $90^\circ\text{C}.\text{min}^{-1}$.

The analogue LVDT was replaced with a Federal Products Co. MAXIMUM digital transducer. The new digital transducer demonstrated a calibrated accuracy of $1\mu\text{m}$ and was not subject to the 'drifting' which plagued its predecessor. The original aluminium/brass housing for the LVDT was replaced with a new housing of a low expansion alloy, Invar® (64wt% Fe, 36wt% Ni) for the digital transducer. Refer to Appendix B for engineering drawings of the modifications.
The expansion coefficient (\( \alpha \)) of Invar\textsuperscript{®} from 20°C to 100°C is only 1.7x10\(^{-6}\) K\(^{-1}\), compared to approximately 10.4x10\(^{-6}\) K\(^{-1}\) for 3CR12\textsuperscript{75}. As the new transducer housing was in a lower temperature environment than the specimen, and also had a lower expansion coefficient, any expansion of the housing could be considered negligible relative to any 3CR12 expansion.

3.5.3 DILATOMETRY TESTING TECHNIQUES

Dilatometry tests were performed in a vacuum, thereby preventing specimen oxidation. For tests determining transformation temperatures, the specimens (50mm x 2mm x 2mm) were heated to 600°C at 20°C.min\(^{-1}\) and thereafter at 1°C.min\(^{-1}\) to 1000°C through the zones of transformation. The 20°C.min\(^{-1}\) heating rate was employed in order to reduce the tests’ duration.

When an alloy’s temperature reaches the \( A_{c1} \), a transformation from (alpha) ferrite to austenite begins, with the maximum austenite content occurring at temperature \( \gamma_{\text{max}} \). If the temperature is increased further, the austenite begins to decompose to a (delta) ferrite phase. This transformation is completed at the \( A_{c5} \), yielding a fully (delta) ferritic phase. As a result, dilatometric curves do not exhibit a sudden change in gradient at the \( A_{c1} \), \( \gamma_{\text{max}} \) or \( A_{c5} \), but rather a gradual change in gradient due to the gradual phase transformations.

![Figure 3.7: Cure's method of determining transformation temperatures](image-url)
Consequently a transformation temperature is not easily determined and a technique suggested by Curé\textsuperscript{76} was employed to estimate the transformation temperatures. Using this technique, the onset at which a curve of temperature vs. extension begins to deviate from linearity would be identified as the transformation temperature. Curé’s technique was used throughout this research to identify the $A_c_1$ and $\gamma_{\text{max}}$. This method is illustrated in Figure 3.7.

For tests in which isothermal annealing was simulated by a dilatometer, specimens were heated at $50^\circ\text{C}. \text{min}^{-1}$ to the desired soaking temperature. The change in extension was then monitored as a function of time. Although the dilatometer was capable of achieving higher heating rates (and thus closer to those used in line annealing), work by Mittemeijer et al.\textsuperscript{77} reasoned that higher heating rates were not advisable. Mittemeijer et al. found that for heating rates exceeding $50^\circ\text{C}. \text{min}^{-1}$, significant temperature gradients would develop in a specimen, thereby leading to erroneous results. As the dilatometric specimens used in this research were of a greater volume than those used by Mittemeijer et al., one would expect the effects due to this phenomenon to be even greater. This led to the decision not to employ heating rates greater than $50^\circ\text{C}. \text{min}^{-1}$.

### 3.6 FURNACE ANNEALING TREATMENTS

Annealing treatments were performed on the alloys in order to simulate batch and line annealing of 3CR12 alloys in industry. Batch annealing is performed at $700^\circ\text{C}$ for approximately 10 hours, excluding several hours of heating and cooling. Line annealing consists of a 15 minute heating step prior to a 2 minute soak at $20^\circ\text{C}$ below the $A_c_1$ of the alloy\textsuperscript{78}. The annealing simulations were performed in a Naber furnace with a built-in temperature controller.

The furnace’s temperature controller was only calibrated in $20^\circ\text{C}$ intervals. It was therefore important to track temperatures of the annealed specimens more accurately. A separate K-Type thermocouple was used to monitor the furnace temperature and maintain the furnace temperature within $5^\circ\text{C}$ of the desired temperature. The furnace
used was incapable of heating specimens to their soaking temperature in the short period of time used for line annealing. Thus it was pre-heated to the soaking temperature before the specimen was placed inside. The same procedure was performed on specimens that were batch annealed. All the specimens were quenched in water following annealing.

Of particular significance (particularly for line annealing simulations) was the time that a specimen would require to reach the soaking temperature in the furnace, known as the 'zero-time'. Although the specimen's temperature could simply be measured with the aid of a thermocouple, it was also decided to compare how accurately heat transfer theory would predict a specimen's temperature. Therefore an investigation was performed concurrently with this work in order to compare empirical data with theory.
4. EXPERIMENTAL RESULTS

4.1 CHARACTERISATION OF AS-ROLLED 3CR12

4.1.1 PHASE PREDICTION REVISITED

As mentioned in section 2.2.2, there are several different techniques available to researchers which allow for the tentative prediction of the phase constitution of a steel with a known chemical composition. The most commonly-used technique for 3CR12 is known as the Kaltenhauser Ferrite Factor Relationship, $F(\alpha)$. More recently its modified form, created by Kaltenhauser and Lefevre $^{20}$, $F(\alpha)'$, has gained acceptance.

<table>
<thead>
<tr>
<th></th>
<th>Alloy A</th>
<th>Alloy B</th>
<th>Alloy C</th>
</tr>
</thead>
<tbody>
<tr>
<td>$F(\alpha)$</td>
<td>13.7</td>
<td>8.3</td>
<td>10.7</td>
</tr>
</tbody>
</table>

Table 4.1: Analysis of the alloys according to Kaltenhauser's Ferrite Factor Relationship, $F(\alpha)$

![Figure 4.1: The predicted phase constitution of the alloys according to Kaltenhauser and Lefevre, $F(\alpha)'$](image)
Table 4.1 shows the values for each alloy as determined by the Kaltenhauser Ferrite Factor Relationship. The alloys' predicted ferrite content in ascending order for the same cooling rate is:

Alloy B, Alloy C, Alloy A.

Therefore, according to the Kaltenhauser Ferrite Factor Relationship, Alloy A is expected to exhibit the most ferrite present in its microstructure, followed by Alloy C and finally, Alloy B.

The modified Kaltenhauser Ferrite Factor Relationship, shown in Figure 4.1, concurs with the prediction made by the Kaltenhauser Ferrite Factor Relationship. The modified relationship also predicts that all three alloys will have (with the same cooling rate) a dual phase martensite + ferrite microstructure. Alloy A's microstructure is expected to be closest to that of a fully ferritic microstructure, while Alloy B's microstructure is expected to be closest to that of a fully martensitic microstructure. Finally, Alloy C is expected to have an intermediate ferrite content relative to the other two alloys. The last deduction can also be made from the Kaltenhauser Ferrite Factor Relationship (Table 4.1).

4.1.2 HARDNESS TESTS

4.1.2.1 MICROHARDNESS TESTS

The results of microhardness tests performed on the martensite phase of the alloys are shown in Figure 4.3. These results indicate that Alloy A's martensitic phase is considerably harder than the martensite in Alloy B or Alloy C. It was not apparent whether Alloy B's martensite was softer or harder than Alloy C's, as differences in hardness between these two alloys fell within the 95% confidence interval* that constituted this research's margin of error.

* A 95% confidence interval implies that one can be (statistically) 95% confident that the average will fall within the given range. Unless otherwise stated, all margins of error featured in this thesis are of this form.
Contrasts in martensite hardness due to different cooling rates following hot rolling were also not discernible in Alloys A or C. However, in Alloy B there does appear to be a clear trend between cooling rate and martensite hardness, as the data points for the two extreme cooling conditions (water quenching and insulatory cooling) fall outside of each other's margin of error. Therefore, for Alloy B, the martensite hardness increases with an increase in the cooling rate following hot rolling. The ferrite phase's hardnesses (Figure 4.4) show little variation between the alloys, with all three alloys' hardnesses ranging between 140HV to 180HV. The only exception is the insulatory cooled form of Alloy B.

![Figure 4.2: Microhardness indents indicating the relative hardness of martensite(α') and ferrite(α) - (Etchant B)](image)

![Figure 4.3: Martensite hardness of the alloys in the as-rolled condition](image)
Experimental Results

There does appear to be a trend present in the ferrite hardness of Alloy C. This trend is similar to that exhibited by the martensite of Alloy B, in that there is a distinct contrast in hardness between the two extreme cooling conditions, i.e. there is an increase in hardness with an increase in cooling rate.

4.1.2.2 MACROHARDNESS TESTS

Macrohardness tests indicate that in all three alloys there is an increase in bulk hardness with an increase in the cooling rate following hot rolling. This is apparent even with the inclusion of the 95% confidence intervals as margins of error. Figure 4.5 overleaf, illustrates that Alloy A is significantly softer than Alloys B or C. The relatively small range of hardnesses due to the different cooling conditions experienced by Alloy B, is also quite noticeable. In Alloy C the range of hardnesses observed, due to the different cooling rates following hot rolling, is considerably larger. Alloy A has an intermediate range of hardnesses relative to the ranges in hardness exhibited by Alloys B and C.
Experimental Results

4.1.3 VOLUME FRACTION ANALYSIS

The 95% confidence intervals which constitute the VFA margins of error are relatively larger than the hardness tests’ margins of error. Therefore there is some overlapping of the VFA margins of error and it is difficult to rank the martensite content based on cooling rates in Alloys A or C, unless one only considers the
Experimental Results

The experimental results show the effects of extreme conditions of cooling (water quenching and insulatory cooling), in which case the martensite content increases with increasing cooling rates. However, Alloy B shows a clear increase in martensite content with increasing cooling rates for all cooling conditions. Alloy A clearly has the lowest martensite content for all cooling conditions, whilst Alloy C exhibits the widest spread of data points, as it did in the macrohardness test results.

### 4.1.4 TENSILE TESTING

For reasons explained in section 3.3.1, the margins of error of the tensile test results in Table 4.2 indicate the standard deviation and not a 95% confidence interval. Usage of a 95% confidence interval for such a small population would result in the margins of error being too large for even general observations to have been made, as this technique is more conservative than the standard deviation.

Alloy A exhibits the lowest UTS and 0.2% proof stress of the three alloys, while its elongation is correspondingly the largest of the three alloys. Alloys B and C show similar UTS values, 0.2% proof stresses and elongations, except in the case of the insulatory cooled form of Alloy C. This condition has a considerably lower UTS and 0.2% proof stress with a higher elongation, which mirrors its low bulk hardness and martensite content values featured earlier.

<table>
<thead>
<tr>
<th></th>
<th>Cooling</th>
<th>UTS (MPa)</th>
<th>0.2% Proof Stress (MPa)</th>
<th>Elongation in 25mm (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Alloy A</strong></td>
<td>Water</td>
<td>501 ± 31</td>
<td>274 ± 15</td>
<td>20 ± 3</td>
</tr>
<tr>
<td></td>
<td>Air</td>
<td>554 ± 4</td>
<td>272 ± 4</td>
<td>26 ± 6</td>
</tr>
<tr>
<td></td>
<td>Insulatory</td>
<td>433 ± 1</td>
<td>235 ± 1</td>
<td>27 ± 9</td>
</tr>
<tr>
<td><strong>Alloy B</strong></td>
<td>Water</td>
<td>878 ± 3</td>
<td>540 ± 23</td>
<td>17 ± 4</td>
</tr>
<tr>
<td></td>
<td>Air</td>
<td>904 ± 1</td>
<td>505 ± 7</td>
<td>19 ± 1</td>
</tr>
<tr>
<td></td>
<td>Insulatory</td>
<td>862 ± 1</td>
<td>432 ± 33</td>
<td>13 ± 1</td>
</tr>
<tr>
<td><strong>Alloy C</strong></td>
<td>Water</td>
<td>898 ± 5</td>
<td>443 ± 22</td>
<td>8 ± 1</td>
</tr>
<tr>
<td></td>
<td>Air</td>
<td>856 ± 6</td>
<td>435 ± 21</td>
<td>16 ± 1</td>
</tr>
<tr>
<td></td>
<td>Insulatory</td>
<td>651 ± 10</td>
<td>304 ± 28</td>
<td>22 ± 2</td>
</tr>
</tbody>
</table>

Table 4.2: Tensile results for the alloys in the as-rolled condition
If one considers only the extreme cases of cooling in each alloy, there is an increase in the UTS and 0.2% proof stress in all three alloys with an increase in the cooling rate. Furthermore, all three alloys show a decrease in elongation in response to an increase in the cooling rate following hot rolling.

### 4.1.5 IMPACT TESTING

The results of the impact tests are presented in Table 4.3. Unlike the results of other tests used to characterise the alloys in their as-rolled condition, there is little difference in toughness between the three alloys, although Alloy B appears to exhibit a slightly higher toughness than Alloys A and C. Alloy C is the only alloy that suggests there may be a relationship between cooling rate and toughness (for extreme cooling conditions only), in that there is a decrease in toughness for an increase in the cooling rate following hot rolling.

<table>
<thead>
<tr>
<th></th>
<th>Cooling</th>
<th>Toughness (J)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Alloy A</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Water</td>
<td>17 ± 2</td>
<td></td>
</tr>
<tr>
<td>Air</td>
<td>22 ± 7</td>
<td></td>
</tr>
<tr>
<td>Insulatory</td>
<td>17 ± 5</td>
<td></td>
</tr>
<tr>
<td><strong>Alloy B</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Water</td>
<td>21 ± 2</td>
<td></td>
</tr>
<tr>
<td>Air</td>
<td>25 ± 8</td>
<td></td>
</tr>
<tr>
<td>Insulatory</td>
<td>17 ± 5</td>
<td></td>
</tr>
<tr>
<td><strong>Alloy C</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Water</td>
<td>17 ± 2</td>
<td></td>
</tr>
<tr>
<td>Air</td>
<td>17 ± 0</td>
<td></td>
</tr>
<tr>
<td>Insulatory</td>
<td>22 ± 2</td>
<td></td>
</tr>
</tbody>
</table>

*Table 4.3: Impact test results for the alloys in the as-rolled condition*

### 4.1.6 MICROSCOPY

The wrought alloys were typified by a banded ferrite and martensite microstructure. Inclusions present in the microstructure were of the 'stringer' form and were identified by energy dispersive x-ray spectroscopy as being MnS inclusions.
Experimental Results

Figure 4.7: Alloy A, water quenched - Typical wrought microstructure of 3CR12 consisting of alternating bands of martensite colonies and recrystallised ferrite (arrowed)

Figure 4.8: Alloy A, water quenched - High angle grain boundaries present in the ferrite phase, indicative of recrystallisation having taken place

Figure 4.9: Alloy A, air cooled - A ferrite grain boundary triple point which has served as a nucleation site for austenite (and subsequently martensite) on cooling

Figure 4.10: Alloy A, insulatory cooled - A 'necklace' of recrystallised ferrite grains on the original ferrite grain boundary. There is a possibility that this 'necklace' could simply be preferential etching in the grain boundary region due to anodic effects.

ROLLING DIRECTION
Figure 4.11: Alloy B, air cooled - This micrograph concurs with VFA by showing a clearly higher martensite content present than in the similarly cooled condition of Alloy A. The only ferrite present in this micrograph is in the form of ferrite stringers.

Figure 4.12: Alloy C, water quenched - Contradicting the VFA, this micrograph shows that this sample has a lower martensite content than the sample in the previous micrograph. This illustrates well the variations in the localised martensite content that can occur in the same sample. Like Alloy B, this alloy also exhibits a higher martensite content than found in Alloy A.

Figure 4.13: Alloy C, air cooled - Typical banded microstructure of wrought 3CR12 (note the arrowed MnS inclusion)

Figure 4.14: Alloy C, insulatory cooled - The dark stripes (lower half of micrograph) in the ferrite phase are prior δ-ferrite, lined on either side by α-ferrite. The α-ferrite grows from the δ-ferrite by means of epitaxial growth, thereby explaining the absence of grain boundaries. It must be noted that the δ-ferrite and α-ferrite constitute one phase (note the arrowed MnS inclusions).

ROLLING DIRECTION
Experimental Results

Figure 4.15: *Alloy C, insulatory cooled* - The high angle grain boundaries are indicative of recrystallisation having taken place.

ROLLING DIRECTION ⇒

Figure 4.16: *Alloy C, insulatory cooled* - This micrograph shows a group of martensite colonies. The prior austenite grain boundaries are clearly visible.

ROLLING DIRECTION ⇒

Figure 4.17: *Alloy C - SEM image of a Charpy impact specimen's fracture surface*. This image clearly shows the early stages of crack development in the rolling direction. (Note the different rolling directions for the SEM images).

ROLLING DIRECTION ↑

Figure 4.18: *Alloy C - SEM image showing the presence of both ductile and brittle failure modes as well as the formation of a larger crack due to the combination of smaller cracks*. The arrow indicates the location of a smaller crack that coalesced with the larger crack.

ROLLING DIRECTION ↑
4.1.7 TRANSFORMATION TEMPERATURES

In order to perform annealing treatments, the \( \text{Ac}_1 \) temperature of each alloy was required. These temperatures were determined by means of dilatometry. Although it is acknowledged that the \( \text{Ac}_1 \) of an alloy is inherently due to its composition, a parallel study was performed in order to determine the effects (if any) of thermomechanical processing on the \( \text{Ac}_1 \).

<table>
<thead>
<tr>
<th>Transformation Temperatures (°C)</th>
<th>Alloy A</th>
<th>Alloy B</th>
<th>Alloy C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water Quenched</td>
<td>830 (911)</td>
<td>762 (888)</td>
<td>801 (906)</td>
</tr>
<tr>
<td>Air Cooled</td>
<td>828 (910)</td>
<td>761 (887)</td>
<td>801 (909)</td>
</tr>
<tr>
<td>Insulatory Cooled</td>
<td>831 (916)</td>
<td>766 (886)</td>
<td>797 (909)</td>
</tr>
</tbody>
</table>

Table 4.4: \( \text{Ac}_1 \) and \( y_{\text{max}} \) (bracketed) as determined by dilatometry

Keeping in mind that the accuracy of each transformation temperature measured by dilatometer was \( \pm \) 2°C, Table 4.4 shows that in most cases every transformation temperature due to a specific cooling rate falls within the margin of error of the other cooling conditions' transformation temperatures (of the same alloy). One therefore cannot draw any conclusions regarding the influence of prior cooling rates on the \( \text{Ac}_1 \) by means of dilatometry.

<table>
<thead>
<tr>
<th>( \text{Ac}_1 ) (°C)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Alloy C - Water Quenched</td>
<td>824</td>
</tr>
<tr>
<td>Alloy C - Air Cooled</td>
<td>821</td>
</tr>
<tr>
<td>Alloy C - Insulatory Cooled</td>
<td>814 &amp; 815</td>
</tr>
</tbody>
</table>

Table 4.5: \( \text{Ac}_1 \) as determined by DTA

Measurements of Alloy C's \( \text{Ac}_1 \) temperature by DTA in Table 4.5 shows that the average \( \text{Ac}_1 \) temperature is about 20°C higher when measured by DTA. Furthermore, the accuracy of the DTA measurements was verified as being \( \pm \) 1°C as evidenced by the two readings taken from different samples of Alloy C in the insulatory cooled condition.
4.2 HEAT TRANSFER THEORY

The determination of the 'zero-time' (described in section 3.6) is of great significance to line annealing treatments owing to this treatment's relatively short duration with respect to the 'zero-time'. Batch annealing is not markedly affected by the 'zero-time', due to the use of considerably longer annealing times. For line annealing, if an estimate for the 'zero-time' was too short, the annealing treatment would not soften the steel sufficiently, whilst if the estimate was too long, the annealing treatment would be commercially inefficient, and in some cases could lead to secondary hardening as described in section 2.3.1.3. Although thermocouples can be used to determine the 'zero-time' accurately, it is considerably less time-consuming to calculate (once the relevant equations have been resolved) the 'zero-time' rather than determine it empirically. An interesting spin-off would be the demonstration of how accurately theory compares with empirical data. These were the motivations for this section of work.

Of the three different modes/types of heat transfer, all are expected to occur inside a furnace, with thermal radiation having the least effect. No suitable method could be found that accounted for the combined effects of all three modes. Consequently, calculations were performed separately for conduction and convection heat transfer.

\[ \begin{align*}
\rho &= 7700 \text{ kg m}^{-3} \\
k &= 25 \text{ W m}^{-1} \text{ K}^{-1} \\
c &= 430 \text{ J kg}^{-1} \text{ K}^{-1} \\
\alpha &= 7.55 \times 10^6 \text{ m}^2 \text{ s}^{-1}
\end{align*} \]

**Figure 4.19:** Assumptions of 3CR12 properties for heat transfer calculations

Thermal radiation's influence was considered negligible since the other forms of heat transfer play far greater roles. As the line annealing temperatures for Alloys A and C were 810°C and 780°C respectively, 800°C was selected as the temperature at which
theory would be compared with empirical data. Convection theory was used to determine the heat transfer coefficient, $h$. The heat transfer coefficient, $h$ (of a cube of dimensions given in Figure 4.19 and placed in air at 800°C), was determined to be 13.47 Wm$^{-2}$K$^{-1}$. For a complete explanation of the calculations used, see Appendix C. Continuing to use convection theory, an equation was derived in which the temperature $T$ of the cube could be determined using only time ($t$) as a variable:

$$T = 800 + \{1.0005 \cdot \exp(-8.1 \cdot 10^{-4} \cdot t)\}^3 \cdot (-780)$$

From conduction theory (section 2.4.1.1) an equation for a cube in similar conditions is also given in the literature:

$$\frac{T - T_\infty}{T_i - T_\infty} = \exp\left(-\frac{6h}{\sigma \rho c}t\right)$$

Comparing the output of these two equations (both with $h = 13.47$ Wm$^{-2}$K$^{-1}$) with empirical data in Figure 4.6, it is apparent that theory predicts a considerably longer 'zero-time' than in reality. This was expected as both equations only accounted for one mode of heat transfer and not two or three. If however, $h$ is increased, this is akin to accounting for the other modes of heat transfer. Therefore, by means of iteration of the equation for conduction heat transfer, it was determined that $h = 85$ Wm$^{-2}$K$^{-1}$.
Using this value, the derived equation yielded a theoretical determination of the 'zero-time' that was almost identical to the empirical 'zero-time'. This is shown by Figure 4.21, which also shows that the 'zero-time' is approximately five minutes.

### 4.3 CHARACTERISATION OF ANNEALED 3CR12

#### 4.3.1 HARDNESS TESTS

Following the determination of the 'zero-time' and the $A_{c_1}$ of each alloy, the alloys were subjected to annealing treatments at the following temperatures:

- Alloy A at 810°C (from $A_{c_1}$ - 20°C)
- Alloy B at 700°C
- Alloy C at 780°C (from $A_{c_1}$ - 20°C)

It must be noted that the 'zero-time' (five minutes) is not included in any of the graphs presented in this section. Furthermore, to prevent any confusion, the 'response' (to annealing treatments) refers to the change in hardness over the test duration, i.e. $\Delta \text{HV/time}$, not $\text{HV/time}$. If the latter were true, the insulatory cooled conditions...
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would always 'respond' faster to annealing treatments, due to their lower starting hardness. Usage of the term ΔHV/time means that the cooling condition that undergoes the largest drop in hardness during annealing (no matter what its starting hardness was) will be seen as having the faster 'response'.

![Figure 4.22: Alloy A at 810°C](image)

It is quite apparent from Figure 4.22 that the water quenched condition of Alloy A responds faster to the annealing treatment than the air or insulatory cooled conditions.

![Figure 4.23: Alloy B at 700°C](image)
In the insulatory cooled condition, there is a very small drop in the alloy’s hardness, whereas in the water quenched condition, there is a decrease of about 20HV. The slight differences in hardness between the starting hardesses in Figure 4.22 and the hardesses given in Figure 4.5 are due to softening occurring during the ‘zero-time’. Alloy A became completely soft after 40 minutes. The slight increase in hardness at four minutes may be attributed to secondary hardening, which was discussed in section 2.3.1.3.

Figure 4.23 shows that Alloy B softens considerably slower than Alloy A, and only becomes completely soft after four hours at temperature. There was very little change in the alloy hardness for the duration of the ‘zero-time’, cf. Figure 4.5. In the water quenched condition this alloy appears to soften faster than in its air cooled condition. The difference in response between the different cooling conditions is not as marked as in Alloy A. At the termination of the test all the differently cooled conditions have very similar final hardesses. This behaviour was also displayed by Alloy A.

Owing to the higher starting hardness of the differently cooled conditions of Alloy C, the annealing response of this alloy is clearest of the three alloys tested. From Figure 4.24, the response of the differently cooled forms of Alloy C are, in ascending order: insulatory cooled, air cooled, water quenched.
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This concurs with the responses shown by Alloy A. Reductions in the alloys' hardness during the 'zero-time' also follow the above sequence, to which Alloy A again shows the greatest reduction in hardness. The final hardnesses of the differently cooled forms of Alloy C, as was the case for Alloys A and B, are very similar, despite the different starting hardnesses. Alloy C became fully soft after approximately 40 minutes at temperature.

Figure 4.25 illustrates, with the benefit of more data points than shown in Figure 4.24, a more complete softening curve for Alloy C (water quenched condition) when it is annealed at 780°C.

![Figure 4.25: Continued annealing leading to a plateau in the softening curve](image)

4.3.2 TENSILE TESTING

The results of tensile tests performed on the alloys following their respective annealing treatments are presented in Table 4.6 overleaf.

Alloys A and C show little difference in UTS, 0.2% proof stress and elongation values between the different cooling rates. The only exception is the air cooled condition of Alloy A, which exhibits a higher UTS and 0.2% proof stress than other conditions of
Experimental Results

this alloy. However, the elongation is similar. Consequently, there is no prevailing trend between cooling rate and UTS/0.2% proof stress/elongation following the annealing treatments in either Alloy A or C.

<table>
<thead>
<tr>
<th>Annealing Treatment</th>
<th>Cooling</th>
<th>UTS (MPa)</th>
<th>0.2% Proof Stress (MPa)</th>
<th>Elongation in 25mm (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alloy A</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>900s @ 810°C</td>
<td>Water</td>
<td>418 ± 19</td>
<td>264 ± 9</td>
<td>28 ± 4</td>
</tr>
<tr>
<td></td>
<td>Air</td>
<td>456 ± 4</td>
<td>286 ± 9</td>
<td>30 ± 2</td>
</tr>
<tr>
<td></td>
<td>Insulatory</td>
<td>401 ± 1</td>
<td>253 ± 18</td>
<td>29 ± 5</td>
</tr>
</tbody>
</table>

| Alloy B             |          |           |                         |                        |
| 120min @ 700°C      | Water    | 430 ± 12  | 230 ± 0                 | 22 ± 4                 |
|                     | Air      | 442 ± 9   | 251 ± 2                 | 35 ± 2                 |
|                     | Insulatory | 441 ± 3  | 248 ± 3                | 32 ± 10                |

| 600min @ 700°C      | Water    | 435 ± 8   | 244 ± 9                 | 37 ± 2                 |
|                     | Air      | 428 ± 0   | 238 ± 0                 | 36 ± 1                 |
|                     | Insulatory | 429 ± 2  | 241 ± 4                | 39 ± 2                 |

| Alloy C             |          |           |                         |                        |
| 900s @ 780°C        | Water    | 475 ± 5   | 279 ± 11                | 32 ± 1                 |
|                     | Air      | 463 ± 4   | 274 ± 8                 | 33 ± 1                 |
|                     | Insulatory | 467 ± 9  | 281 ± 2                | 30 ± 2                 |

Table 4.6: Tensile results for the alloys in various annealed conditions

Two different times of annealing were selected for Alloy B, viz. two hours and ten hours, owing to the extended length of the annealing treatment. As was the case with Alloys A and C, there appears to be little variation between the differently cooled forms of Alloy B. The exception is the water quenched condition of Alloy B at two hours, which shows a slightly lower UTS and 0.2% proof strength and a considerably lower elongation. Again, there is no relationship demonstrated between cooling rate and UTS/0.2% proof stress/elongation. Annealing for ten hours has slightly decreased the UTS and 0.2% proof stress further, whilst increasing (very slightly) the elongation.

4.3.3 IMPACT TESTING

Charpy impact tests were performed on the alloys after their respective annealing treatments. The results are shown in Table 4.7 overleaf.
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### Table 4.7: Impact test results for the alloys in the annealed condition

<table>
<thead>
<tr>
<th>Annealing Treatment</th>
<th>Cooling</th>
<th>Toughness (J)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Alloy A</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>900s @ 810°C</td>
<td>Water</td>
<td>21 ± 4</td>
</tr>
<tr>
<td></td>
<td>Air</td>
<td>24 ± 6</td>
</tr>
<tr>
<td></td>
<td>Insulatory</td>
<td>19 ± 3</td>
</tr>
</tbody>
</table>

| **Alloy B**         |         |               |
| 120min @ 700°C      | Water   | 191 ± 26      |
|                     | Air     | 215 ± 36      |
|                     | Insulatory | 232 ± 40 |

|                     | Water   | 232 ± 44      |
|                     | Air     | 251 ± 12      |
|                     | Insulatory | 257 ± 7    |

|                     | Water   | 46 ± 7        |
|                     | Air     | 28 ± 20       |
|                     | Insulatory | 29 ± 7    |

In Alloys A and C, there is little difference in toughness between the differently cooled conditions of each alloy, the exception being the water quenched condition of Alloy C, which exhibits a considerably higher toughness than the differently cooled forms of the same alloy. The excessively large margin of error associated with the air cooled form of this alloy also makes it difficult to determine any prevalent trend. Therefore, there does not appear to be any relationship between cooling rate and impact energies of these two alloys.

There is a very large increase in the impact toughness of Alloy B following its annealing for two hours. These values again increased slightly following the ten hour annealing treatment. In addition, there appears to be a trend based on the cooling rate following hot rolling for both annealing conditions of this alloy, despite the overlapping of the margins of error for this alloy, i.e. the impact toughness decreases with increasing cooling rates.
4.3.4 MICROSCOPY

Figure 4.26: Alloy A, water quenched and annealed at 810°C for 20min. Complete decomposition of the martensite into ferrite and carbides has taken place. The carbides line the prior martensite/ferrite grain boundaries and the inside of what was once the lath boundaries of the martensite phase.

Figure 4.27: Alloy B, air cooled and annealed at 700°C for 30min. The martensite and ferrite phases can still be very clearly discerned, and there is little evidence of carbide precipitation.

Figure 4.28: Alloy C, insulatory cooled and annealed at 780°C for 15min. There has been complete decomposition of the martensite into ferrite and carbides. The latter line what was the ferrite/martensite grain boundary. Darker bands of what was δ-ferrite are lined by lighter α-ferrite bands.

4.3.5 DILATOMETRY

Section 2.3.2.2 discussed how dilatometry has been used in the past to evaluate the response of a steel to isothermal annealing treatments. Nevertheless, usage of this technique is still fairly limited and as far as it can be ascertained, no published literature has employed this technique to compare the annealing response of different alloys. Consequently, in the course of using this novel technique, several problems arose.
- Analogue LVDT's could not be used for this type of work due to electronic drift over extended periods.
- The response of the alloys at high temperatures could not be determined by dilatometry.

The first problem was solved by replacing the analogue LVDT with a digital transducer (as described in section 3.5.2). The second problem was caused by the alloys tempering whilst being heated. The tempering was a result of the dilatometer's relatively slow heating rate of approximately 50°C.min⁻¹. In this section, the term 'response' implies the change in length over time, i.e. Δlength/time, not length/time, for reasons already covered in section 4.3.1.

![Figure 4.29: Alloy B annealed at 700°C](image)

Consequently, for high annealing temperatures, the specimens had already annealed sufficiently such that any differences in the annealing response were undetectable. This meant that the response of the differently cooled forms of each alloy to the annealing treatments were identical. This phenomenon is illustrated by Figure 4.29. As a result, the isothermal annealing had to be performed at lower temperatures in order to slow the transformation kinetics so that any differences in the annealing
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responses were detectable. Polynomial curves were fitted to the data in order to display the prevailing trends more clearly.

![Graph showing experimental results](image)

**Figure 4.30: Alloy A at 600°C**

Owing to the reasons explained above, attempts at measuring Alloy A's dilatometric response to isothermal annealing treatments at temperatures above 600°C were unsuccessful.

At 600°C, however, Figure 4.30 shows that there is a difference in the annealing response of the differently cooled conditions of Alloy A. There is a greater reduction in the length of the water quenched condition, followed by the air cooled and finally the insulatory cooled conditions.

When annealed at a lower temperature (Figure 4.31) Alloy A again illustrates different responses due to differences in the cooling rate, with the same order exhibited in terms of response as in Figure 4.30, where it was annealed at a higher temperature. In Figure 4.31, however, there is an equal difference between the annealing responses of

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*The term $R^2$ displayed in these graphs is the coefficient of correlation which attests to the accuracy of the fitted curve. A value near 0 indicates a poor fit, whilst a value near 1 indicates an excellent fit.*
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Figure 4.31: Alloy A at 500°C

the water quenched and air cooled conditions, and the air cooled and insulatory cooled conditions.

Figure 4.32: Alloy B at 600°C

Alloy B (Figure 4.32) shows a response similar to that of Alloy A to annealing. As the cooling rate following hot rolling increases, so there is an increase in the response of the alloy to the annealing treatment. The insulatory and air cooled conditions
Experimental Results display a similarly slow response, whilst the water quenched condition shows a considerably greater response to the annealing treatment.

As was the case with Alloys A and B, in terms of the extreme cooling conditions there is an increase in the annealing response of Alloy C with an increase in the cooling rate following hot rolling. However, the response of the insulatory cooled and air cooled conditions are reversed when compared to the order shown by Alloys A and B, i.e. the insulatory cooled condition shows a greater response to the annealing treatment than the air cooled condition. This anomaly can be easily accounted for as follows. The digital transducer which measures changes in extension has a resolution of 1µm. One will notice that the differences in extension between the air and insulatory cooled conditions fall inside this 1µm resolution due to the polynomial curve fitting. Therefore, these two curves could very well be in the reverse order.

Nevertheless, there may still be some scepticism about the accuracy of this method in qualitatively comparing the annealing responses of different conditions of the same alloy. This led to the decision to perform tests which would verify whether or not this technique was yielding accurate information (the reliability had already been established by performing numerous tests on the same material). A sample of Alloy C (water quenched condition - although for these purposes the cooling history was of no
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major significance) was annealed to yield a considerably softer and dislocation-free material compared to its earlier condition, or for that matter, any other cooling condition of Alloy C. The pre-annealed specimen’s response to a simulated annealing treatment was then compared to previously unannealed specimens of Alloy C. Differences in the annealing response between the pre-annealed specimen and the insulatory, air and water cooled samples are shown in Figure 4.34. This figure shows that the pre-annealed sample experienced only a modest change in length with respect to the unannealed specimens, i.e. the structure with less strain exhibited a smaller response to the annealing treatment than the more highly strained structures.

This test was repeated at lower annealing temperatures, yielding similar results. This was not unexpected owing to the high heating rates (50°C.min⁻¹) used to attain the soaking temperature (it would be reached in under 16 minutes). Although the unannealed samples would have had the opportunity to anneal to a degree during the heating step, the fact that none of the unannealed specimens (exhibiting three different cooling histories) presented an annealing response similar to that of the pre-annealed sample, indicates that none of these unannealed specimens became fully annealed in the heating step.

![Figure 4.34: Alloy C at 780°C](image)
Furthermore, owing to the high annealing temperature, the response of the insulatory cooled, air cooled and water quenched samples is almost identical for reasons explained earlier (see Figure 4.29).

The relatively large drop in all the specimens' extensions in the early stages of the tests may be explained by the dilatometer's temperature 'overshooting' the desired temperature during the heating stage. This 'overshoot' was due to the usage of a high heating rate. This led to the Ac₁ being exceeded for no more than ± 15 seconds which would lead to austenite formation, but due to the short duration in which the Ac₁ was exceeded, this austenite formation was not expected to play a large role. The 'overshoot' would have led to an increase in the length of the sample, which would have decreased as the dilatometer's temperature returned to the annealing temperature. Tests performed at lower temperatures also experienced 'overshooting', again due to the high heating rates that were employed.
5. ANALYSIS AND DISCUSSION

5.1 CHARACTERISATION OF AS-ROLLED 3CR12

5.1.1 PHASE PREDICTION RELATIONSHIPS

Despite this research noting comments by at least one other worker that phase prediction relationships were of little use due to their imprecision, these relationships do still play an important role. This is evidenced by the presence of the Kaltenhauser Relationship in many (recently) published papers, despite the proliferation of computer-aided phase diagrams. Irrespective of their inaccuracies, these relationships continue to serve as an inexpensive and expeditious means of determining the phase composition and/or ranking of the ferrite contents in different alloys.

The two models used in this research (the Kaltenhauser Ferrite Factor Relationship and a modified form of the Kaltenhauser Ferrite Factor Relationship) predicted that the three alloys featured in this research would exhibit:

- A dual phase ferrite + martensite microstructure.  
  (Predicted by the modified Kaltenhauser Relationship)
- A ferrite content in ascending order:  
  Alloy B, Alloy C, Alloy A.  
  (Predicted by the both forms of the Kaltenhauser Relationship)

Mentioned earlier (section 2.2.2) in the literature review was the fact that these models dealt with a welded metal’s structure and not the equilibrium structure. Therefore, for the following section (which compares the predicted microstructures with the observed microstructures) it was decided that it would be more prudent to compare the predicted microstructure with the microstructure of the air cooled alloys. This is because air cooled alloys’ cooling rate (and not water quenched or insulatory cooled alloys) is the closest to that experienced by a welded metal.
5.1.2 THE OBSERVED AS-ROLLED MICROSTRUCTURE

Microstructural studies showed that all three alloys exhibited a dual phase microstructure of ferrite and martensite, for all cooling rates. Therefore, the modified Kaltenhauser Relationship, $F(\alpha')$, correctly predicted the phases present in the three alloys’ microstructures. Furthermore, volume fraction analysis (VFA) utilising optical microscopy demonstrated that Alloy A had considerably more ferrite present in its microstructure than Alloys B or C, thereby corroborating the prediction made by the Kaltenhauser Relationship, $F(\alpha)$.

However, both these relationships also predicted an intermediate ferrite content for Alloy C with respect to Alloy A (a very high ferrite content) and Alloy B (a very low ferrite content). According to VFA, this prediction was incorrect. VFA showed that Alloy C’s air cooled (and water quenched) condition had less ferrite present than the similarly cooled Alloy B. This was contrary to what was predicted. However, Alloy C’s insulatory cooled condition did have a higher amount of ferrite present compared to the similarly cooled condition in Alloy B. Therefore, in terms of insulatory cooling, the prediction was accurate, but this correlation is not significant since a welded plate would not be expected to cool at the same rate as an insulatory cooled plate. Consequently, according to VFA, both the Kaltenhauser Relationship and the modified Kaltenhauser Relationship incorrectly predicted the ranking of the ferrite content in the three alloys.

Section 3.2.1.1 describes why some workers reasoned that VFA utilising optical microscopy was not an entirely accurate method. In order to determine whether or not these inaccuracies would affect the conclusions drawn in the above paragraph, bulk hardness tests were performed on the same samples that were subjected to VFA.

Assuming that the martensite and ferrite hardness does not vary (this assumption will be critically analysed later in this Chapter), bulk hardness tests also showed that the ferrite content in Alloy A was higher than in Alloys B or C, concurring with both predictive models and VFA. However, the hardness tests showed that the air cooled (and insulatory cooled) form of Alloy C is softer than its similarly cooled counterpart.
in Alloy B, suggesting that there is in fact more ferrite present in Alloy C than in Alloy B. Thus the results of the bulk hardness tests concurred with the predictive models on this point, and not VFA.

5.1.3 AS-ROLLED BULK HARDNESS vs. VFA

Apart from the exception mentioned in the previous section, the results of bulk hardness tests (section 4.1.2.2) correlated very well with those of VFA (section 4.1.3). The other noticeable difference between these two sets of data was the margins of error. The average margin of error for the hardness tests was approximately 1.5% of each data point. For VFA, however, the margin of error was ten times larger, approximately 15% of each data point. If one also considers that a minimum of five results was needed for a bulk hardness data point, compared to 29 for VFA, it can be seen that hardness tests were considerably less time-consuming than VFA and most importantly, more accurate.

It could be argued that increasing the number of results obtained by VFA would eventually reduce the VFA margin of error to smaller than that of the hardness tests' margin of error. However, the number of hardness test results could also be increased, further reducing their margin of error and thereby nullifying any reduction in the margin of error associated with VFA.

Figure 5.1 illustrates how bulk hardness varies as a function of the martensite content. This graph was constructed from data in Figures 4.5 and 4.6 and shows how bulk hardness increases with an increase in the martensite content. It is interesting to note that when the best-fit lines of these data points are extended to allow for the determination of the hardness of a fully ferritic (0% martensite) microstructure, they show a large variation in hardness. Clearly the hardesses of the fully ferritic alloys do not correspond to the ferrite phases' hardness shown in Figure 4.4. A similar result emerges if one also extends these lines to a fully martensitic (0% ferrite) condition. Had the hardesses of the fully ferritic or martensitic microstructures corresponded more closely to the ferrite or martensite phases' hardesses respectively, one could
Analysis and Discussion

draw the conclusion that hardness of the ferrite phase (and the martensite phase) do not fluctuate with different cooling rates. However, these results indicate the contrary.

![Image of graph showing variation in bulk hardness due to changes in martensite content]

**Figure 5.1:** Variation in the bulk hardness due to changes in martensite content

From Figure 5.1, Alloy B appears to have a much harder form of martensite than Alloy C, whilst Alloy A’s martensitic hardness increases very drastically with an increase in the martensite content. Once again, these observations are only valid if the ferrite and martensite hardness are assumed to remain fairly stable for different cooling rates. Figure 4.4 (which illustrates ferrite hardnesses) does not show any outright relationships between ferrite hardness and cooling rate in all three alloys. However, if one examines the hardness of the differently cooled conditions in Alloy C, the ferrite hardness does not appear to be independent of cooling rate. A similar situation applies to the martensite hardness of Alloy B in Figure 4.3. Even more weight is therefore added to the assumption that it is unlikely that ferrite and martensite’s hardness are independent of the cooling rate. This tentative conclusion is further supported by a discussion in section 5.1.4 which discusses possible influences on the phase’s hardness.
5.1.3.1 HARDENABILITY CURVES

Owing to the different cooling rates applied to each alloy, and the fact that the martensite content is a function of the cooling rate, it is possible to derive a hardenability curve for each alloy.

Although only three different cooling rates were used in this research, one can nevertheless create an approximate hardenability curve for each alloy, as shown in Figure 5.2, by plotting the martensite content (determined from VFA) against its respective cooling rate. From the above graph, the hardenability of the three alloys of interest in ascending order is:

Alloy A, Alloy C, Alloy B.

It is well known that an alloy's hardenability is a function of its composition. Alloys B and C have higher carbon contents than Alloy A, and as carbon has been shown to increase the hardenability of an alloy (section 2.2.3.1), this is one of the causes of these two alloys' high hardenability. Likewise, nickel and manganese additions have also been found to cause an increase in the hardenability of an alloy. It may be noted that these elements are all very strong austenite formers, which stabilise the austenite phase and consequently allow the formation of martensite from austenite on cooling.
Nitrogen, another strong austenite former, is therefore also expected to assist in increasing the hardenability of the alloys, despite there being no mention of its influence on hardenability in the papers reviewed in this thesis. Table 5.1 indicates how Alloys B and C have consistently higher contents of carbon, nickel, nitrogen and manganese (to a lesser extent) relative to Alloy A, thereby explaining the higher hardenability of these two alloys.

<table>
<thead>
<tr>
<th></th>
<th>C</th>
<th>Ni</th>
<th>N</th>
<th>Mn</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alloy A</td>
<td>0.016</td>
<td>0.10</td>
<td>0.0169</td>
<td>0.55</td>
</tr>
<tr>
<td>Alloy B</td>
<td>0.019</td>
<td>0.46</td>
<td>0.0229</td>
<td>1.14</td>
</tr>
<tr>
<td>Alloy C</td>
<td>0.027</td>
<td>0.37</td>
<td>0.0196</td>
<td>0.40</td>
</tr>
</tbody>
</table>

Table 5.1: The content of elements in each alloy that contribute towards hardenability (note how the lowest level of each alloying element features most often in Alloy A)

### 5.1.4 DIFFERENCES IN PHASE HARDNESS

Alloy A exhibits a minimal fluctuation in the hardness of the martensite phase due to changes in the cooling rate. It is interesting to note that the hardness of the martensite in this alloy in all three differently cooled conditions is about 40HV greater than the hardness of the martensite in the other alloys. The higher martensite hardness exhibited by this alloy was unexpected.

One would expect a slightly higher martensite hardness in Alloys B and C due to the higher levels of carbon and nitrogen present in these two alloys (although as mentioned in section 2.2.3.2, there is not total agreement by workers regarding nitrogen) which would increase martensite hardness. Table 5.1 shows that Alloy A has the lowest carbon and nitrogen contents of all three alloys. If there were higher levels of alloying elements such as titanium or niobium in Alloys B and C than in Alloy A, then this could have also explained these alloys’ softer martensite. This is because titanium and niobium remove the interstitial elements from solution to form Ti(C,N) or Nb(C,N). However, niobium was only present in trace amounts in all three alloys and titanium levels were highest in Alloy A, not Alloys B or C as one would have expected. A similar situation exists for the carbide-forming elements, chromium
Analysis and Discussion

and vanadium. Alloy A has higher vanadium and chromium contents than both Alloys B or C. Consequently, it is unlikely that these elements removed carbon from solution of Alloys B and C to make their martensite phase softer, as there was an even higher vanadium and chromium content in Alloy A, and thus one would expect Alloy A’s martensite to be even softer than that of Alloy B or C.

The explanation for these apparent contradictions lies in the martensite content of the three alloys. Figure 4.6 demonstrates that Alloy A has a considerably lower martensite (and prior to its formation, austenite) content than Alloys B or C. Therefore, for similar bulk contents of, for example carbon and nitrogen, in all three alloys, there will be a higher concentration of carbon and nitrogen in the austenite of the alloy with the lowest austenite content, viz. Alloy A. If one recalls that these interstitial elements will increase the hardness of any martensite developing from the parent austenite, it is obvious that the hardness of the martensite phase in Alloy A will be greater than that of the martensite phase in Alloy B or C, due to the higher concentrations of carbon and nitrogen. This is related to partitioning and dilution effects.

It was mentioned in an earlier section of this Chapter that the ferrite phases’ hardnesses were fairly similar in all three alloys, but that it could be argued that the water quenched condition of each alloy did exhibit a slightly higher hardness. This certainly appears to be true for Alloy C. The reason for this increased hardness is a result of a more highly strained ferrite with a higher dislocation density. Thus there would be a high driving force for recovery and also recrystallisation. The recrystallisation is evidenced by the development of high angle grain boundaries in the ferrite. It can be seen that in the water quenched condition (Figure 4.7) there are considerably more recrystallised grains present than in the insulatory cooled condition (Figure 4.10).

Returning to the martensitic hardness of each alloy, although there were no apparent trends present in the martensitic hardness of Alloys A or C, in Alloy B there did appear to be an increase in the martensitic hardness with an increase in the cooling rate. In other words, the parent austenite appeared to be more dislocated for cases in
which there was an increase in the cooling rate following annealing. This dislocated condition should affect the martensite morphology in some manner, thereby possibly influencing the hardness. Changes in the martensite phase would be best detected by transmission electron microscopy and coercivity measurements. This work would lend qualitative and quantitative support respectively to an increase in dislocation density (and thus microhardness) in the martensite phase. Unfortunately this work could not be performed due to time constraints.

5.1.5 ANALYSIS OF THE $A_C_1$

The $A_C_1$ of each alloy was measured by means of dilatometry and DTA. The results featured in section 4.1.7 are summarised in Table 5.2 below.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>$A_C_1$ $^{\circ}C$</th>
<th>Dilatometry</th>
<th>DTA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alloy A</td>
<td>830 ± 2</td>
<td>not performed</td>
<td></td>
</tr>
<tr>
<td>Alloy B</td>
<td>764 ± 2</td>
<td>not performed</td>
<td></td>
</tr>
<tr>
<td>Alloy C</td>
<td>800 ± 2</td>
<td>820 ± 1</td>
<td></td>
</tr>
</tbody>
</table>

Table 5.2: Average $A_C_1$ of alloys

Measurement of Alloy C’s $A_C_1$ by means of dilatometry and DTA yielded a different temperature for the $A_C_1$ ($\pm 20^\circ C$ difference) depending on the technique used. This finding was not unexpected, since a similar variation of the $A_C_1$ appeared in the work of Kosikiniemi et al.\textsuperscript{22}. The variation of the $A_C_1$ can be attributed to differences in the heating rates employed by DTA and dilatometry. The reader may recall that tests performed with DTA employed heating rates of $10^\circ C.min^{-1}$ (section 3.4), whilst heating rates in the dilatometer were considerably lower, being $1^\circ C.min^{-1}$ (section 3.5.3). Consequently, the martensite was able to undergo a greater degree of tempering when exposed to the slower heating rates in the dilatometer. The higher levels of tempered martensite in the dilatometry specimens led to a depression of the $A_C_1$, as their microstructures became more similar to that of an equilibrium microstructure. The fact that the $A_C_1$’s for all cooling conditions of each alloy were
very similar, further indicates that these alloys had almost attained an equilibrium microstructure during the heating stages in the dilatometer.

Although it is accepted that the $A_{c1}$ is intrinsically dependant on an alloy’s composition, no prior work has attempted to determine whether or not thermomechanical processing would alter the $A_{c1}$. As mentioned earlier, results yielded by dilatometry were inconclusive due to tempering of the microstructures as a result of the slow heating rates. DTA was thus performed on the samples because of the higher heating rates associated with this technique, which would reduce large-scale tempering. A comparison of the results of the tests performed on the same alloy by these two techniques is given in Table 5.3.

<table>
<thead>
<tr>
<th>Alloy C</th>
<th>$A_{c1}$ (°C) Dilatometry</th>
<th>$A_{c1}$ (°C) DTA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water Quenched</td>
<td>801 ± 2</td>
<td>824 ± 1</td>
</tr>
<tr>
<td>Air Cooled</td>
<td>801 ± 2</td>
<td>821 ± 1</td>
</tr>
<tr>
<td>Insulatory Cooled</td>
<td>797 ± 2</td>
<td>815 ± 1</td>
</tr>
</tbody>
</table>

Table 5.3: Comparison of the measured $A_{c1}$'s of Alloy C by dilatometry and DTA

There is no apparent trend present in the dilatometry results of Alloy C (as was the case for the other alloys, see Table 4.4) due to the close proximity of the $A_{c1}$'s. There is, however, a clear trend present in the measurements made by DTA. With an increase in the cooling rate following hot rolling, there is an increase in the $A_{c1}$ of Alloy C. This relationship is clearly not a coincidence as shown by the accuracy of the DTA results in Table 4.5 for separate tests of the same alloy. In addition, the margin of error is sufficiently small enough not to play a role.

This relationship is analogous to the phenomenon described earlier in which the $A_{c1}$ varied depending on the technique used to measure it. In this case, however, the $A_{c1}$ is not affected by differences in the heating rate for the same microstructure as was the previous case, but rather by differences in the microstructure for the same heating rate. Alloys subjected to slower cooling rates had more ferrite present in their microstructure, and thus had microstructures closer to that of an equilibrium
microstructure. Their Ac₁'s were consequently closer to the Ac₁ of an equilibrium microstructure, thereby explaining why the Ac₁ decreased with decreasing cooling rates.

Therefore, the cooling rate during thermomechanical processing will influence the Ac₁ of 3CR12. This may alter the temperature difference between the Ac₁ and the furnace temperature during annealing, which in turn will influence the annealing response of 3CR12.

### 5.1.5.1 THE ROLE OF ALLOYING ELEMENTS

In order for the subsequent discussion to be clear, the iron-chromium phase diagram is shown in Figure 5.3. This phase diagram shows the location of the Ac₁ and \( \gamma_{\text{max}} \) in addition to some of the other transformation temperatures found in 3CR12.

Section 2.2.1 explained how austenite and ferrite formers are responsible for increasing or decreasing the size of the austenite field. Consequently, if an element affects the size of a phase field, it will also affect the boundaries of the phase field, i.e., the transformation temperatures. Thus the austenite and ferrite formers are also responsible for affecting the Ac₁ (and the Ac₃, Ac₄ and Ac₅) of the alloys.

Alloy A had the highest addition of the most powerful ferrite former, titanium. In addition it had the highest contents of chromium and silicon which are also ferrite formers. The addition of these elements reduces the size of the austenite phase field, thereby raising the Ac₁ relative to its original position. Consequently, Alloy A exhibits the highest Ac₁ of the three alloys studied. Alloy B had the second highest carbon content and the highest levels of manganese, nickel and nitrogen. These alloying elements are the most powerful austenite forming elements. Therefore, these elements' presence led to an increase in the size of the austenite phase, thereby depressing the Ac₁ and Ac₃. Consequently, Alloy B's Ac₁ was the lowest measured.

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*The \( \text{Ac}_2 \) (or Curie Temperature) occurs at approximately 600°C and does not signify a phase transformation, but rather the loss of 3CR12's magnetic properties.*
Alloy C was alloyed with intermediate levels of the various austenite and ferrite formers, thus its $\text{Ac}_1$ was intermediate with respect to the $\text{Ac}_1$'s of Alloys A and B.

![Fe-Cr phase diagram with vertical line indicating the approximate position of 3CR12](image)

**Figure 5.3:** The Fe-Cr phase diagram, with the vertical line indicating the approximate position of 3CR12

### 5.1.6 MECHANICAL PROPERTIES OF 3CR12 IN THE AS-ROLLED CONDITION

All the Charpy impact specimens failed by means of brittle fracture. This can be visually confirmed by the presence of transgranular cleavage facets on the fracture surfaces, such as those seen in Figure 4.17. Transgranular cleavage and the associated ‘river lines’ are clearly visible in this micrograph. This failure mode can be ascribed to the high martensite content present in the microstructure. Brittle fractures also exhibit a very poor impact energy, as indicated by the low impact energies shown in Table 4.3.

Owing to the very low impact energies recorded and the fairly large margins of error, it is very difficult to discern between samples of the same alloy with different cooling
Analysis and Discussion

rates. The two extreme cooling conditions of Alloy C do, however, indicate that there may be a slight increase in the impact energy in response to a decrease in the cooling rate.

A glance at the tensile test results (Table 4.2) shows that these results were slightly more forgiving in terms of the presence of trends. Alloy C exhibits an increase in elongation for a decrease in the cooling rate. Furthermore, there is a clear decrease in the alloy's UTS values and 0.2% proof stress, with a decrease in the cooling rate following hot rolling. These findings can be ascribed to the increase in the alloy's martensite content as a response to increased rates of cooling. As seen earlier, the martensite is considerably harder (yet more brittle) than ferrite and so any alloy with a higher martensite content will exhibit a higher strength, but a much lower ductility.

Quite noticeable in Figure 4.17 of the fracture surface of a Charpy impact specimen is the presence of small cracks, which are parallel to the anisotropic 'pancake-like' microstructure of the hot-rolled 3CR12. The smaller cracks have a similar length to the MnS inclusions shown in Figure 4.14. Owing to MnS inclusions being anisotropically-shaped third phase particles, and thus likely sites for the initiation of decohesion, a possible scenario is that some of these cracks have developed from the MnS inclusions, a view supported by Knutsen and Hutchings. The small cracks (20µm to 50µm long) join together to form larger cracks such as in Figure 4.18, which shows an arrowed smaller crack amalgamating with a larger crack. Once the crack has reached a critical size, it could then exploit the anisotropic microstructure of 3CR12 by preferentially extending between grain boundaries and coalescing with smaller cracks in the same region.

One could expect MnS inclusions to initiate the delamination, because if delamination were initiated arbitrarily between the ferrite and/or martensite grain boundaries without the presence of a third phase particle, many of the ferrite and martensite grain boundaries should delaminate, leading to a massively delaminated fracture surface. However, visual examination of the fracture surface reveals a fairly small number of cracks, thereby suggesting that this does not play a predominant role. Knutsen and Hutchings agreed that non-metallic inclusions were mainly responsible for the
splitting in Charpy impact specimens and attempted to explain the crack formation by means of the initiation of a triaxial stress system developing at the root of the V-notch. Other workers have attempted to explain the development of these cracks by means of bulk texture analysis\textsuperscript{79}. 

The results thus far can be summarised as follows. For 3CR12 steel in the as-rolled condition, with an increase in the cooling rate following hot rolling there is a corresponding:

- increase in bulk hardness
- decrease in impact energy
- decrease in elongation
- increase in the UTS
- increase in the 0.2% proof stress

5.2 HEAT TRANSFER

In order for heat transfer theory to correctly predict the temperature of an object, an accurate value of $h$ (heat transfer coefficient) is required. This research showed that convection theory was unable to accurately determine $h$. The heat transfer coefficient was therefore rather determined empirically as 85 Wm$^{-2}$K$^{-1}$, which is significantly higher than the 13 Wm$^{-2}$K$^{-1}$ predicted by theory.

However, substitution of this empirically determined value into the lumped-heat-capacity theory allowed for the derivation of a pseudo-empirical equation which accurately predicted the change in temperature of a 1cm$^3$ block of 3CR12 placed in a furnace. Furthermore, this equation can be modified for application to any material in cube form with a known density and specific heat. The equation in its final form is:

$$T = T_\infty + (T_i - T_\infty) \cdot \exp\left(\frac{s}{k_\rho c} \cdot \tau\right)$$
Therefore, a cube of material (with side $a$) of density ($\rho$), specific heat ($c$) and initial temperature ($T_i$), will have a temperature $T$ after time $\tau$ in a furnace of temperature $T_\infty$.

### 5.3 THE RESPONSE TO ANNEALING

#### 5.3.1 THE ROLE OF ALLOYING ELEMENTS

It is reasonable to expect that the addition of any substitutional alloying element may retard diffusion to some extent, thereby retarding the tempering response of an alloy. Nevertheless, Chapter Two has clearly demonstrated that at least one alloying element may accelerate rather than retard the annealing response of an alloy. Irvine et al.\textsuperscript{25} concluded that the effects of alloying elements on annealing treatments was dependent on whether the alloying element was a ferrite or an austenite former. Section 2.2.1 in conjunction with the phase diagram in Figure 5.3 supports this conclusion by Irvine et al. by demonstrating that the addition of a ferrite former will cause an increase in the $AC_t$, whereas the addition of an austenite former will cause a reduction in the $AC_t$. An increase in the $AC_t$ will permit the annealing temperature to be raised which will permit an increase in the annealing response (recall: the greatest decrease in hardness over the annealing period), owing to increased diffusion. Conversely, there will be retardation of the annealing response if the $AC_t$ is reduced.

<table>
<thead>
<tr>
<th>Does element retard tempering response?</th>
<th>Yes</th>
<th>No</th>
</tr>
</thead>
<tbody>
<tr>
<td>Niobium ($\alpha$ former)</td>
<td>×\textsuperscript{25}</td>
<td></td>
</tr>
<tr>
<td>Titanium ($\alpha$ former)</td>
<td>×\textsuperscript{34}</td>
<td>×\textsuperscript{5}</td>
</tr>
<tr>
<td>Nickel ($\gamma$ former)</td>
<td>×\textsuperscript{25}</td>
<td></td>
</tr>
<tr>
<td>Manganese ($\gamma$ former)</td>
<td>×\textsuperscript{25}</td>
<td></td>
</tr>
<tr>
<td>Carbon ($\gamma$ former)</td>
<td>×\textsuperscript{22}</td>
<td></td>
</tr>
</tbody>
</table>

Table 5.4: Summary of the effects of alloying elements on tempering response and the relevant literature references
However, this conclusion appears to be more of a generalisation, as a survey of the literature used in this research revealed that Irvine's statement was more correctly applicable to the stronger ferrite and austenite formers, as shown in Table 5.4.

Nevertheless, as this research was concerned with comparing the annealing response of different forms of the same alloy, the effects of any individual alloying element would not have been of much consequence.

5.3.2 AS-ROLLED vs. ANNEALED MECHANICAL PROPERTIES

The decomposition of the hard, yet brittle martensite phase into ferrite and carbides (most likely of the form Cr$_2$C$_6$ - section 2.3.1.1) as a result of annealing treatments was shown to affect the mechanical properties of the alloys markedly. The precipitation of these carbides, mainly on the martensite/ferrite and martensite/martensite lath boundaries, is quite apparent from Figures 4.26 and 4.28.

The 'loss' of martensite resulted in the formation of a softer and more ductile steel. As a result, all three alloys experienced increases in elongation and impact energies, and a corresponding decrease in the UTS and 0.2% proof stress following their annealing treatments. The impact and tensile tests performed on the three alloys following annealing did not yield any discernible relationships between impact toughness, strength (UTS and 0.2% proof stress) and elongation with changes in the cooling rate.

The impact tests performed on the alloys following annealing yielded some startling results. Alloys A and C experienced very modest increases when compared to Alloy B's increase of over 900% in its impact energy. Although an increase in impact toughness was expected due to the replacement of the brittle martensite by a more ductile ferrite, there was a very large discrepancy between Alloy B and Alloys A and C. Owing to the different annealing parameters applied to each alloy, one clearly cannot compare the alloys' annealing treatments without the aid of the Holloman-Jaffe Parameter (P), which accounts for both annealing times and temperatures. It was therefore surprising to find that all three alloys, at the conclusion of the annealing
treatments, had very similar P-values, approximately 16.5 as can be seen by Figures 5.4 to 5.6 later in this section. One would have expected there to be a large difference in P-values owing to differences in composition and the mechanical properties following annealing. A possible explanation for Alloy B’s high impact energies is that it had a considerably higher martensite content (in all three cooling conditions) than the other alloys. Following annealing it experienced the greatest volume of martensite decomposition into ferrite and carbides, leading to it experiencing the greatest reduction in UTS values, 0.2% proof stress and the greatest increase in elongation and impact toughness of the three alloys. Chemically, Alloy B had the lowest titanium content of the three alloys, which would also have assisted in increasing its toughness with respect to Alloys A and C, due to TiC acting as sites for cleavage fracture.

All three alloys’ hardnesses decreased to a final hardness of approximately 140HV, despite there being considerable variations in the annealing times and temperatures. As the different alloys were subjected to different annealing parameters of time and temperature, the Holloman-Jaffe Parameter (section 2.3.1.3) was applied in an attempt to account for these differences. Figures 5.4 to 5.6 illustrate the Holloman-Jaffe Parameter vs. hardness for each alloy.

![Graph showing Holloman-Jaffe Parameter vs. hardness for each alloy](image)

**Figure 5.4:** Response of Alloy A to annealing using the Holloman-Jaffe Parameter
The resultant graphs still have hardness represented along the y-axis and consequently the same margins of error apply as in the more conventional time vs. hardness graphs. The margins of error were omitted in this graph and later graphs for greater clarity. Alloy A did not soften greatly, although it is quite evident that there is a greater reduction in hardness with an increase in the cooling rate. This is due to the presence of a higher initial (and more highly strained) martensite content in the specimens subjected to higher cooling rates. Owing to the more highly strained condition of the faster cooled martensite, there is a correspondingly greater annealing response. As mentioned earlier, work quantifying these statements could not be performed due to time constraints.

A very interesting aspect of the annealing response of Alloy A, which was not noticeable in the conventional graph using the same data (Figure 4.22), was the appearance of a secondary hardening peak where $P \approx 16$. Although the peak is inside the margins of error of the hardness readings (as can be seen from Figure 4.22), the fact that all three differently cooled conditions exhibit this peak implies that the possibility of this being a coincidence is very unlikely. Hence, at this point replacement of the coarse Fe$_3$C particles by the finer Cr$_2$C$_6$ particles is most likely occurring. Alloy A has the highest levels of titanium and vanadium. These two alloying elements have been shown in Chapter Two to produce secondary hardening effects in 12wt% Cr steels by forming TiC and VC respectively.

<table>
<thead>
<tr>
<th></th>
<th>Alloy A</th>
<th>Alloy B</th>
<th>Alloy C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Titanium</td>
<td>0.016</td>
<td>0.006</td>
<td>0.008</td>
</tr>
<tr>
<td>Vanadium</td>
<td>0.12</td>
<td>0.08</td>
<td>0.07</td>
</tr>
</tbody>
</table>

Table 5.5: Vanadium and titanium contents of the alloys studied

The softening curve of Alloy B illustrates a more marked softening process than that which occurs in Alloy A. Just as Alloy A reached its lowest hardness at $P \approx 16$, Alloy B reaches its lowest hardness at a similar value of the Hollomon-Jaffe Parameter, despite the completely different annealing parameters. Unlike Alloy A, there does not appear to be any secondary hardening occurring in this alloy and there is no influence of prior cooling rate on the tempering behaviour.
Alloy C shows more clearly the difference in response to annealing treatments due to the different cooling rates. It can be seen quite clearly that with an increase in the cooling rate following annealing, there is a faster response (in this case, implying ΔHV/P) to the annealing treatment. The reasons for this response have been explained earlier.
The simulation of isothermal annealing by means of dilatometry demonstrated that this novel technique was a viable means of comparing the annealing response of different alloys. This technique could be used qualitatively and quantitatively to compare the response of alloys to annealing treatments, i.e. the determination of which alloy experiences a greater level of martensitic decomposition into ferrite and carbides. As outlined in section 2.3.2.2, this technique also has several advantages over the conventional means of measuring an alloy’s annealing response. The dilatometry technique is considerably quicker, less labour intensive and gives a continuous indication of the annealing response of an alloy.

The only disadvantage that emerged from the research of this technique was that the alloys’ response could not be ascertained at temperatures above approximately 650°C. All the alloys began to anneal during the relatively slow heating stage to the soaking temperature, and at temperatures above 650°C any difference in the annealing response (and thus change in length) would be ‘lost’, and therefore the annealing responses during the subsequent soaking stage would be almost identical. The obvious means of rectifying this situation would be to increase the heating rate, but, as explained in section 3.5.3, this would lead to temperature gradients developing in the specimen. If the specimens were wafer-thin, one could possibly discount this problem. Unfortunately, in the dilatometer the specimen is connected to a spring-loaded digital transducer - such a thin specimen would bend under the spring’s force.

The only other option available would be to measure the specimen’s extension by non-mechanical means, by employing a laser beam. However, such a task is beyond the scope of this thesis.
6. CONCLUSIONS

1. For all three alloys of 3CR12 investigated, an increase in the cooling rate following annealing was found to increase the martensite content in the microstructure. This increase in martensite resulted in an increase in the bulk hardness, UTS values and 0.2% proof stress, whilst causing a corresponding decrease in the alloys' impact toughness and elongation. The \( A_c \) was also found to decrease with decreasing cooling rates. The hardness of the martensite and ferrite phases also appear to increase with higher cooling rates following hot rolling.

2. An increase in the cooling rate following hot rolling was found to cause the alloys to experience a greater and more immediate response to subsequent annealing treatments, i.e. the decomposition of martensite to ferrite and carbides was accelerated. However, at the completion of the annealing treatment, the differently cooled conditions of each alloy had similar microstructures and mechanical properties.

3. Dilatometry can be used to evaluate the annealing responses of alloys of 3CR12 steel. This technique allows for the qualitative and quantitative comparison of 3CR12 alloys, provided that tests are performed at temperatures below 650°C.

4. Heat transfer utilising an empirical form of the lumped-heat-capacitance theory can accurately predict the temperature of a cube in a furnace using the equation:

\[
T = T_\infty + (T_i - T_\infty) \exp\left(-\frac{5100}{\rho \cdot c \cdot \alpha} \cdot t\right)
\]
7. REFERENCES

60. S D Gertstriken, N N Novikov & B F Slyusar, Metallurgizdat 34, 180 (1963).
References

75. BS prEN10088-1 List of stainless steels (1995).

NOTE: References that feature in appendices are listed at the end of the relevant appendix.
APPENDIX A

(TestPoint Program Listing)
Objects in panel "DilaData 4.0 - (1997)":

- Container1
- Container2
- Container3
- Container4
- Container5
- Container6
- Math1
- Math2
- Math3
- Math4
- Math5
- Math6
- Label1
- Label2
- Loop1
- Loop2
- Sampling Time (s)
- Datum Length (μm)
- Length (μm)
- Temperature (°C)
- Elapsed Time (s)
- Temperature vs Length
- Time vs Length
- Condition1
- Condition2
- Condition3
- A/D PC73
- RS232 1
- RUN TEST
Objects in panel "DilaData 4.0 - (1997)": ...continued

- Time1
- File1
Settings for Panel object "DilaData 4.0 - (1997)":

BG Color: Lt Gray
X: -1
Y: -1
Multitasking mode: Yield at end of loops

Math1

Settings for Math object "Math1":

Formula: a * 1000

Math2

Settings for Math object "Math2":

Formula: e + 1

Math3

Settings for Math object "Math3":

Formula: a + 1

Math4

Settings for Math object "Math4":

Formula: a - b

Math5

Settings for Math object "Math5":

Formula: a - b
Settings for Math object "Math6":

Formula: \( a + 1 \)

Settings for Display object "Datum Length (\(\mu m\))":

- Type: Text
- Number Format: Auto
- # digits: 5
- Text if no data: STANDBY
- BG Color: Black
- Text Color: White
- Text Size (dots): 24
- Visible: 1
- Initial Value:
- Bezel: 1
- Caption: 1

Settings for Display object "Length (\(\mu m\))":

- Type: Text
- Number Format: Auto
- # digits: 5
- Text if no data: STANDBY
- BG Color: Black
- Text Color: White
- Text Size (dots): 24
- Visible: 1
- Initial Value:
- Bezel: 1
- Caption: 1
**Temperature (°C)**

Settings for Display object "Temperature (°C)"

- Type: Text
- Number Format: Auto
- # digits: 5
- Text if no data: STANDBY
- BG Color: Black
- Text Color: White
- Text Size (dots): 24
- Visible: 1
- Initial Value:
- Bezel: 1
- Caption: 1

**Elapsed Time (s)**

Settings for Display object "Elapsed Time (s)"

- Type: Text
- Number Format: Auto
- # digits: 5
- Text if no data: STANDBY
- BG Color: Black
- Text Color: White
- Text Size (dots): 24
- Visible: 1
- Initial Value:
- Bezel: 1
- Caption: 1

**Condition1**

Settings for Condition object "Condition1"

- Expression: \(a - b - (c \cdot d) \geq d\)

**Condition2**

Settings for Condition object "Condition2"

- Expression: \(\text{strequal}(a,\text{"none"})\)

**Condition3**

Settings for Condition object "Condition3"

- Expression: \(a = 50\)
Label1

Settings for Label object "Label1":

- Text: DilaData
- BG color: Lt Gray
- Visible: 1

Label2

Settings for Label object "Label2":

- Text: 4.0
- BG color: Lt Gray
- Visible: 1

Sampling Time (s)

Settings for Data-Entry object "Sampling Time (s)":

- Visible: 1
- Enabled: 1
- Exec. actions at initialize: 0
- Initial Value:
- Numeric: 0
- Min. value:
- Max. value:
- Bezel: 1
- Caption: 1
- Multi-line: 0

File Name

Settings for Data-Entry object "File Name":

- Visible: 1
- Enabled: 1
- Exec. actions at initialize: 0
- Initial Value: none
- Numeric: 0
- Min. value:
- Max. value:
- Bezel: 1
- Caption: 1
- Multi-line: 0
Temperature vs Length

Settings for Graph object "Temperature vs Length":

- **Mode:** Line
- **X vs Y:** 1
- **X step (if not XvsY):** 1
- **Left:** 20
- **Right:** 90
- **Top:** 8
- **Bottom:** 70
- **BG Color:** White
- **Visible:** 1
- **Bezel:** 1
- **Caption:** 1
- **Trace Number:** 1
- **Color:** Black
- **Style:** Solid
- **Shape:** None
- **Width:** 0
- **Size (pts):** 5
- **Y Axis:** Y1
- **Axis:** X
- **On:** 1
- **From:** 0
- **To:** 10
- **Color:** Black
- **Intercept (% full scale):** 0
- **Step:** 1
- **Position:** Left/Below
- **Title:** °C
- **Color:** Black
- **Major:** 0
- **Minor:** 0
- **Color:** Black
- **Logarithmic:** 0
- **Auto:** 1
Time vs Length

Settings for Graph object "Time vs Length":

Mode: Line
X vs Y: 1
X step (if not X vs Y): 1
Left: 20
Right: 90
Top: 8
Bottom: 70
BG Color: White
Visible: 1
Bezel: 1
Caption: 1
Trace Number: 8
Color: Brown
Style: Solid
Shape: None
Color: Black
Width: 0
Size (pts): 5
Y Axis: Y1
Axis: Y1
On: 1
From: 0
To: 10
Color: Black
Intercept (% full scale): 0
Step: 1
# Minor: 0
Position: Left/Below
Title: μm
Major: 0
Color: Black
Minor: 0
Color: Black
Logarithmic: 0
Auto: 1
Settings for A/D object "PC73":

- Board #: 1
- Demo mode: 0
- Raw data mode: 0
- Log to disk: 0
- Filename: data.dat
- Type: ASCII
- Format: width: 7
- decimal pl.: 3
- Auto-increment name: 1
- Mode: Append
- Apply scaling: 1

Settings for RS232 object "RS232 1":

- COM port #: 1
- Default output term.: CR
- Default input term.: CR
- Timeout (sec): 5
- Event on receiving character:
- Input queue size: 1024
- Output queue size: 1024
- Demo mode: 0
RUN TEST

Action list for Switch object "RUN TEST":

1) Clear Container1
2) Clear Container2
3) Clear Container3
4) Clear Container4
5) Clear Container5
6) Clear Container6
7) Set mode of RS232 1 baud rate=9600, parity=None, bits=8, stop
   bits=1
8) Output to RS232 1 with "R1", term.=CR, wait for completion?=0
9) Enter from RS232 1 up to 256 bytes, stop on EOS=CR
10) Append to Container1 from RS232 1
11) Calculate Math1 with a=RS232 1
12) Set Datum Length (µm) to Math1
13) Store in Container1 from Math1
14) Start Time1 interval=1
15) Store in Container2 from Time1
16) Set Math2 to 0
17) Store in Container3 from Math2
18) Do loop Loop2 while RUN TEST is true (non-zero)
19) If/Then Condition1 with a=Time1 b=Container2 c=Container3
d=Sampling Time (s)
20) Calculate Math3 with a=Container3
21) Store in Container3 from Math3
22) Output to RS232 1 with "R1", term.=CR, wait for completion?=1
23) Enter from RS232 1 up to 256 bytes, stop on EOS=CR
24) Store in Container4 from RS232 1
25) Acquire A/D PC73 #samples=1, rate=1 Hz, channel(s)=0
26) Calculate Math1 with a=PC73
27) Calculate Math4 with a=Math1 b=Container1
28) Calculate Math5 with a=Time1 b=Container2
29) Set Temperature (°C) to PC73
30) Set Length (µm) to Math4
31) Set Elapsed Time (s) to Math5
32) Add point(s) to Temperature vs Length from PC73, Math4, max. # points=10000
33) Add point(s) to Time vs Length from Math5, Math4, max. # points=10000
34) Append to Container5 from Math5, PC73, Math4
35) Calculate Math6 with a=Container6
36) Store in Container6 from Math6
37) If/Then/Else Condition2 with a=File Name
38) Else if not Condition2
39) If/Then Condition3 with a=Container6
40) Set filename of File1 to File Name
41) Output to File1 with Container5, term.=none
42) Clear Container5
43) Clear Container6
44) End If Condition3
45) End If Condition2
46) End If Condition1
47) End Loop2
48) If/Then/Else Condition2 with a=File Name
49) Else if not Condition2
Action list for Switch object "RUN TEST": ...continued

50) Set filename of File1 to File Name
51) Output to File1 with Container5, term.=none
52) End If Condition2

Settings for Switch object "RUN TEST":

Style: Slide Switch
Label:Off: Stop
Label:On: Start
Visible: 1
Enabled: 1
Exec. actions at initialize: 0
Initial Value: 0
Bezel: 1
Caption: 1

Time1

Settings for Time object "Time1":

Time format: Secs. elapsed (since Jan. 1 1970)

File1

Settings for File object "File1":

Filename initial value:
Update disk on each output: 0
'Save As' style (else 'Open'): 0
Warn on create (if 'Open'): 1
Must exist (if 'Open'): 0
Warn on existing (if 'Save As'): 1
Default extension:
Dialog title:
File name filter:
Visible: 0
Enabled: 1
Execute actions at init: 0
Bezel: 1
Caption: 1
APPENDIX B

(Drawings of Dilatometer Modifications)
END PLATE (AS VIEWED FROM MIDDLE PLATE)

1. All dimensions in mm
2. Scale 2:1
3. All other dimensions to your discretion
4. Material: Invar

MIDDLE PLATE (AS VIEWED FROM FRONT PLATE)

1. All dimensions in mm
2. Scale 2:1
3. All other dimensions to your discretion
4. Material: Invar
CONNECTING RODS

- ALL DIMENSIONS IN MM
- SCALE: 2:1
- ALL OTHER DIMENSIONS TO YOUR DISCRETION
- MATERIAL: INVAR

FRONT PLATE (as viewed from front of dilatometer)

- ALL DIMENSIONS IN MM
- SCALE: 2:1
- ALL OTHER DIMENSIONS TO YOUR DISCRETION
- MATERIAL: INVAR
APPENDIX C
(Heat Transfer Calculations)
\[
T_{\text{BOUNDARY FILM}} = \frac{T_w + T_{\infty}}{2} = \frac{1073 + 293}{2} = 683 \text{ K}
\]

**Properties of air @ 683K**

\begin{align*}
\nu &= 63.62 \times 10^{-6} \text{ m}^2 \text{ s}^{-1} \\
\gamma &= 9.8 \text{ m s}^{-2} \\
\beta &= \frac{1}{T_{\text{BOUNDARY FILM}}} = 1.46 \times 10^{-3} \text{ K}^{-1} \\
k &= 0.0514 \text{ W m}^{-1} \text{ K}^{-1} \\
\Pr &= 0.683 \text{ (Prandtl Number)}
\end{align*}

\[
Gr = \frac{g \cdot \beta \cdot |T_w - T_{\infty}| \cdot x^3 \cdot Pr}{\nu^2}
\]

(Grashof Number)

where \(x\) (characteristic length), is the distance travelled by a fluid particle in the boundary film.

\[
L = 10 \text{ mm}
\]

\[
\therefore \text{ characteristic length} = L/2 \text{ (base)} + L \text{ (side)} + L/2 \text{ (top)} = 2L = 20 \text{ mm}
\]

\[
\therefore Gr = 1.51 \times 10^4
\]
Now using the equation

\[ Nu = C(Gr \cdot Pr)^m \]

according to Lienhard\(^b\), for irregularly-shaped solids,

\[ C = 0.52 \text{ and } m = 0.25 \]

\[ \therefore Nu = 0.52 (1.51 \times 10^4 \times 0.68)^{0.25} \]
\[ = 5.24 \]

since \( Nu = \frac{h \cdot x}{k} \)

\[ \therefore h = \frac{Nu \cdot k}{x} \]
\[ = 13.47 \text{ W m}^{-2} \text{ K}^{-1} \]

---

**Properties of 3CR12\(^c\)**

\[ \rho = 7700 \text{ kg m}^{-3} \]
\[ k = 25 \text{ W m}^{-1} \text{ K}^{-1} \]
\[ c = 430 \text{ J kg}^{-1} \text{ K}^{-1} \]
\[ \alpha = \frac{k}{\rho \cdot c} = 7.55 \times 10^{-6} \text{ m}^2 \text{ s}^{-1} \]

Now
\[ \frac{k}{h \cdot l} = 371.27 \]

and \( Bi = 1/\frac{k}{h \cdot l} \) (Biot Number)
\[ = 0.00269 \]

Heisler\(^d\) showed that if \( \frac{\alpha x}{l^2} > 0.2 \), the solution for the centre temperature could be approximated to within 1 percent using the term

\[ \frac{\theta_0}{\theta_i} \approx C_0 \cdot \exp\left(-A_0 \cdot \frac{\alpha x}{l^2}\right) \]  

...(1)
where \( L/2 = l \), and \( C_B \) and \( A_B \) (which are functions of the Biot number), can be expressed as

\[
A_B \cdot (\tan A_B) = Bi = \frac{hl}{k}
\]

\[
C_B = \frac{4 \sin A_B}{2A_B + \sin 2A_B}
\]

the arguments of the trigonometric equations being in radians.

Solving for \( A_B \) and \( C_B \)

\[
A_B = 0.0518
\]

\[
C_B = 1.0005
\]

(1) can then be simplified to

\[
\frac{\theta_o}{\theta_i} = 1.0005 \cdot \exp\left(-8.1 \times 10^{-4} \cdot \tau\right)
\]

in which \( \tau \) is time in seconds.

Consequently, the temperature \( T \) of a cube after exposure to a temperature \( T_{\infty} \) is expressed in the form

\[
T = T_{\infty} + \left(\frac{\theta_o}{\theta_i}\right)^3 \cdot (T_{\infty} - T_{\infty})
\]

which when simplified becomes

\[
T = 800 + \left\{1.0005 \cdot \exp\left(-8.1 \times 10^{-4} \cdot \tau\right)\right\}^3 \cdot (-780)
\]

References

c BS EN 10088-1 List of stainless steels (1995).
APPENDIX D
(Published MSSA '97 Abstract)
During the production of alloy steels, annealing treatments are often employed in the thermomechanical process cycle. This thermomechanical process initially involves hot rolling of a cast slab and may be concluded with a cold rolling procedure. Intermediate annealing treatments are performed to both soften the material for further processing, and to control microstructural development. Annealing treatments of a 12wt% Cr steel (3CR12) transform the martensite phase, which is present after hot rolling, to a mixture of ferrite and carbides. As the microstructure of these steels is dual phase, any reduction in the martensite volume fraction and resultant increase in ferrite volume fraction, will reduce the hardness, thus yielding a parallel increase in ductility. 3CR12 alloys transform to austenite typically at temperatures between 750°C to 850°C (Ac3). Hence to prevent austenite and corresponding martensite formation, annealing treatments need to be performed below the Ac3. It is more desirable for annealing to be performed at temperatures close to the Ac3, as the kinetics of transformation are greater at higher temperatures, which results in the period of annealing required being considerably shorter, and thus more economically favourable. Further, it is thought that differences in the microstructure due to different cooling rates following hot rolling, may influence the rate of annealing. Consequently a study of the annealing response of 3CR12 steel when subjected to different post hot rolling cooling treatments, may aid in developing improved annealing characteristics for this steel.

A series of 12wt% Cr base alloys were subjected to various cooling treatments immediately following hot rolling in order to study their annealing response. This was accomplished by water quenching, air cooling and controlled cooling in an insulatory material of the hot rolled plates. A study of the material in the hot rolled condition comprised of dilatometry, optical microscopy, hardness testing and volume fraction analysis. Using Nomarski interference contrast on a Reichert MeF3-A optical microscope, the etched microstructures were studied and photographed for analysis in an image analyser. The image analyser was able to discern between phases due to etching contrasts and hence measure the volume fraction of ferrite or martensite in the hot rolled or annealed conditions.

The ferrite and martensite develop from an austenite phase on cooling, with proportionately more martensite forming at higher cooling rates than ferrite. Hot rolling causes the martensite and ferrite phases to develop in bands forming an anisotropic microstructure as shown in Figure 1. Even following subcritical annealing treatments, persistent anisotropic behaviour has been shown to be exhibited by 3CR12 steel, as a result of the hot rolling. Figure 2 illustrates the nucleation of martensite on a prior austenite (now ferrite) grain boundary.

Preliminary results indicate that samples with higher cooling rates after hot rolling, respond faster to annealing treatments than samples subjected to lower cooling rates after hot rolling. Hence post hot rolling cooling treatments do appear to influence subsequent subcritical annealing treatments of 3CR12 steel.

The assistance and financial support of Columbus Stainless and Boart Longyear Research Centre are gratefully acknowledged.

References