HEWITT, J. High-chromium controlled-hardenability steels. *INFACON 6. Proceedings of the 1st International Chromium Steels and Alloys Congress, Cape Town*. Volume 2. Johannesburg, SAIMM, 1992. pp. 71–88.

High-Chromium Controlled-Hardenability Steels

J. HEWITT

Middelburg Steel and Alloys (Pty) Ltd, Middelburg, South Africa

The paper first describes the development of a process in which the composition of coils of corrosion-resisting steels and their natural cooling rates are matched to ensure essentially complete transformation to ferrite + carbides during cooling after hot-rolling. This produces uniform properties throughout large coils so that the steel is ready for dispatch without any further heat treatment. In this slow-cooled condition the large coils have mechanical properties equivalent to those of material after annealing, and give products that meet the mechanical-property ranges of existing 11 per cent chromium steel specifications, which are equivalent to, or slightly stronger than, those for mild steel.

The paper next describes how work, on more than 500 experimental and production heats, has established the effects of each of up to 18 elements, individually and particularly in combination, on the proportion of the phases present, and on their rate of transformation during the continuous cooling of these high-chromium steels.

It is shown how these results are applied in the development of new high-strength high-chromium general-engineering steels that have mechanical properties, corrosion resistance, and weldable behaviour satisfying a wider range of national and international standards. The uniqueness of this development is that the composition of the steel is predetermined so that these properties are achieved without the need for any further heat treatment after hot-rolling. This effects a considerable simplification over the process routes currently applied to stainless and high-chromium steels. Consequently, the savings in production costs are significant in terms of energy cost and increased production rates.

Finally, it is shown that these steels can be rolled on conventional carbon-steel rolling mills, with only minor adjustments to roll-pass sequencing to accommodate the higher spread found in high-chromium steels. It is not necessary to recut profiles or to have separate, expensive roll sets.

These developments are aimed at general-engineering and construction steel applications, and offer cost-effective solutions to many of the corrosion problems facing that sector of the steel marketplace. The results are believed to represent a significant improvement in our understanding of ferritic stainless steels, and many opportunities for commercial exploitation have clearly emerged from this work.

Introduction

Corrosion costs form a significant proportion of each country's Gross National Product (GNP). Estimates vary, by country and author, from between 1,5 and 5 per cent of GNP. Methods used to combat these corrosion problems in general-engineering and construction steels are many and widely varied. They range from simple to advanced and complex paint schemes, and to coatings of zinc, aluminium, chromium, and such like 'skin-deep' approaches. Additions of alloying elements to these steels, aimed at through-thickness protection, include the copper additions of 'weathering steels', which rely on copper's promotion of a tightly adhering corrosion product to lessen further attack. At the top end of the range of options are the ferritic and then the austenitic stainless steels.

For general-engineering and construction purposes, the use of stainless steels has been severely limited by their cost, so that until recently they were rarely used outside applications where the corrosive environment is so severe as to make their use obligatory. In recent years, there has been a steady (exponential?) growth in the application of the 11 to 12 per cent chromium micro-duplex steels in areas of general engineering and construction. These steels, typified by 3CR12[1], have been shown to give cost-effective solutions in harsh, wet-corrosive and abrasive environments such as in the coal, sugar, and transportation industries.

Their success has bred look-alike's and, over the past two or three years, X2CR11 (Krupp, Germany), 5CR12 (Thyssen, Germany and Australia), Highfab 3/12 (British Steel), and F12N (Ugine, France) have been launched in the marketplace. Jointly, these manufacturers are predicting that market sales will climb to some 1 Mt/a over the next five years. Whilst this figure suggests a fair degree of double counting, it is nonetheless an impressive target in a total stainless-steel market of about 10 Mt/a. However, this is a very small fraction of the market for general-engineering and construction steels, where a more interesting notion would be a 1 per cent penetration of the carbon-steel market. This would require a doubling of the present stainless-steel production and associated chromium supplies!

Several factors limit a more rapid growth for these high-chromium steels.

(a) First, is undoubtedly the cost since the market price at first sight bears little, if any, relationship to the cost of the alloying elements they contain. The reasons for the high costs are that, at present, these steels are generally produced on highly sophisticated stainless-steel facilities of low-tonnage output, which preclude the economies of scale of the bulk steel producer. The fixed-cost element of their production is thus high, particularly when coupled with the current requirement for the steel to be given an often complex heat treatment to develop the required (specified) properties. This is particularly true of the higher-strength steels as formulated at present.

(b) The general belief that ferritic stainless steels have low impact resistance and poor weldability, and thus require more skilled handling in their fabrication. This belief is generally correct for the single-phase varieties of these steels, but is certainly not applicable to the dual-phase steels with which we are now concerned.

(c) The general opinion of the mechanical properties of these steels as low, thus limiting a higher-strength, thinner-section approach. This belief is true, unless cold-worked steels, or the even-more expensive and sophisticated precipitation-hardening steels, are employed.

(d) Other general constraints associated with, for example, resistance to proprietary steels compared with the credibility offered by national or international standards.

(e) The broad approach to construction projects in which the initial costs are regarded as paramount, and such techniques as lifecycle costing are not used.

(f) The general resistance to change.

The last three issues are not addressed in this paper, but are nevertheless very real.

Background

Late in 1984 and early in 1985, trials started on sampling coils of 3CR12 (as set out in Figure 1) to determine the property variations throughout these coils in the as-rolled condition. This work was necessary because at that time some 10 to 15 per cent of production heats were proving difficult to soften or had variable properties after continuous line annealing of coil or roller-hearth annealing of plates. These required re-annealing, thus adding to the cost and slowing the production.

These trials revealed several things about coiled 3CR12. With hindsight, none now seems too surprising but, as they formed the nucleus for what followed, they are summarized first. The trials showed that

(1) small coils were hard throughout their length,

(2) large coils were fully soft throughout their length, except for a hard lap or two on the inside and outside ends,

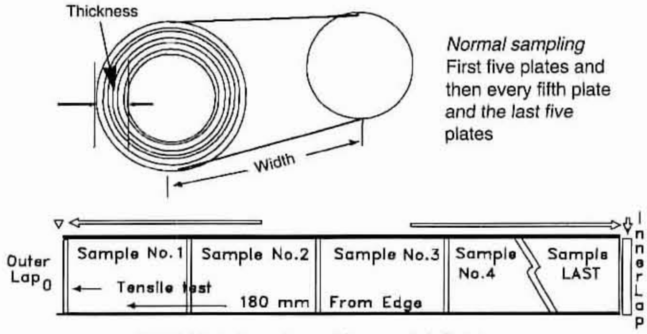


FIGURE 1. Sample positions and definitions

Note: Sample 1 is *before* the First Plate
Sample 2 is *before* the second plate, and so on
The last sample is *after* the last plate cut

(3) water on the mill, for cooling purposes, hardens the steel and gives erratic properties through the as-rolled coil,

(4) stoppages during rolling, for example to check gauge, also harden the steel.

These effects are shown in Figures 2 to 4, where 0,2 per cent proof stress is plotted versus distance on either side of the centre line of the thickness of the coil. Short lines then identify small coils, and long lines represent large coils. (The parameters are given in US units.)

The results were consistent, and led to a proposal that the major proportion of the plates cut from large coils were already 'self-annealed', and that these portions could be sold direct off the mill; only the hard ends needed to be annealed. This proposal met with a mixed reception, because the concept of as-rolled products is not normal in the stainless-steel industry. This is in contrast to the carbon-steel industry, where well over 90 per cent of hot-rolled products receive no further heat treatment after rolling. About 70 t were trialed in the marketplace before the route was suspended in October 1985. No problems arose from these 70 t.

In March 1987 a full order book led to the idea of 'self-annealed' coils being resurrected since each tonne of 3CR12 taken off the annealing lines by this process allowed about 2 extra tonnes of austenitic steel to be produced. On the first coil of this second series of trials, A.B. Victor (Mills Metallurgist) tossed an insulating blanket over the coil as it came off the downcoiler in an attempt to slow down the cooling rate, particularly on the ends. It worked, and the properties were uniform through the full length of the coil and in specification, as shown in Figure 5.

As tossing hairy insulating blankets over coils coming off the hot-rolling mill is not an attractive production route, within a short time J. Nysschen (Hot-Mill Engineer) had made a simple box with fibre-insulated sides – the first hood. A further four were added later. All subsequent trials used these hoods over the coils. The results, when analysed, showed that uniform properties throughout a coil could be obtained provided that the coil thickness (as defined in Figure 1) exceeded about 300 mm. With our mandrel size of 760 mm, this is achieved at 6 t on a 1050 mm wide coil, at 11 t on a 1300 wide coil, and at 14 t on a 1580 mm wide coil (shown in Figure 6). Water and mill stoppages still needed to be avoided.

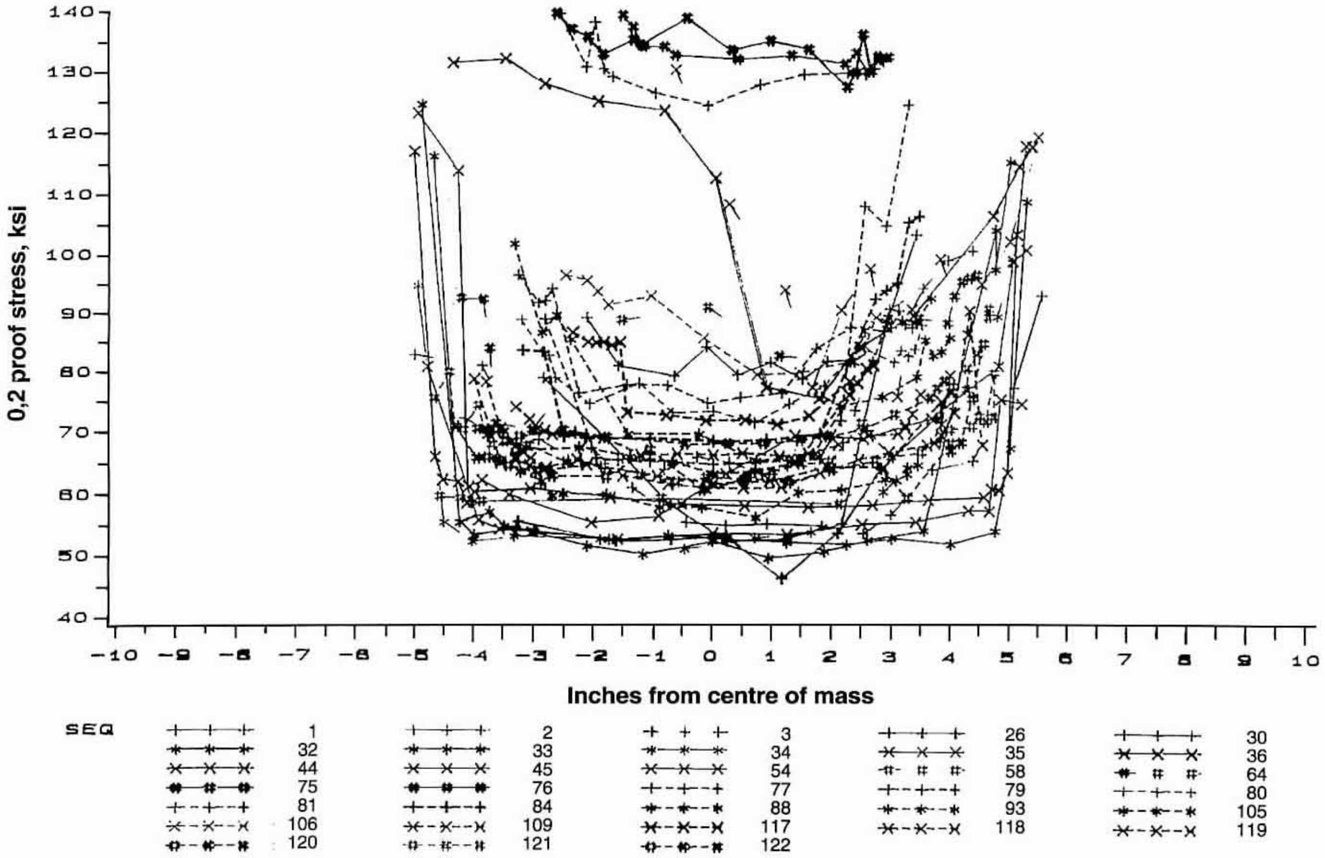


FIGURE 2. Proof stress versus coil position: Water and stoppages on the mill

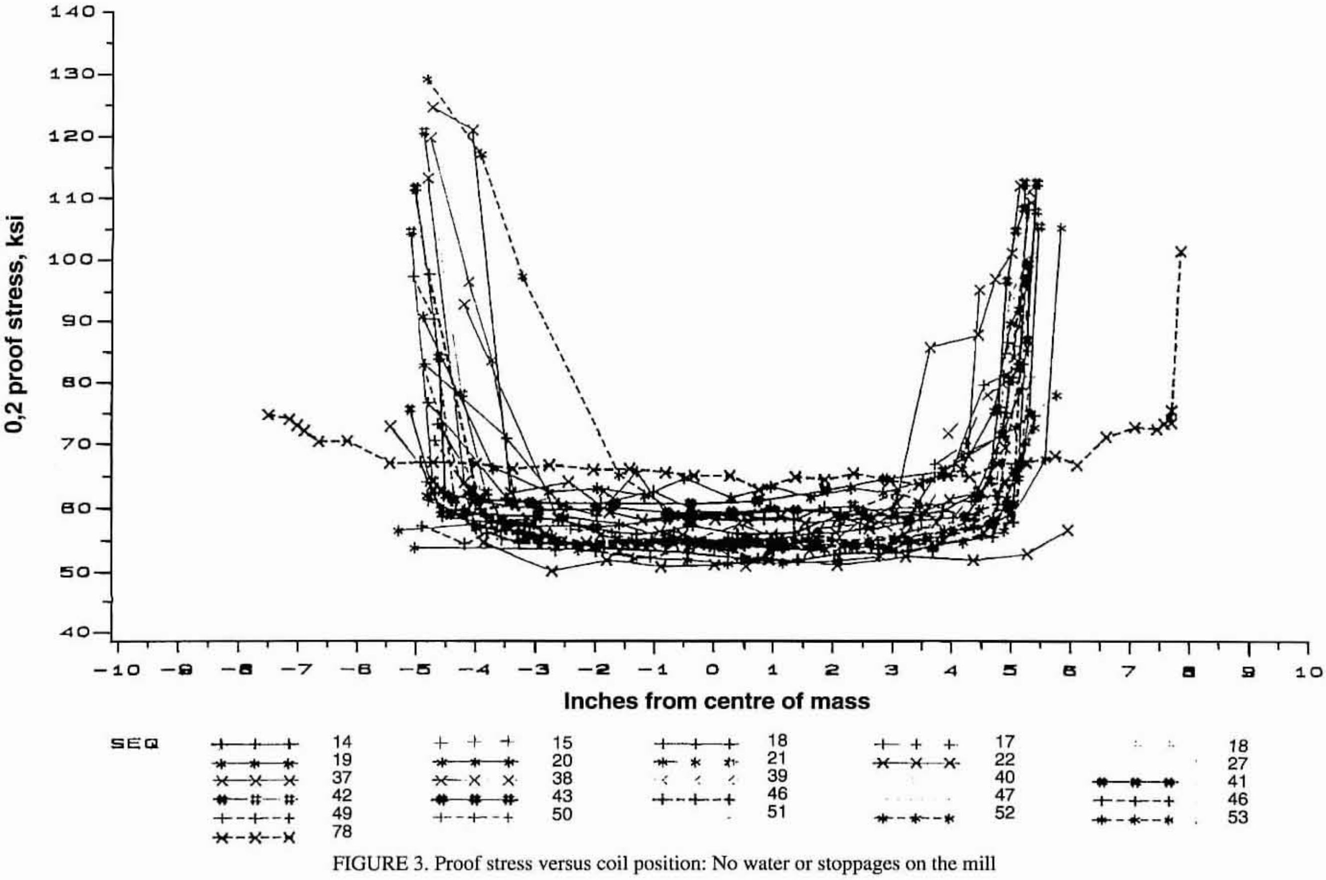


FIGURE 3. Proof stress versus coil position: No water or stoppages on the mill

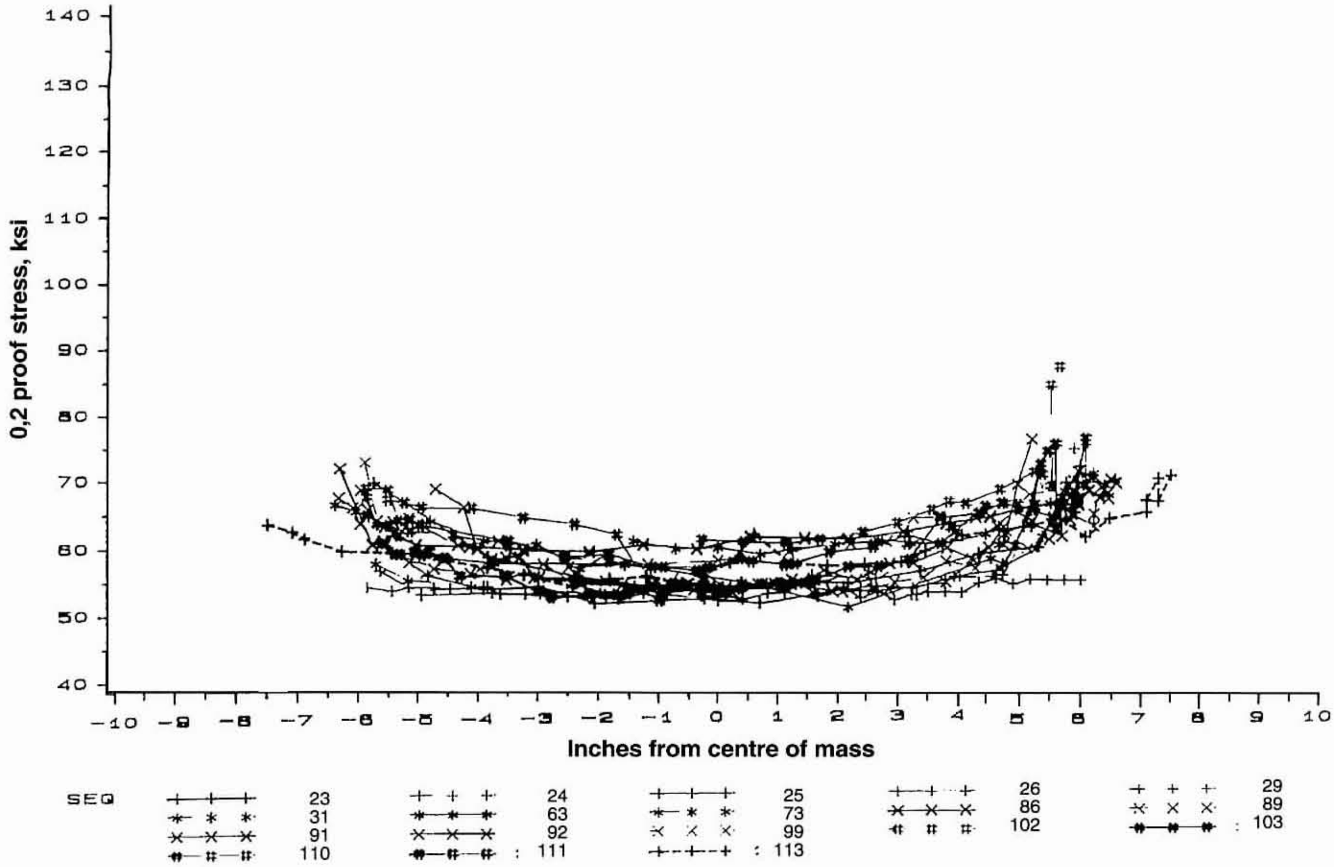


FIGURE 4. Proof stress versus coil position: Properties of coils meeting required criteria

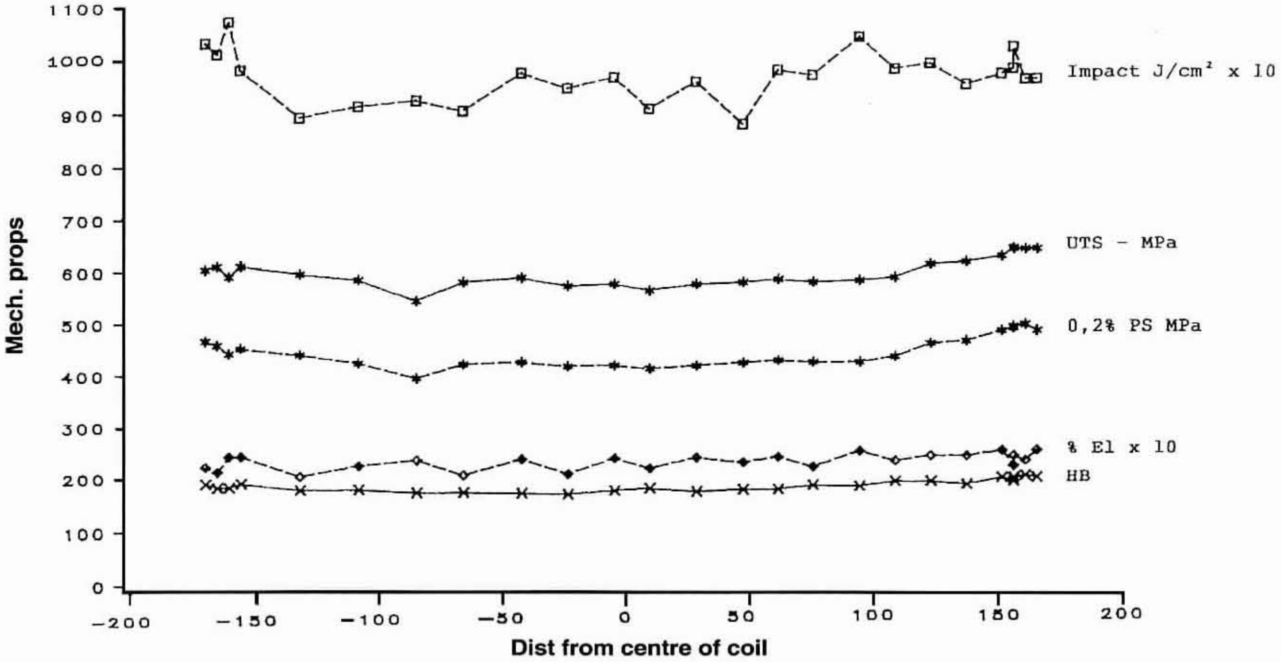


FIGURE 5. Through-coil properties of hood-cooled coil (mass 11420 kg, width 1250 mm)

There was a fundamental inconsistency in the initial metallurgical interpretation that the coils were soft because of 'self-annealing', i.e. the heat in the coil tempered the martensite formed on cooling. This interpretation problem arises because the formation of martensite is completed at relatively low temperatures (M_f about 300°C), when most of the heat energy has gone. Processes such as tempering are known to be very slow at these low temperatures.

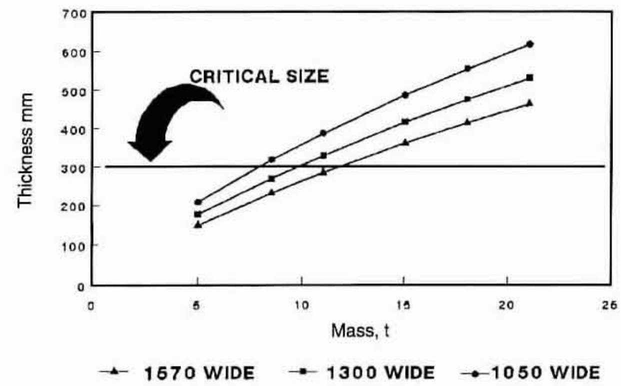


FIGURE 6. Relationship between mass and width thickness for a mandrel size of 760 mm

In order to resolve this problem, Professor G.T. van Rooyen (University of Pretoria) was asked to produce continuous-cooling transformation diagrams (CCT diagrams) for typical heats of 3CR12, i.e. to measure the rate of progress of transformation at different cooling rates. If we were to use these CCT diagrams effectively, we also needed to establish in detail, how quickly the different parts of a coil cool. This was done by placing thermocouples in coils that were subsequently processed, i.e. reheated, through the batch-annealing unit, and by using MFT computing[3] to model the cooling process by finite-element analysis. This work was completed in 1988.

The early CCT diagrams, e.g. Figure 7, showed clearly what was happening. Examination of Figure 7 shows that, if the cooling rate is slow enough, the austenite fully transforms to ferrite + carbides, and no martensite is formed at all. At higher cooling rates (> 60°C/min), the austenite in the steel fully transforms to martensite, and the steel is uniformly hard. At intermediate cooling rates, a mixture of ferrite + carbide and martensite is formed, with consequent intermediate properties, depending on what proportions of these soft and hard phases are present. The concept of 'self annealing' or 'self tempering' does not have to be invoked since the behaviour patterns seen are *fully* explained by the CCT diagrams.

Results from further CCT work at the University of Pretoria on a range of compositions also indicated that it was not necessary to use titanium and nickel to achieve typical 3CR12 properties, since identical results could be obtained with alternative suitably balanced compositions. The cost savings and the reduction of surface defects associated with the avoidance of titanium additions were clearly attractive targets. A major exercise was set in motion to explore this possibility. In total, over 4200 tensile tests were evaluated on laboratory and production heats, together with tests on impact, fatigue, high-temperature properties, weldability, and, corrosion resistance, and side-by-side forming tests at customers' locations. The surface quality improved by about 1,5 per cent in terms of reject levels, with much reduced spot conditioning.

In February 1989, these results, together with data from assorted costing exercises, were presented to the Executive of Middelburg Steel & Alloys (MS&A). The costing work showed a saving of more than 20 per cent from reduced alloy costs, yield gains, and not having to anneal. In addition the 'black coil' route, in a full order-book situation, gave a significant potential extra capacity for export austenitic steels. The decision to switch to 3CR12L was, not surprisingly, taken at this meeting. In October 1991, production tonnages passed the 60 kt level. The process is patented[2].

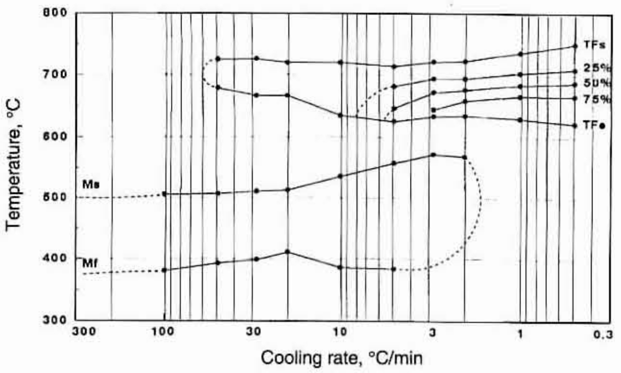


FIGURE 7. An example of a CCT diagram for 3CR12

Gauge Project

From the early results, it was clear from the way that the CCT diagrams changed with relatively minor changes in composition that, if one could determine how composition changes moved these transformations around, the possibility would exist for controlling the hardenability of these steels. Essentially, the question is how does each individual element in high-chromium steels affects the amount of austenite in the steel and the rate at which it transforms. If these two parameters could be controlled in a systematic and reproducible way, then a range of new possibilities would become available for the development of steels that have attractive combinations of properties and ease of production.

The objective of the first phase of the project was therefore to try to establish how the various elements in a steel affect the amount of each phase present in high-chromium steels, and the speed at which these phases are formed or transformed.

Techniques Employed

Ultra-linear high-sensitivity dilatometers (designed by Professor G.T. van Rooyen, University of Pretoria) were used, together with highly accurate programmable temperature controllers. Principally, these devices measure the progress of transformations by length change over a series of controlled cooling rates in the range 100°C/min to 0,1°C/min. Figure 8 shows an example of the plots from a dilatometer. This output is first converted to tabular form, as illustrated in Table I, and then to a continuous-cooling transformation diagram (CCT curves), as shown in Figure 9.

At high temperatures, i.e at hot-rolling temperatures, these steels usually contain a mixture of austenite and ferrite. On cooling, the austenite phase can transform to ferrite + carbides, or to martensite, or in extreme cases remain as retained austenite (e.g. 304 types!). The percentage of the total available austenite present that transforms to martensite is measured for each cooling rate, and is included in the results table.

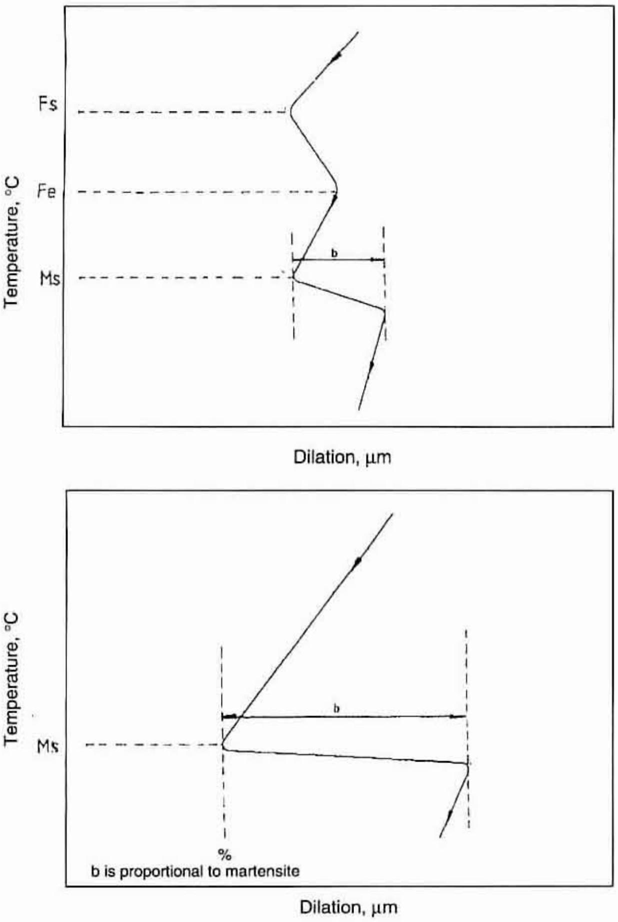


FIGURE 8. Examples of dilatometer output

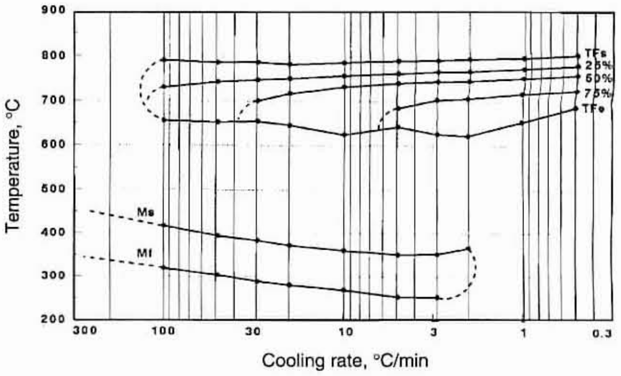


FIGURE 9. A further example of a CCT diagram for 3CR12

It is also essential to know the total amount of austenite available for transformation. This is determined by the following.

(a) Water-quenching from high temperature (20 minutes at 1000°C) and the preparation of micrographs. Selective etching to highlight the martensite then allows the measurement of the percentage martensite with an image analyser. Etching techniques are critical on high-chromium steels, which are difficult to attack chemically.

(b) An alternative method for determining the percentage of austenite can be used if the dimensions of the sample are measured accurately, and the thermal-expansion coefficients of the austenite and ferrite are also known or determined accurately.

The results of the two methods agree, and they can be used together for cross- checking.

TABLE I
TYPICAL RESULTS FROM DILATOMETER OUTPUT

Steel no.	M_s	A_{C_1}	°C/min	F_s	F25	F50	F75	Fe	M_s	M_f	% Tran.
128986	410	796	100	791	731	–	–	656	417	319	34
(M_f = 322)			50	787	744	–	–	653	395	304	49
			30	788	749	702	–	655	384	289	55
			20	784	752	718	–	646	373	281	61
			10	787	758	733	–	625	361	270	71
			5	791	763	741	685	643	351	254	80
			3	792	767	745	704	626	352	253	88
			2	795	768	746	707	622	367	–	93
			1	798	774	753	718	654	–	–	100
			0,5	802	782	760	725	688	–	–	100

% martensite = 97,3 (water-quenched from 1000°C)

M_s	Temperature at which martensite starts to form *on cooling*
A_{C_1}	Temperature at which austenite starts to form *on heating*
°C/min	Controlled cooling rate, °C/min
F_s	Temperature at which austenite starts transforming to ferrite
F25	Temperature at which 25% of austenite transforms to ferrite
F50	Temperature at which 50% of austenite transforms to ferrite
F75	Temperature at which 75% of austenite transforms to ferrite
Fe	Temperature at which austenite to ferrite transformation ends
M_f	Temperature at which martensite transformation ends
% Tran.	% of the *total available* austenite transformation at that cooling rate
% EDT	% of the *total available austenite* (measured by image analyser)

The flow of data from the University of Pretoria, was supplemented by the purchase of four dilatometers at the Works; this increased the rate of progress. The difficulties in establishing the percentages of each phase present in production and experimental steels were largely resolved by work done at Mintek[4], and the results became consistent.

Interpretation of the Results

Initially, it proved difficult to quantitatively compare two or more CCT curves and extract the effects of compositional changes on the transformation behaviour. Alternative methods to allow such comparisons had to be devised. What emerged from this part of the work was that, if the effects of the cooling rate on the percentage martensite are plotted, they can be shown to provide a simple yet very powerful method of characterizing each steel.

The effect of the cooling rate on the percentage of martensite is first determined using a probability density-function type of equation adopted for this purpose. This method provided a consistent approach to the difficulty of determining the start of transformation (5 per cent transformed) and the end of transformation (95 per cent transformed). The technique also has the advantage that the transformation behaviour of a steel can be described by only two parameters; these can then be studied in relation to the compositional changes.

This novel approach is, to date, the most useful way found to summarize and compare results. Figure 10 shows examples of a plot of percentage martensite versus cooling rate for the data of Figures 7 and 9. We are, in effect, studying the steel's hardenability, and the plots in Figure 10 can be regarded as hardenability diagrams similar to, but more sophisticated than, those for a Jominy hardenability test.

To further characterize the steel, the hardness was measured after water-quenching, and after slow, controlled cooling of 0,5°C/min. The results are added to the graph for percentage martensite versus cooling rate when they are of particular interest. These data also permit the calculation of the individual hardness of the ferrite and martensite phases, which is useful for separating the characteristics of the two phases and checking for anomalies.

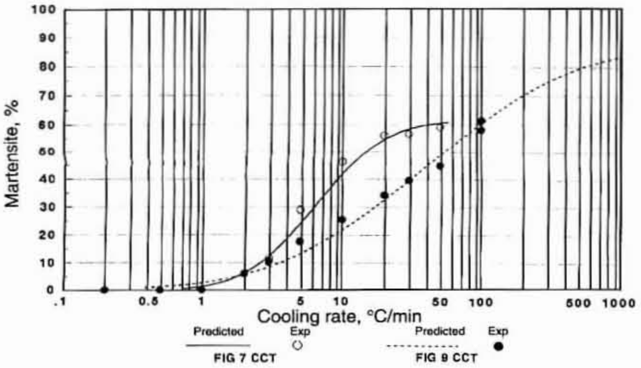


FIGURE 10. Martensite versus cooling rate (CCT diagrams in Figures 7 and 9)

Effect of Composition

It was obviously impossible to study individually each of the possible alloying elements that could be used to modify transformation behaviour; the number of heats required would have been prohibitively large. (The variation of 8 elements at 3 levels, for example, would require 6561 heats.) Instead, the known effects of these elements on mild steel and low-alloy steels were first examined, on a 12 per cent chromium base, concentrating mainly on elements that strongly interact with the interstitials (carbon and nitrogen). The data assembled from the previous work at universities and research institutes were used to initially set composition starting-points for the investigations into the effect of compositional changes. These data have now been discarded because much of this work lacked what are now considered essential details (for example, their full analyses were rarely available), and the transformation data are relatively inaccurate by current standards. The compositions and relevant transformation parameters studied are summarized in Table II, where the most relevant columns are, perhaps, those showing the minimum and maximum values. Steels with higher alloy additions, other than chromium, are discussed by Schmid and Knutsen[5], and by Knutsen and Hutchinson[6] in companion papers in these Congress proceedings.

The data available for interpretation are currently from a total of 544 heats made up as follows:

100 production heats of 3CR12 (three variants)
21 production heats of type 409*
25 production heats of type 430*
201 laboratory heats of 11 – 13% Cr and 'Adds'
12 laboratory heats of 14 – 16% Cr and 'Adds'
71 laboratory heats of 16 – 18% Cr and 'Adds'
50 laboratory heats of 18 – 20% Cr and 'Adds'
16 laboratory heats of more than 20% Cr and 'Adds'
3 type 410/420 martensitic cutlery steels*
5 3CR12 'look-alike's'*

* Includes steels from Argentina, Japan, USA, Brazil and Europe.
'Adds' comprise aluminium, boron, copper, cobalt, molybdenum, niobium, tungsten, vanadium, and zirconium, as well as rare-earth treatments, and deliberate variations of nickel, titanium, silicon, and manganese. All the 'Adds' were kept relatively small.

Reliance was placed on the power of modern computer statistical-analytical packages[7] in the study of the wealth of data generated, and the extraction of the information required on individual elements. All possible cross-terms and parameter square terms were examined, i.e. the relationships were limited to second-order equations. A maximum of 60 terms was set for each of the parameters of interest. Whilst this may well represent an over- specification in statistical terms, it yielded satisfactory constitutive equations for practical application on the variables listed in Table II, as is demonstrated in what follows.

These data analyses successfully allowed the effect of each element to be established, and such analyses are carried out as each batch of results becomes available. The effect of the various elements quickly stabilized (became consistent) and, on the assumption of linear relationships, typical results are given in Table III.

TABLE II
SUMMARY OF COMPOSITIONS AND VARIABLES STUDIED

Factor	Unit	Mean	Minimum	Maximum	No.
Carbon	wt%	0,029	0,006	0,166	530
Sulphur	wt%	0,008	0,001	0,029	530
Phosphorus	wt%	0,025	0,004	0,117	530
Manganese	wt%	0,952	0,13	2,93	530
Silicon	wt%	0,563	0,05	2,97	530
Copper	wt%	0,131	0,001	0,85	530
Cobalt	wt%	0,033	0,003	1,69	530
Titanium	wt%	0,088	0,001	1,71	530
Molybdenum	wt%	0,135	0,008	1,93	530
Chromium	wt%	13,80	8,13	27,72	530
Nickel	wt%	0,54	0,01	6,88	530
Aluminium	wt%	0,015	0,001	0,503	530
Niobium	wt%	0,042	0,001	0,657	530
Vanadium	wt%	0,089	0,02	0,589	530
Nitrogen	wt%	0,0364	0,0066	0,276	530
Cerium	wt%	0,0011	0,0001	0,012	530
Boron	p.p.m.	14,30	0	340	530
Ferrite factor		12,31	-15,95	32,82	530
Chromium equivalent		15,86	8,42	31,78	530
Nickel equivalent		2,86	0,65	14,84	530
Ratio Cr/Ni		7,27	1,49	27,00	530
Transformation data					
Austenite		57,3	0	100	491
A_{C_1}	°C	810	550	984	339
M_s	°C	368	-40	585	352
M_f	°C	260	-60	485	320
Quenched hardness	HB	245	123	389	469
Slow-cooling hardness	HB*	160	118	388	460

* Hardness after slow cooling at 0,5 °C/min

TABLE III
GENERAL EFFECTS OF EACH ELEMENT ON TRANSFORMATION, ETC.

Factor	Unit	A_{C_1}, °C	M_s, °C	M_f, °C	% Mart.
Carbon	1%	-280	-133	-300	+290
Sulphur	1%	-100	+85	+530	-495
Phosphorus	1%	+435	-275	+300	-220
Manganese	1%	-54	-34	-20	+6,2
Silicon	1%	+34	-44	-40	-32
Copper	1%	-23	+9	+13	+24
Titanium	1%	+83	+360	+350	-60
Cobalt	1%	-21	+19	-0,5	-0,4
Molybdenum	1%	+45	-17	-1,5	-2,0
Chromium	1%	+13	-32	-27	-8,3
Nickel	1%	-70	+24	-1,0	+12,6
Aluminium	1%	+40	+23	-120	+12
Niobium	1%	+15	+53	+60	-45
Vanadium	1%	+78	-12	-4,5	-13
Nitrogen	1%	-230	-93	-450	+100
Zirconium	1%	+36	-73	-90	-110
Cerium	1%	+88	+900	+1250	+1420
Boron	10 p.p.m.	0,14	+1,20	-0,3	-0,4

Note: The above factors show the average general effects from linear analyses about the mean composition given in Table I. There are strong inter-element effects that have to be taken into account for more accurate estimation and design purposes

The value of the coefficients listed in Table III show the effect of 1 per cent of each element (except boron, where 10 p.p.m. is used), and thus, not only indicate the effect of the element, but also show how natural variations around meltshop aim-points will affect the final product; in other words, how tight the specification will have to be if that element is used. Note, for example, the effect of titanium: a change of +0,1 per cent drops the austenite by 6,5 per cent, raises the A_{C_1} by 10°C and the M_s temperature by 35°C, drops the as-quenched hardness by 18 points, and increases the cooling rate at which transformation starts by about 33 per cent. Add to this, that titanium is a difficult element to 'hit' accurately during steelmaking and that it gives surface defects, and we have a good picture of what titanium additions are all about!

In an examination of the results in Table III, it must be remembered that the effects measured are the overall effects of what may well be a series of separate events. To again take the effect of titanium as an example, an addition of titanium will undoubtedly fix at least some of the carbon and nitrogen (starting in the liquid state), and perhaps some of the sulphur; and any spare after these reactions could give hardening of the ferrite – and not necessarily in that order! A comparison with one's previous perceptions and/or previously published data could thus be misleading. It is the overall effects that we can use to practical advantage.

For a given base composition, the effect of each element on the various transformation parameters can be readily modelled. Examples of the effect of titanium, chromium, and nickel are shown in Figures 11 to 13. Note that these effects apply only to this base composition, and should NOT be extrapolated to other bases since strong interaction terms are involved in the models. The overall predictability of behaviour of these steels is satisfactory, as can be seen from Figures 14 to 16, which show actual A_{C_1}, M_s, and percentage martensite (quenched from 1000°C) versus values predicted from the numerical analysis. This is in contrast to such parameters as Kaltenhauser Ferrite Factor [8] (see Figure 17), Gamma max[9], nickel equivalents[10] (Figure 18), chromium equivalents[11], and ratios of the last two. We have found that these factors do not provide any useful guidance to any of the parameters studied in our work, as seen from Figures 17 and 18.

An overview of the results relating to the effect of composition on phase balance, and what needs to be addressed to achieve, for example, a 40 to 60 per cent Martensite 'target' range, are illustrated in Figure 19.

Significance of the Results

If the cooling rate of a particular product shape is known, then its properties can be inferred from these diagrams. For example, we know that coils of wire rod are controlled to cool at 40°C/min on the Stelmore rolling process. Examination of the curve showing percentage martensite for a given steel at this cooling rate tells us what structure to expect, and therefore what the properties will be after this process.

We also know that water cooling can give cooling rates of up to about 25 000°C/min. The severe effect of water on the mill or coiler system *found in the earlier* investigations is now easy to understand.

We know from measurements, and particularly from finite-element modelling, that the outside laps of a 10 t coil cool in air at about 15 to 20°C/min, and the centre of the mass at about 2°C/min. Under properly used hood-cooling conditions, these values become 4 and 1°C/min respectively.

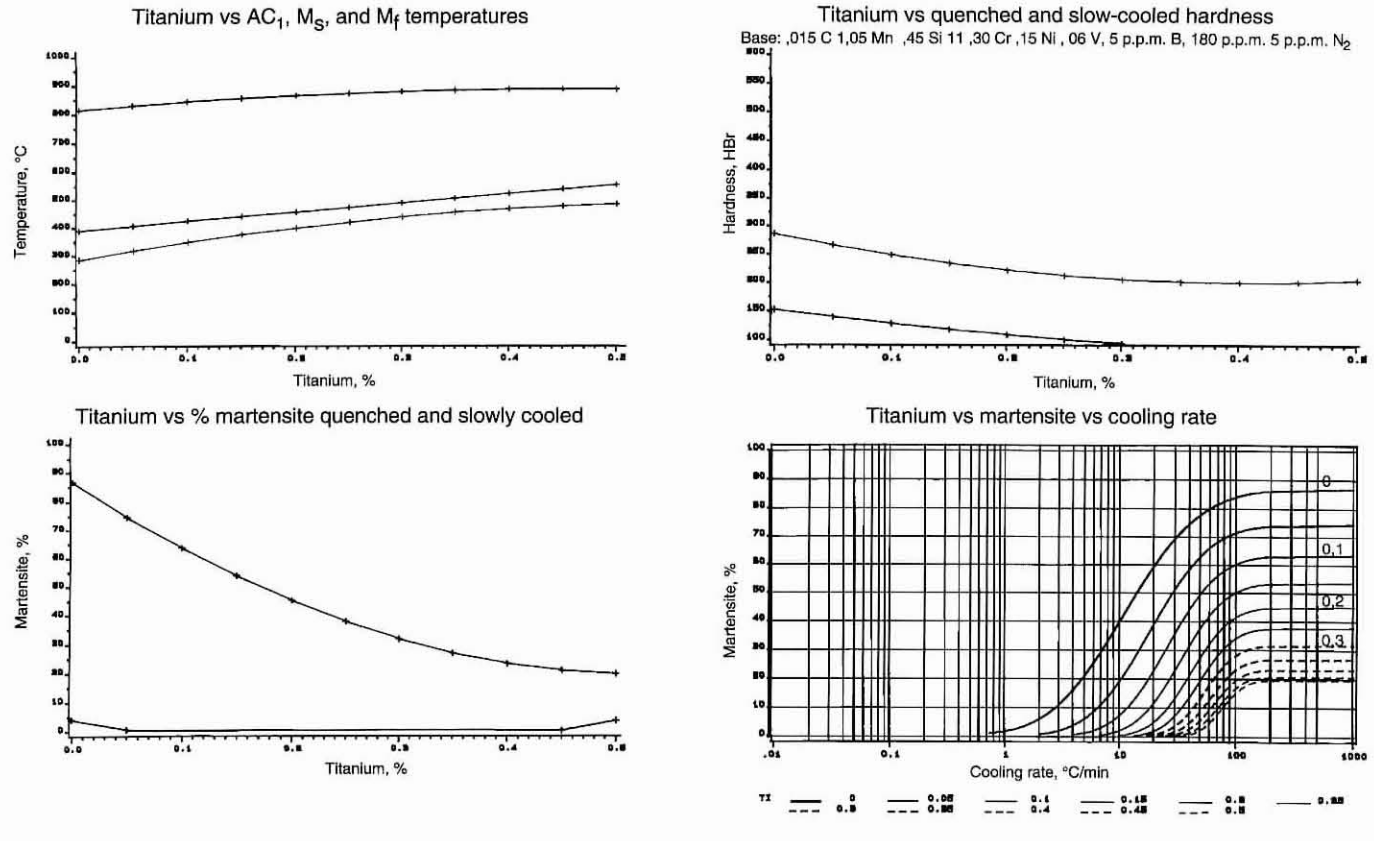


FIGURE 11. The effect of titanium

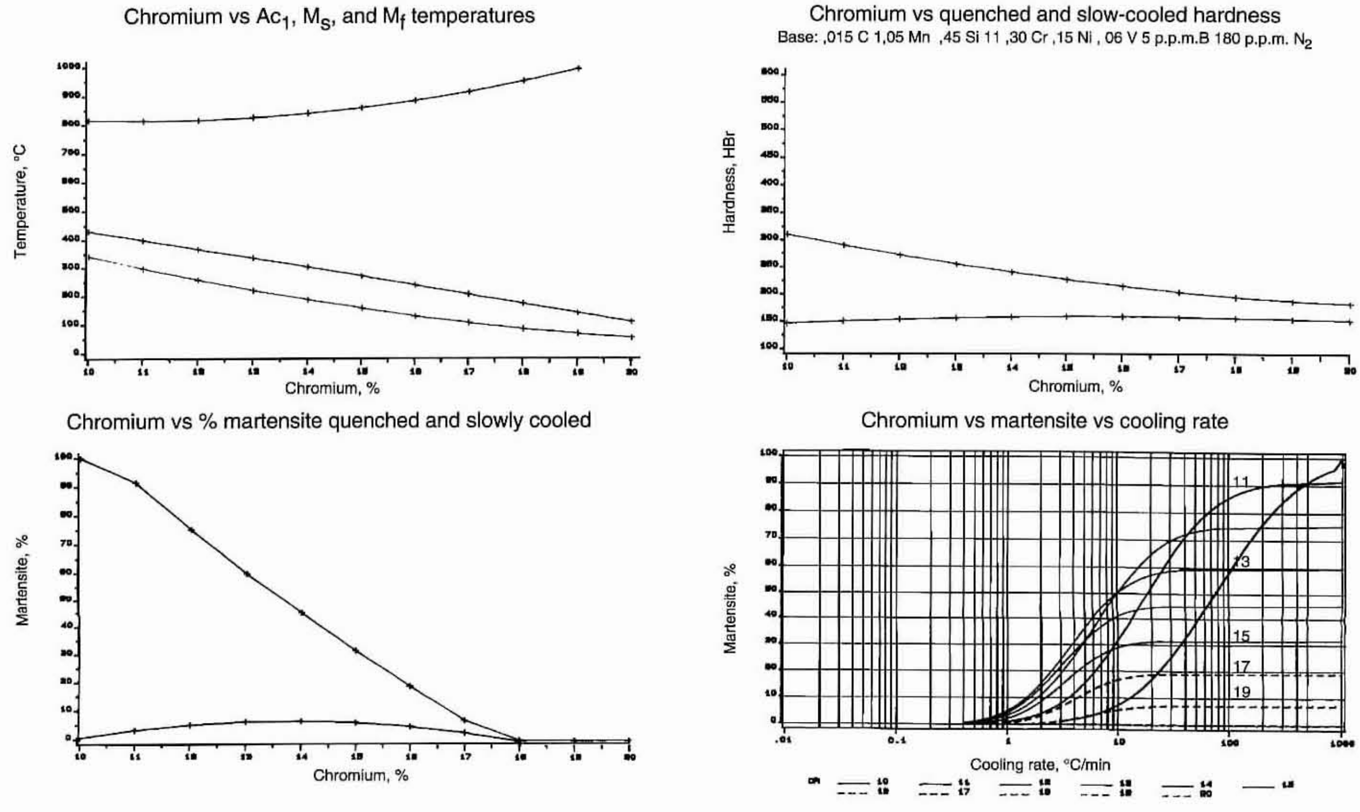
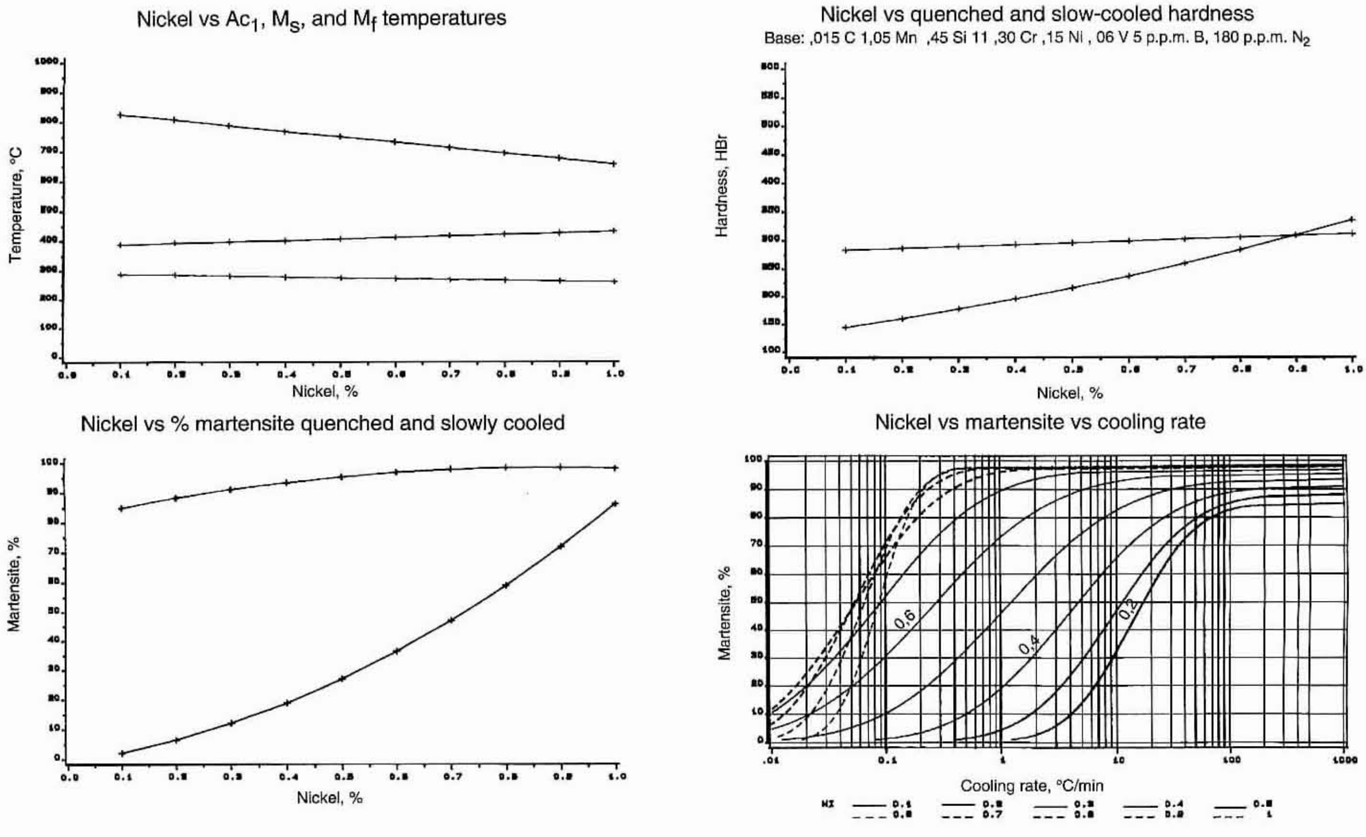


FIGURE 12. The effect of chromium



Nickel vs Ac_1, M_s, and M_f temperatures

Nickel vs quenched and slow-cooled hardness

Base: ,015 C 1,05 Mn ,45 Si 11 ,30 Cr ,15 Ni , 06 V 5 p.p.m. B, 180 p.p.m. N_2

Nickel vs % martensite quenched and slowly cooled

Nickel vs martensite vs cooling rate

FIGURE 13. The effect of nickel

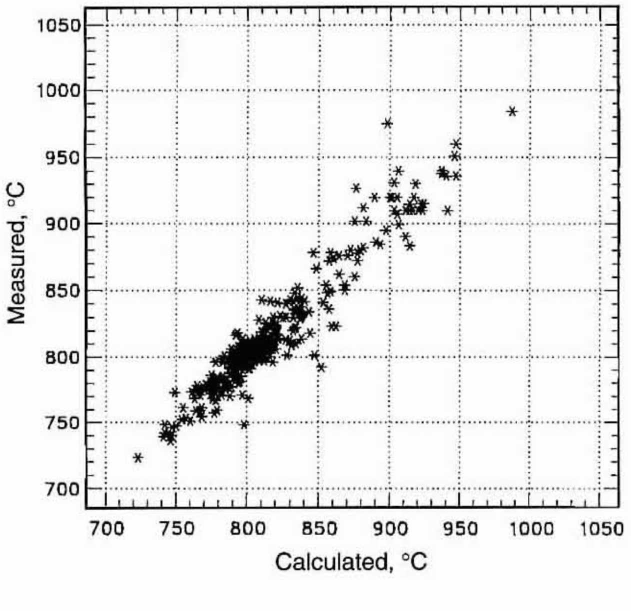


FIGURE 14. Actual versus calculated values for A_{C_1} temperatures

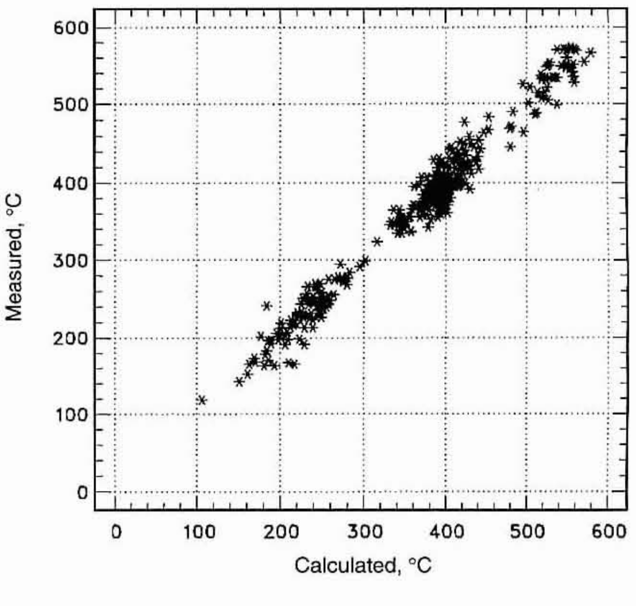


FIGURE 15. Actual versus calculated values for martensite starting temperature

Examination of the type of diagram given in Figure 10 immediately shows the response to be expected and the variability in the percentage martensite (and hence in the properties of the coil) that will result from these variations of cooling rate through an air-cooled coil, and the effects to be expected from the use of hoods.

Typical industrial cooling rates for a range of products have been collected from the literature, and from direct measurements in the plant and laboratory. If these are added to the plots for percentage martensite versus cooling rate, their usefulness in giving a total picture of the behaviour of a steel becomes clear. Figure 20 shows an example for several alloys, together with the known cooling rates for a variety of product shapes of practical significance superimposed on the same plot.

Understanding Figure 20 is important to an understanding

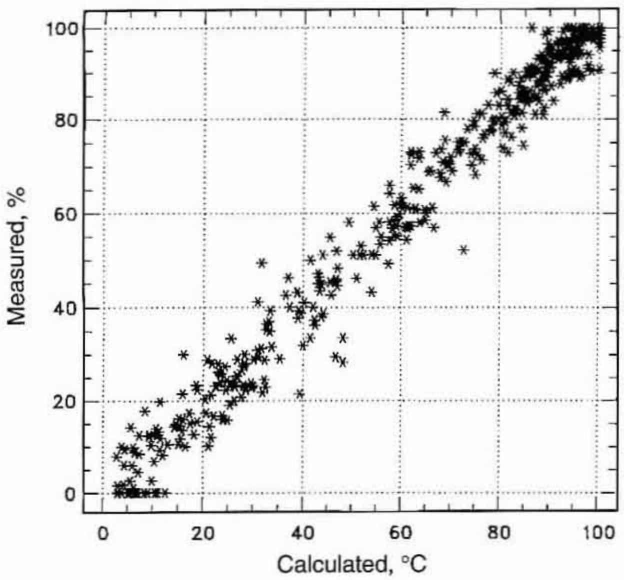


FIGURE 16. Actual versus calculated values for martensite quenched at 1000°C

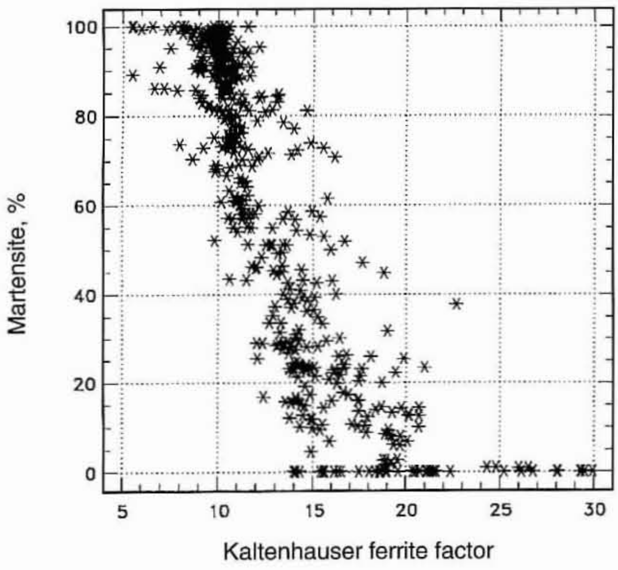


FIGURE 17. Percentage martensite versus the ferrite factor

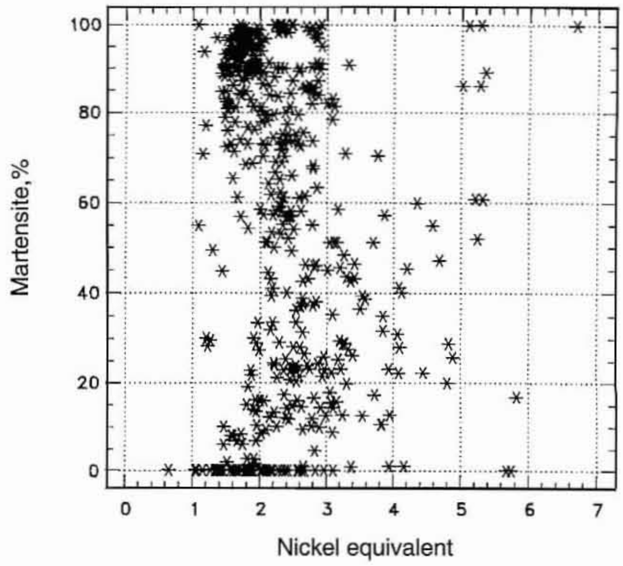


FIGURE 18. Percentage martensite versus the nickel equivalent

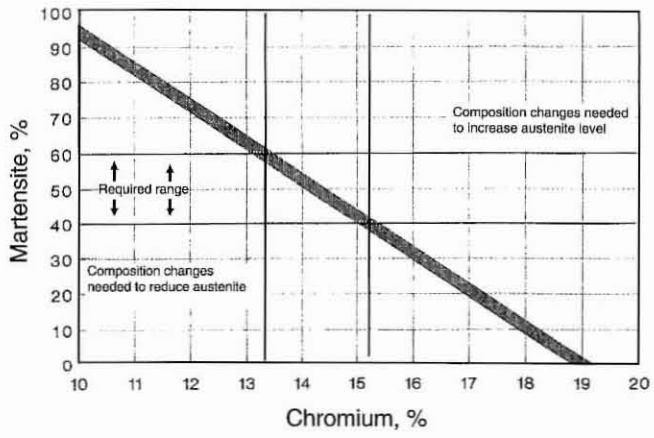


FIGURE 19. Schematic diagram showing a natural phase balance for low-carbon chromium steels

of the behaviour of a steel (and what this project was all about), since it allows an accurate assessment to be made of the steel's behaviour for ALL the practical cooling conditions that steel is likely to meet. These conditions can vary from water quenching and welding (where cooling rates are around 25 000°C/min) to heat treatment in a batch-annealing type of furnace, where cooling rates of around 0,1°C/min have been measured. This range of 250 000:1 encompasses all known product forms and cooling processes.

Closer examination of Figure 20 shows the variability of closely similar 11 per cent chromium steels, and how this relates to the typical cooling rates found in industry. The behaviour of the sample of 410 cutlery steel is straightforward. At all cooling rates greater than 4°C/min, the steel is fully hard. Between 1 and 4°C/min, the structure is mixed. At 1°C/min and slower, the steel is fully soft. Note that this fully soft structure is produced by cooling from finish rolling temperature to about 600°C; below 600°C, the cooling rate is not important because the transformation of austenite to ferrite + carbides is complete. It would be possible to modify the composition (without necessarily changing the carbon content) so as to move this curve towards the right, thus ensuring a soft product from natural cooling in coil form. No further processing in annealing facilities needs follow this cooling cycle, and the steel would be ready for stamping into cutlery. The 409 would produce fully soft coils, even under air-cooling, but mixed properties on sections and bars. 3CR12 is seen to give soft coils if large coils are hood-cooled, while giving relatively hard or strong sections if the section size is small. The experimental alloy (marked 'Exp') would be very suitable for plate, sections, and small bars, and leads to less variability in larger sections than 3CR12 for example.

All of this behaviour arises from the location of the curve showing transformation versus cooling rate in relation to the natural cooling rates of products of industrial

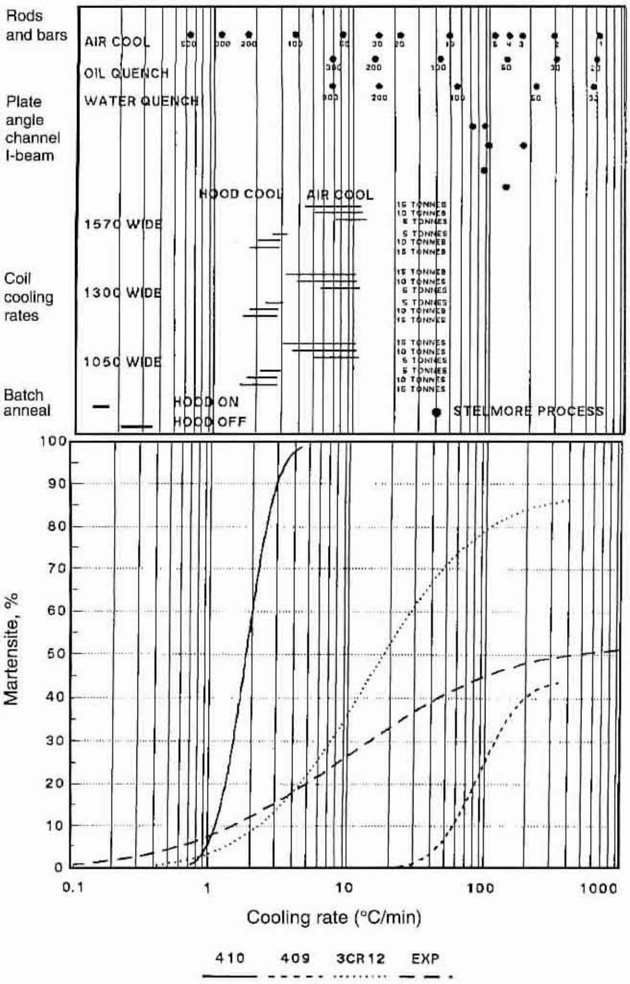


FIGURE 20. Cooling rates in industry superimposed on transformation curves

importance. The variability that can exist in the properties of hot-rolled products can be explained by this diagram. It is also evident that the variability can be further exacerbated by the high martensite content of some of the steels.

The results obtained can be interpreted in several other ways, but essentially they give a model with which it is possible to predict the behaviour of existing steels – our own and those of our competitors. The use of the results from the data analyses in the form of a model is instructive, and often surprising; the model predicted, for example, that type 409 and type 430 grades were not fully ferritic steels, but could contain relatively large amounts of martensite. It also predicted that the speed of transformation of 409 and 430 is very rapid so that, under normal production conditions (cooling rates), the steels will be fully transformed, i.e. soft, and thus almost always appear as 100 per cent ferrite (+ a few carbides) when examined under a microscope. Only at high cooling rates will martensite be formed and found; this has significant implications on the welding behaviour of 409 and 430 grades. These predictions have been shown to be correct; all the samples of type 430 steels examined, our own and those from other producers, have been found to be duplex structured steels. It also illustrates that the broad categorization of ASTM types 409 and 430 as fully ferritic stainless steels is not strictly correct. Type 409 may be be either fully ferritic or dual phase, depending on its composition and the cooling rate from high temperature. All the type 430 steels we have examined are dual-phase, as is simply shown from a hardness measurement after water-quenching from, say, 1000°C.

The composition ranges of existing steel specifications are fairly wide, enabling each manufacturer to select his own aim range for each element. Additionally, each steelmaker has residual element levels that may be quite different from those in other countries. For example, residual vanadium levels can vary from 0,02 to 0,12 per cent, boron levels from 0 to 10 p.p.m., cobalt from 0,003 to 0,10 per cent, aluminium levels from 0,001 to 0,080 per cent, and so on; these factors can alter the amount of austenite and its transformation behaviour significantly. This is illustrated in Figure 21, which compares samples from various manufacturers. This illustrates very clearly the problem of variability in as-rolled properties with the present technology.

Long Products

It has been obvious for some time that there are major technical difficulties associated with the use of 11 per cent chromium steels for long products, i.e. angles, beams, rounds, flats, rebars, rods, and the like. The problem is particularly relevant to the production of an 11 to 12 per cent chromium steel in the form of concrete reinforcing, which has been shown by Callaghan of the CSIR[12] to be unattacked by corrosion even under severe salt-spray conditions for up to 5 years, and to offer excellent resistance to the exfoliation problems besetting bridges and structures in coastal areas and in countries using salt for de-icing. They have further been shown by Kemp[13] and Rankine[14] at the University of the Witwatersrand to offer design advantages associated with their continuous yielding behaviour, corrosion resistance being a bonus of less significance in this case.

The technical difficulties involve the large degree of variability in the properties of as-rolled long products from these existing grades as shown in Figure 22. This variability would be unacceptable in the marketplace. Further, when these products are annealed, the resulting properties meet only the specifications for lower-strength

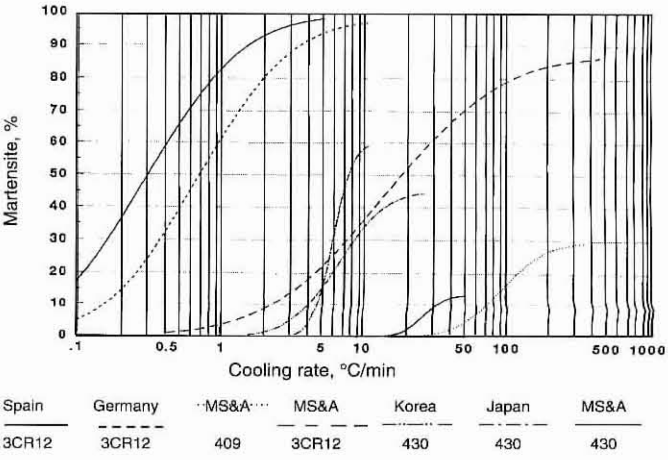


FIGURE 21. Variability in 'as rolled' properties

construction steel, i.e. the same properties as those for mild steel. This seriously limits the steel's competitive position in the marketplace.

To achieve properties that would meet the higher specifications for construction steel with current 11 per cent chromium compositions would entail heat treatment to introduce a controlled amount of martensite into the structure. As the A_{C_1} (the temperature at which austenite starts forming on heating) varies significantly on a heat-to-heat basis, this in turn would mean a different temperature for each heat. Therefore, keeping identity on each product and keeping heats separate would be essential – clearly, in total an impracticable and unacceptable proposition for a production route.

What is required is a steel that has an essentially 'flat-topped' response curve, as illustrated in Figure 23; in other words, a controlled-hardenability steel. The transformation behaviour needs to be flat only over the range of the characteristic cooling rates of whatever long products we wish to produce. These characteristic cooling rates are already collected together in Figure 20.

Further assumptions built into this work were as follows:

(1) If possible, the product should have the desired mechanical properties in the as-rolled, naturally cooled condition. The cost and capacity implications are obvious.

(2) If this is not possible, the heat treatment required must be simple and fast, e.g. simple tempering at maximum speed on the annealing unit for a plate or long product, or the use of hoods on coils.

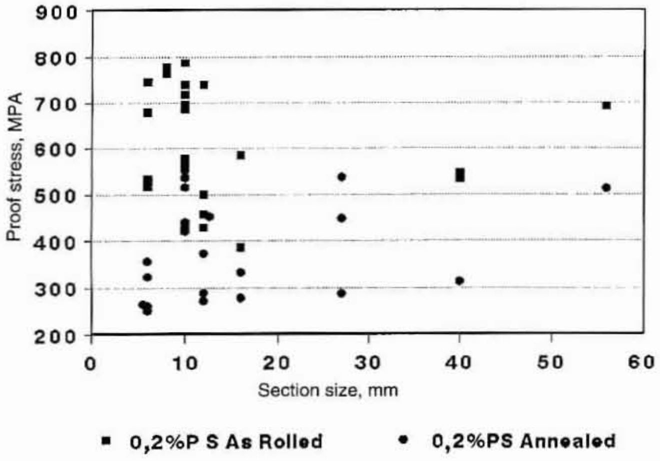


FIGURE 22. Mechanical properties of normal types of long products

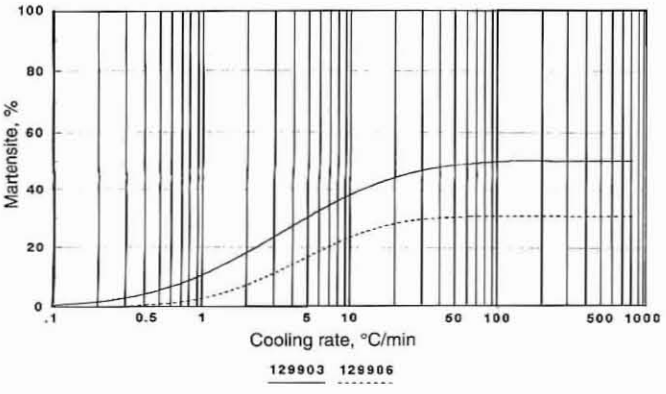


FIGURE 23. A 'flat-topped' response curve

(3) Dual-phase structures are desirable since they inhibit grain growth during casting, and during subsequent rolling and any heat treatment that may be required. Single-phase structures, in turn, lead to rapid grain growth at high temperatures (>650°C) and, for example, the need to hot-charge fully ferritic steels at high chromium levels.

(4) Dual-phase structures have much better impact-resistance properties since the presence of a second phase inhibits crack propagation in itself. The finer grain size also inhibits crack propagation.

As a consequence of this logic and results from laboratory heats, several experimental steel compositions were directed to this objective of 'flat-top' behaviour, and certain compositions were identified as having these required characteristics. Figure 23 shows the response curves for two of these. The compositions and transformation data are included in Table IV.

The compositions of these first two experimental steels (one slab heat no. 129906, and one ingot heat no. 129903) were fixed on evidence from the less extensive data available at that time. Thus, they were based on 3CR12 with a nickel + titanium base. The ingots were rolled to blooms at Iscor with no metallurgical problems and no changes to the pass schedules. The blooms were then ground and rolled at Iscor Newcastle to a range of section sizes and products.

The CCT response curves for these heats, Figure 23, predict uniform properties. As-rolled properties on 70 x 70 x 8 mm angles rolled at Iscor are given in Table V. They can only be described as 'excellent'. To obtain this combination of properties by any heat treatment would be a notable event since they satisfy the requirements for the higher-strength constructional steel specifications (Table VI); to produce these results from 'as-rolled off the mill' products is considered a significant achievement. Of equal significance is the fact that the trials showed these steels could be produced on carbon-steel facilities with only minor changes to the pass sequencing on some shapes to allow for the 'closed pass' sections. The controlled-hardenability steel products trialed to date are summarized in Table IV, where the predicted and actual results achieved are compared. Sections rolled on carbon-steel facilities are given in Table VII. The results are considered to be very satisfactory.

The implications of these results are best understood by reference to Figure 24. All the products shown, with the possible exception of the forgings, should have the same excellent properties as shown in Table V, 'As-rolled' from any mill.

Higher-chromium Steels

The published literature usually shows that the 3CR12 type of duplex structure can be achieved only up to about 16 per cent chromium. For this reason, the range of 16 to 18 per cent chromium was at first explored only briefly.

Work in 1988 at the University of Cape Town had already produced a 3CR16 variant, i.e. containing 16 per cent chromium, but, whilst giving an attractive combination of mechanical properties, this alloy has the disadvantages

TABLE IV
DETAILS OF EXPERIMENTAL PRODUCTION HEATS

Analyses, wt%

Heat	C	Mn	Si	Ti	Mo	Cr	Ni	Al	Nb	V	N_2 p.p.m.	FF
129903	0,024	1,23	0,59	0,389	0,050	11,90	0,57	0,033	0,002	0,87	80	13,15
129906	0,027	1,28	0,59	0,506	0,040	12,10	0,61	0,077	0,003	0,073	210	12,45
131377	0,018	1,20	0,62	0,291	0,035	12,06	0,66	0,034	0,004	0,079	295	11,71
131399	0,021	1,26	0,70	0,366	0,048	11,79	0,61	0,035	0,003	0,078	102	12,98
131412	0,018	1,11	0,80	0,365	0,036	11,83	0,56	0,034	0,003	0,082	191	12,14
131413	0,018	0,82	0,54	0,013	0,026	11,20	0,17	0,002	0,002	0,059	215	10,75
134006	0,021	0,94	0,87	0,004	0,030	12,18	0,17	0,001	0,286	0,066	325	13,98

Transformation data

	°C/min						°C										W.Q. 1000°C			
	CR95		CR50		CR05		A_{C1}		T_{Fs}		T_{Fe}		M_s		M_f		Mart, %		Hardness	
Heat	A	P	A	P	A	P	A	P	A	P	A	P	A	P	A	P	A	P	A	P
129903	0,3	0,1	3	2	45	45	808	834	780	760	629	638	545	542	397	410	51	49	218	226
129906	0,7	1,0	5	5	30	27	817	813	753	742	640	646	533	534	351	350	31	32	179	181
131377	0,1	0,4	1,2	3	32	21	806	810	743	755	623	643	525	494	390	335	52	49	235	217
131399	0,01	0,01	0,3	1	163	100	826	818	746	755	660	647	546	552	428	413	34	37	229	227
131412	2,0	1,0	16	17	150	180	822	839	746	742	658	648	488	509	390	416	25	31	178	194
131413	2,0	3,0	14	29	198	230	810	810	803	810	648	649	383	383	283	287	97	90	281	294
134006	1,1	1,6	13	11	47	60	821	810	852	820	679	682	395	390	262	279	32	32	218	210

A = Actual measured value P = Predicted values

TABLE V
MECHANICAL PROPERTIES OF LONG PRODUCTS
(EXPERIMENTAL STEELS)

Condition	0,2 % proof	UTS	Elong, %	Hardness
70 x 70 x 8 mm angles. Heat 129903				
As-rolled:				
a	425	585	32	179
a	433	589	33	184
b	442	590	28	189
c	428	578	20*	185
d	419	586	26	194
e	440	589	27	188
Lab-annealed:				
a	331	507	43	153
a	342	496	38	157
12 mm plates. Heat 129906	474	595	13	193
	537	630	14	203
	494	619	10*	203
60 x 60 x 6 mm angles. Heat 131377				
	446	593	20	185
	444	585	23	182
	452	591	24	186
	452	605	24	186
203 x 133 x 6 mm I-beams. Heat 131399				
	554	643	23	235
	574	657	24	236
	567	650	21	225
	562	648	21	219
10 mm plates. Heat 131412	424	517	11*	–
	404	513	16*	–
20 mm plates. Heat 131412	416	548	35	185
	385	544	34	174
3 mm coil. Heat 131412	466	588	16	190
	489	614	18	201
	497	625	18	197
	492	625	19	185
	513	618	20	201
	505	618	18	206
	531	636	17	196
	510	620	20	211
	498	589	22	195

* Broke outside the gauge length

of a high nickel content of about 3,5 per cent, and a requirement for a lengthy batch-annealing heat treatment of about 60 hours. Initial belief that this sluggish response to heat treatment was a function of the high total alloy content was later doubted. It is now known that, for this particular alloy, transformation is at a low temperature and requires diffusion of nickel and chromium, also at these relatively low annealing temperatures; this type of diffusion is known to be slow. The long times at temperature are understandable. It also follows that, if this second explanation is correct, transformation speeds could be much improved by the substitution of nitrogen for nickel. Nitrogen, a strong austenite former, is also an interstitial element and can move very much faster as a consequence; transformation then should be much faster. The costs of nitrogen can be taken as zero, against about R350 per tonne for each 1 per cent of nickel. This logic was tested and found to work; as can be seen from Figure 25, these higher chromium + nitrogen steels transform fast.

Encouraged by these results, more laboratory heats were made so that the chromium limit could be determined for the 3CR12 type of duplex structure; the chromium level was increased up to a maximum of 27,5 per cent on a few experimental heats. The results are shown in Figure 26 and, again, it can be seen that duplex structures were obtained, thus far to a maximum chromium level of about 20 per cent. In addition, the transformation behaviour is 'interesting' since some of these steels would appear to be hood-coolable, i.e. capable of being produced fully soft in the off-the-mill condition.

Several of the higher-chromium experimental steels showed apparent 'failure' in that no transformation was observed during the investigation stages, and they were simply labelled as fully ferritic. A more recent analysis of the data suggests that this conclusion may be premature, and that the M_s temperature of some of these steels may be

TABLE VI
TYPICAL PROPERTY SPECIFICATIONS FOR HIGHER-STRENGTH STRUCTURAL STEELS

	0,2 PS	UTS	Elong., %	Impact, J
BS 4360 '50B':				
Up to 16 mm	355 min	490 min 640 max	20 min	27
16 to 40 mm	345 min	640 max	20 min	27
40 to 63 mm	340 min	640 max	20 min	27
ASTM A 752 Grade 50:	345 min	450 min	18 in 8"	–
Heavy structural shapes	(50 ksi)	(65 ksi)		
ASTM A572 Grade 60:	415 min	520 min	16 in 8"	20 at –29°C
Flat bars	(60 ksi)	(75 ksi)		
ASTM A572 Grade 65:	450 min	550 min	15 in 8"	20 at –29°C
Flat bars	(65 ksi)	(80 ksi)		
SAE 970X:	485 min	550 min	14 in 8"	20 at –29°C
Flat bars	(70 ksi)	(80 ksi)		
ASTM A572 Grade 80:				
Flat bars	550 min	620 min	12 in 8"	20 at –29°C
Highway trailer cross members	(80 ksi)	(90 ksi)		

TABLE VII
PRODUCTS ROLLED AT ISCOR

Product	Size mm	Pass schedule	Result
Window sections	F7		
	FX7	No changes	Good
	F4B	No changes	Good
	T14		
Rounds	100 to 250	No changes	Good
	13,5	No changes	Good
I-beams	152 x 152	Modified	Good
	203 x 133	Modified	Good
	203 x 203	Modified	Good
Blooms/billets	80 x 80	No changes	Good
Wire rods	5,5	No changes	Good
	6,5		
Channels – parallel	200 x 75	Modified	Good
	180 x 70	Modified	Poor
	100 x 50	No changes	Good
	100 x 50	Modified	Good
Channels – taper	180 x 70	Modified	Poor
Small angles	40 x 40 x 5	No changes	Good
	45 x 45 x 3	No changes	Good
	45 x 45 x 5	No changes	Good
	50 x 50 x 6	No changes	Good
	60 x 60 x 6	No changes	Good
	70 x 70 x 8	No changes	Mixed
	80 x 80 x 8	No changes	Good
Rebars	16	Modified	Good
IPE – sections		Modified	Good
Flat bars		No changes	

below room temperature, i.e. the austenite is present but not transforming. Some of these are 'triple phase' steels consisting of ferrite + carbide, martensite, and retained austenite.

General

It is interesting to speculate that the upper limit in chromium content that can be used to produce duplex micro-structures is fixed not only, as supposed, at about 16 per cent chromium by closure of the dual-phase region of the phase diagram; it can also be fixed by the M_s temperature of these steels being pushed below room temperature, so that martensite transformations are not seen under normal testing conditions. This suggests that the structure of these steels at room temperature should be austenite and ferrite. If the M_s temperature is not too far below room temperature, the steel would be 'metastable', i.e. it would transform on sub-zero treatment or on cold-working at ambient temperatures. This has interesting implications for the formability of these steels because they are expected, and have been shown, to exhibit 'TRIP' behaviour.

Research work on the weldability of alloys has been carried out at the University of Pretoria[15,16] and is reported in these proceedings by Zaayman and Van Rooyen[17]. Apart from the elegance of the experimental technique and its ability to produce testpiece-size heat-affected zones, the most significant conclusion has to be the clear evidence that the martensite in the welds is the tough phase, even when present at the grain boundaries, and the ferrite phases are the most brittle. The techniques developed are already able to explain in more fundamental terms the need to restrict the heat input during the welding of high-chromium alloys, whereby it is simply a question of allowing a dual-phase structure to redevelop in the weld zone.

Research work on the effect of different proportions of martensite in these alloys on general and pitting corrosion, as carried out at the University of the Witwatersrand by Van Bennekom *et al.*[18], has shown that there is a slight decrease in general corrosion resistance and a slight increase in pitting resistance as the martensite fraction increases. Thus, there are no significant corrosion problems associated with the as-rolled concept.

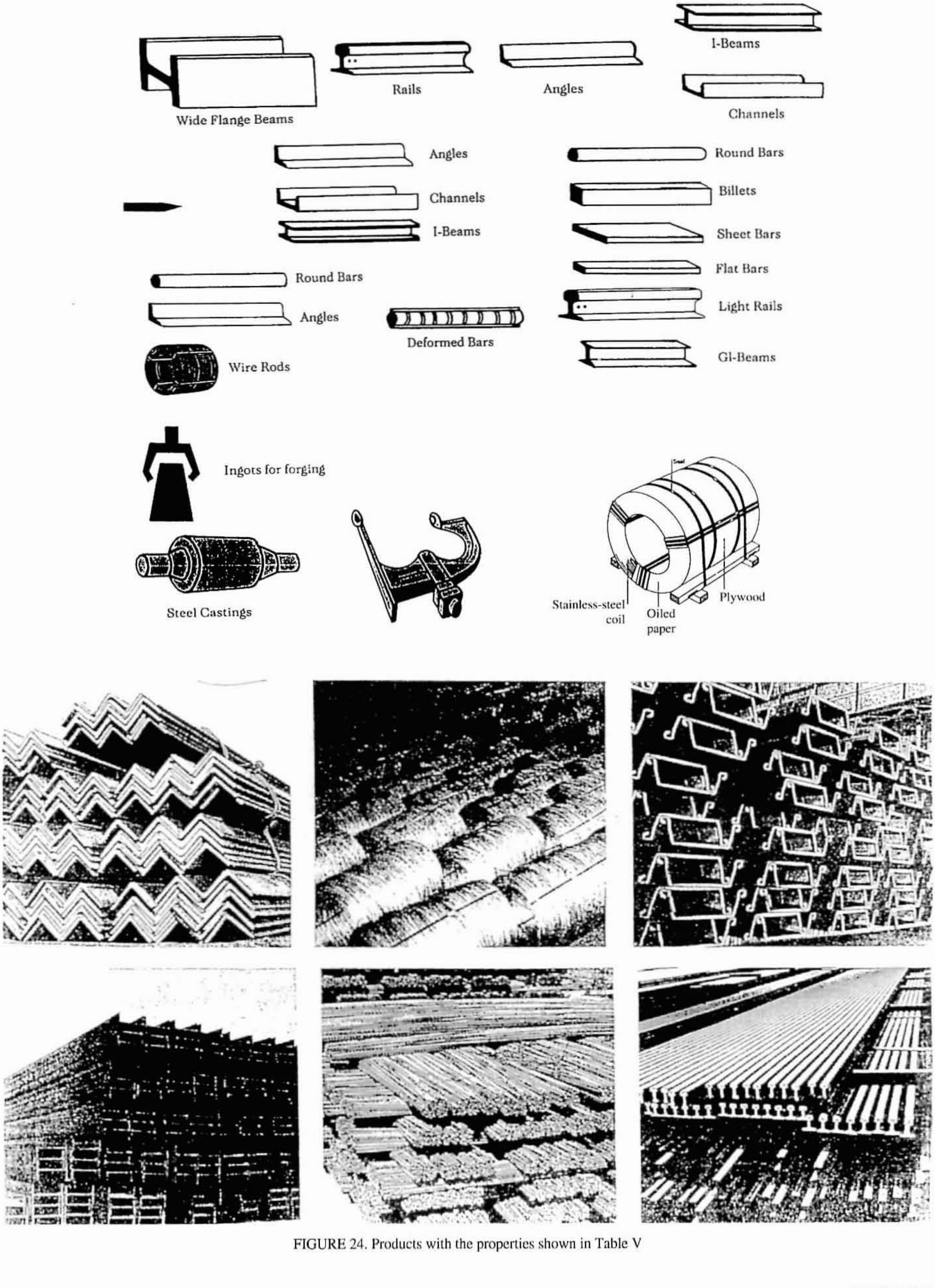


FIGURE 24. Products with the properties shown in Table V

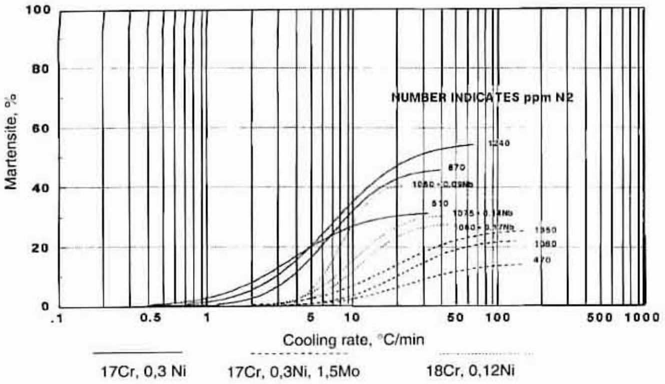


FIGURE 25. Transformation of higher-chromium and nitrogen steels (the numbers on the graphs refer to the N_2 content in p.p.m.)

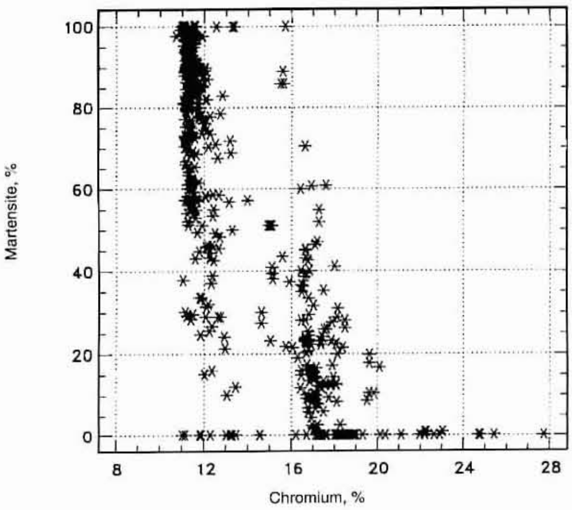


FIGURE 26. Percentage martensite (water-quenched) versus chromium content

The possibility that steels with more than about 18 per cent chromium could well be subject to sigma-phase embrittlement was recognized. This was examined by Mintek on a range of chromium levels, with and without molybdenum additions. Sigma was found only in one steel containing 23 per cent chromium + molybdenum, where about 3 per cent sigma was detected by X-ray techniques only after a treatment time of 100 hours.

Conclusions

This paper records some of the more interesting work carried out by Middelburg Steel & Alloys, with major contributions from the various research institutions and universities in South Africa over the past six years.

- The work has established the transformation behaviour of 10 to 28 per cent chromium steels to a major degree of understanding – far in advance of our previous knowledge.
- It has demonstrated that this transformation behaviour can be controlled and exploited by the selection of a steel's composition. The effects of individual elements, singly and particularly in combination, are now known.
- It has fully explained the cause of the earlier variation in the mechanical properties of steels containing 12 per cent chromium.
- It has shown that the production of long products from existing grades of 12 per cent chromium alloys is not a viable proposition. Alternative grades have been developed and shown to work on several laboratory heats and on slabs, large blooms, and angles, and I-beams from five plant heats. The properties are excellent and meet the higher-strength structural specifications. It has also shown that these steels can be rolled on conventional carbon-steel mills.
- It has shown that type 410 cutlery steels can be produced fully soft off the mill by hood-cooling. Data analyses indicate that this can also be done on type 420 steels.
- It is predicted from data analyses that all type 430 and most type 409 steels are also dual-phase steels. This has been confirmed, and has implications related to welding problems and, perhaps, slab cracking of 430 steels.
- It has established that dual-phase 3CR12 type steels can be produced up to chromium levels of at least 20 per cent.

It is clear that the questions posed earlier as to whether or not we can establish meaningful control of the amount of each phase, and the speed at which it transforms, can be answered with a very definite 'YES'. The work has also established an overall appreciation of chromium level versus martensite content, and what has to be done to achieve a pre-selected amount.

The combination of techniques outlined in the paper permit a much more reliable method of designing new steels, or improving existing ones, than the trial-and-error methods that had to be used in the absence of this wealth of information. It is an effective design kit for new steels and for re-examination of established grades.

The work has shown clearly that high-chromium steels exhibit very similar characteristics to those of high-strength low-alloy steels (HSLA steels). The well-established technologies of HSLA steels can be adopted in producing their high-chromium counterparts. That satisfactory higher-strength properties can be produced in the as-rolled state is regarded as an important development, which, coupled with the ability to roll these steels on carbon-steel facilities, can only reduce production costs significantly. Constraints on a more rapid growth for high-chromium steels as discussed in the opening section have therefore been addressed by this work, and have been shown to be solvable. Whether or not 1 per cent penetration of the carbon-steel market can be achieved remains the most significant variable left to be determined; perhaps to a major extent by contributors and delegates at this Congress?

Acknowledgments

This report summarizes major work carried out at the Universities of Pretoria, Cape Town, and the Witwatersrand; at M.F.T Computing (Johannesburg); at Mintek (phase resolution and sigma studies); the CSIR (corrosion, high-temperature properties, and fatigue testing); and in the laboratories and production units at Middelburg Stainless and at various Iscor mills.

The major inputs of Professor G.T. van Rooyen, and Mr Pieter Pistorius at the University of Pretoria are particularly noted and acknowledged. The finite-element analyses of the cooling of coils in air and under hoods was done under contract by Roland Prukl, Mike Shapiro, and Rick Raubenheimer of M.F.T. Computing (Pty) Ltd, Rivonia, and their contributions are gratefully acknowledged.

The contributions of Dave Smith, John Tarboton, Arthur Alford, and the laboratory and test-house teams, Dr. Keith Barker and Francesca Schwamborn (programming and graphics), and Ken Dewar (long-product developments) are also gratefully acknowledged.

Special thanks are due to Don Maxwell of Cromweld Steels U.K.; and to Athol Victor and Lucien Matthews at MS&A for their superb support and encouragement in the darker hours of the project. Last, but not least, thanks go to the Executive of Middelburg Steel & Alloys for permission to publish this work.

References

1. *Cromweld 3CR12 User Manual*, Cromweld Steels Ltd, The Old Vicarage, Tittensor, Stoke on Trent, Staffordshire ST12 9HD, U.K.
2. R.S.A. Patent no. 883551. The controlled hardenability technology is currently protected by provisional patents.
3. M.F.T. Computing (Pty) Ltd, P.O. Box 221, Rivonia 2128, R.S.A.
4. Dalton, H.J., Smith, M., and De Visser, P. Phase differentiation in duplex stainless steels by potentiostatic etching. *Stainless Steel '87*, May 1988, The Institute of Metals, pp. 554–557.
5. Schmid, O.E. and Knutsen, R.D., University of Cape Town. Reducing the nickel content in metastable austenitic stainless steel. INFACON 6, 1992.
6. Knutsen, R.D., and Hutchison, R., University of Cape Town. Duplex ferrite–martensite steels containing 16 wt per cent chromium. INFACON 6, 1992.
7. SAS (R) System Software, SAS Institute Inc., Cary N.C., U.S.A.
8. Kaltenhauser, R.H. (1971). *Met. Eng. Quarterly*, 11 May, pp. 41–47.
9. Tricot, R., and Castro, R. (1966). *Rev. Met.*, LXIII, No. 718, pp. 657–684.
10. Briggs, J.E., and Parker, T.D. (1965). *The super 12% Cr steels*. Climax Molybdenum Co.
11. Schneider, H. *Foundry Trade Journal*, 1960. Vol. 108, p. 562.
12. Callaghan, B.G., and Hearn, I.R. Division of Materials Science and Technology, CSIR. The use of 3 CR12 as reinforcing in concrete. *Corrosion & Coatings S.A.* August/September 1990, pp. 2–10.
13. Kemp, A.R. Strength and ductility of reinforced concrete beams. Private Communication.
14. Rankine, R.D.G. MSc. Thesis, University of the Witwatersrand. 1990. Appropiate properties for a new corrosion resisting reinforcing steel.
15. Mostert, R.J., and Van Rooyen, G.T. Novel model for accurate calculation of hardenability and continuous cooling transformation. *Mat. Science and Technology*, Sept. 1991, vol. 7, pp. 802–811.
16. Pistorius, P.G.H., and Van Rooyen, G.T. *Meas. Sci. Technol.* 2, (1991), pp. 1220–1222.
17. Zaayman, J.J.J. and Van Rooyen, G.T. University of Pretoria. The toughness of the heat-affected zone welds in 11,5% chromium steels. INFACON 6, 1992.
18. Van Bennekom, A., Matthews, L.M., Tarboton, J.N., and Robinson, F.P.A. University of the Witwatersrand. The effect of martensite content on the corrosion and mechanical properties of dual-phase 12% chromium steels. INFACON 6, 1992.