

Duplex Ferrite–Martensite Steels Containing 16 Wt Per Cent Chromium

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The grain structure of ferritic steels containing 16 to 17 wt per cent chromium was refined by modification of the ratio of ferritizing elements to austenitizing elements in the steel chemistry. Suitable nickel additions (approximately 2.5 wt per cent) were determined to provide alloys with sufficient austenitizing ability to refine the high-temperature δ -ferrite phase, and consequently produce a duplex ferrite–martensite microstructure. Tempering of these alloys at 700 °C resulted in a lamellar ferrite–martensite structure that gave rise to an attractive combination of impact and tensile properties that may provide a stainless steel with superior cost-effectiveness to that of austenitic grades.

In addition, attempts were made to lower the nickel content of such steels while increasing the nitrogen content in order to maintain a desirable ferrite–martensite phase balance. Analysis of the microstructure and properties of these nitrogen-rich steels showed that the high content of interstitial elements is deleterious to the ductility of both the ferrite and the martensite phases. A comparison of these properties with those of the nickel-rich alloy indicated the desirable toughness of nickel-containing martensite.

Introduction

Strength, toughness, and ductility are the most important properties specified for structural steels. As corrosion is prevalent in many engineering applications, a suitable structural steel is one that combines these properties with good corrosion resistance. Ferritic stainless steels represent the lower-cost family of chromium-containing corrosion-resistant steels but, what these steels gain in their resistance to corrosive attack, they generally lose in terms of their ductility, toughness, forming, and welding properties. The introduction of commercial methods of obtaining low levels of interstitial elements in ferritic stainless steels has improved the properties of these steels remarkably, but it is well known that grain-coarsening occurs readily in these steels owing to the greater atomic mobility in body-centered cubic structures, and poor toughness is a consequence. Furthermore, ferritic stainless steels, like mild steels, show a ductile–brittle cleavage transition, but their impact-transition temperature is considerably higher than that for mild steel because of the embrittling effect of chromium dissolved in the ferrite. This impact-transition temperature can be reduced, while also increasing the upper-shelf energy, by decreasing the grain size but, owing to the non-transformable nature of ferritic grades, the coarse grain size is a major problem.

Because ferritic stainless steels with chromium contents greater than 16 wt per cent are generally considered to have single-phase microstructures, the ferrite formed during solidification (δ -ferrite) remains stable down to room temperature. This means that any refinement of the large grains produced at elevated temperatures generally occurs only

due to the rolling and subsequent recrystallization process. Reheating to elevated temperatures, for example during welding, will reverse this process, and a large grain structure will once again be produced. Additional grain refinement, however, could be achieved by transformation reactions induced by modification of the steel chemistry. Transformation, or partial transformation, of the large-grained δ -ferrite to austenite during cooling from the high-temperature region may lead to either fully austenitic or duplex ferrite–austenite structures at intermediate temperatures. Further cooling to ambient temperature can then result in the regression of austenite to α -ferrite, the formation of martensite, or the retention of stable austenite. These transformations will, of course, ultimately depend on the steel chemistry and the cooling rate. In this way, the decomposition of the high-temperature δ -ferrite, by suitable minor alloy addition, can modify the properties of the original ferritic stainless steel both in terms of a more refined microstructure after rolling, and improved weldability due to the presence of a duplex structure at elevated temperature.

Refinement of Grain Structure

To a steel containing 16 to 17 wt per cent chromium and carbon levels of less than 0.03 wt per cent, sufficient nickel needs to be added to provide the necessary $\delta \rightarrow \gamma$ decomposition reaction to refine the δ -ferrite grain structure. The pseudobinary Fe–Ni phase diagram for 17 wt per cent chromium in Figure 1 illustrates the effect of nickel on the nature of phase transformations. This diagram indicates that, if one assumes equilibrium cooling conditions, then

complete decomposition of δ -ferrite to austenite can be achieved only for nickel equivalents greater than 4. Nickel additions above that equivalent value will increase the tendency to achieve a fully austenitic structure at intermediate temperatures. However, in deciding on the upper limit in nickel addition, the essential cost factor needs to be taken into account. The idea of modifying ferritic stainless steels is to achieve improved engineering alloys while maintaining low cost. Care is therefore required in the determination of a suitably balanced chemical composition.

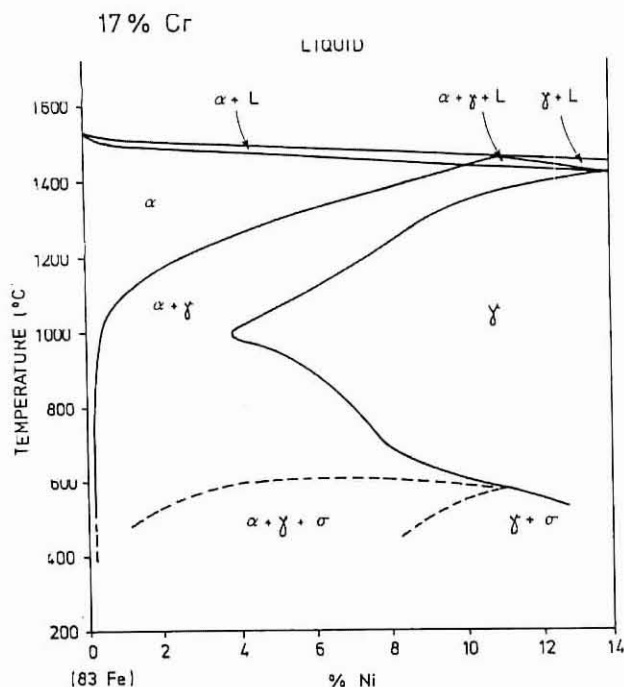


FIGURE 1. Pseudobinary Fe-Ni phase diagram for an isopleth at 17 wt per cent Cr (drawn from isothermal sections given in reference 1)

Experimental

Microstructural analysis

The microstructural behaviour of three experimental alloys (E1 to E3, Table I) was assessed. The alloys were laboratory cast into 5 kg ingots (50 mm thick) and were hot-rolled to plate thicknesses in the range 6 to 8 mm. The final reduction was terminated at 850 °C. The solution treated (1000 °C for 2 hours, oil quenching) microstructure and dilatometer trace for each of these alloys are shown in Figures 2 to 7. Phase-transformation temperatures are indicated by the points of inflection in the dilatometer traces, which were produced at heating and cooling rates equal to 4 °C/min.

TABLE I
COMPOSITION OF ALLOYS E1 TO E3 (IN WT PER CENT)

Alloy	C	N	S	P	Mn	Si	Ti	Cr	Ni
E1	0,013	0,030	0,01	0,02	1,4	0,5	0,29	18,2	2,00
E2	0,025	0,029	0,01	0,02	1,5	0,3	0,34	16,7	1,97
E3	0,027	0,026	0,01	0,02	1,0	0,4	0,00	15,9	2,44

The microstructure of alloy E1 in the solution treated condition, which is shown in Figure 2, indicates a large-

grained (200 to 300 μm) ferritic matrix. Martensite islands occur very occasionally at grain boundaries. The dilatometer trace in Figure 3 does not indicate the occurrence of any substantial transformations during the heating and cooling cycles, although minor austenite formation is indicated between 500 and 600 °C during heating. It is apparent that any austenite that may have formed as a result of partial δ -ferrite decomposition during cooling has regressed to α -ferrite in the region of 600 °C. There is no evidence of a martensite-start (M_s) temperature.



FIGURE 2. Large-grained ferrite microstructure of alloy E1 (1000 °C)

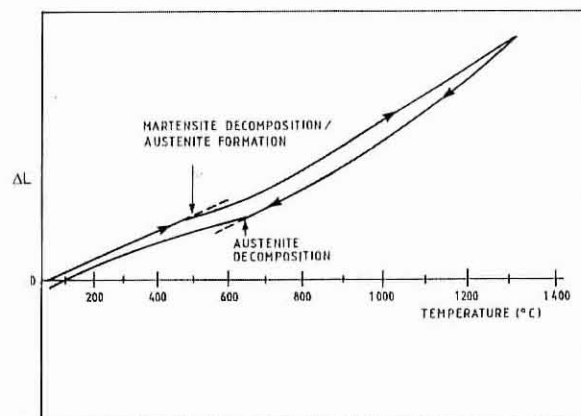


FIGURE 3. Dilatometer trace for alloy E1

Alloy E2 exhibits a duplex ferrite-martensite microstructure in the solution treated condition (Figure 4). This is manifested by the occurrence of elongated martensite fibres in a ferritic matrix. The dilatometer trace (Figure 5) indicates a reasonably well-defined point of inflection just below 600 °C during the heating cycle, and a well-defined M_s temperature at 300 °C during cooling.

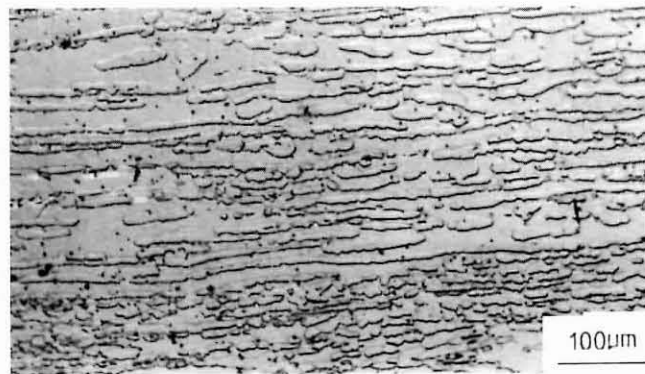


FIGURE 4. Microstructure of alloy E2, indicating martensite fibres in a ferritic matrix (1000 °C)

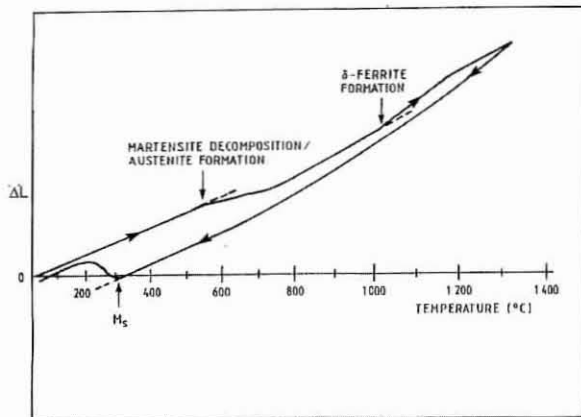


FIGURE 5. Dilatometer trace for alloy E2

Alloy E3, on the other hand, displays an elongated ferritic structure in a martensitic matrix (Figure 6). The dilatometer trace for this alloy shows a much more exaggerated inflection just below 600 °C during the heating cycle (Figure 7). During cooling, a considerable degree of δ -ferrite decomposition is indicated, and a corresponding degree of martensite formation is detected at approximately 220 °C.

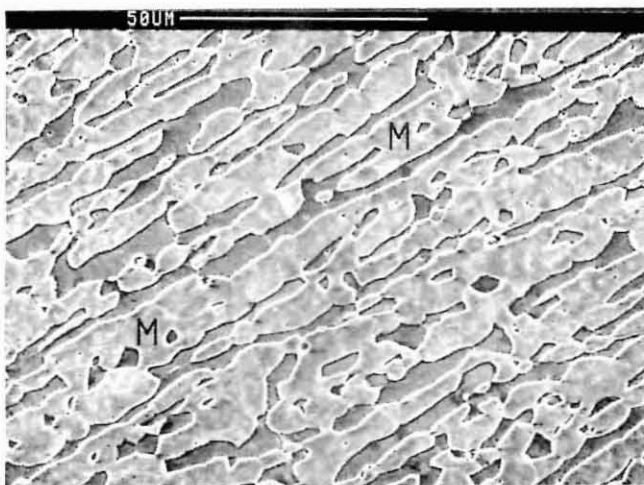


FIGURE 6. Alloy E3 exhibits residual δ -ferrite in a martensite matrix (1000 °C)

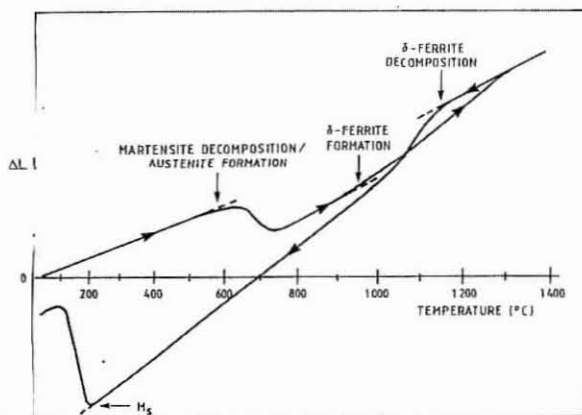


FIGURE 7. Dilatometer trace for alloy E3

The microstructures of alloys E1 to E3 emphasize the fact that appreciable grain refinement is achieved only when extensive δ -ferrite decomposition occurs. In other words, the higher the austenite (martensite) content of the steel, the greater is the tendency for grain refinement. A comparative study of the microstructures of the three alloys indicates a much more refined microstructure in the case of alloy E3. The microstructure of alloy E2 is indicative of fairly minor solid-state $\delta \rightarrow \gamma$ transformation, and it is apparent that the austenite occurred mainly as a result of the precipitation of grain-boundary allotriomorphs during the partial δ -ferrite decomposition. In the case of alloy E3, however, a much more advanced $\delta \rightarrow \gamma$ transformation occurred, and the structure is reminiscent of an interlath residual δ -ferrite-austenite structure, which results from advanced Widmanstätten growth of austenite from ferrite. Consequently, the original δ -ferrite grains become much more broken, and the overall grain size is considerably reduced. The deleterious effect of the large grain size associated with alloy E2 and, conversely, the grain refinement produced by the advanced δ -ferrite decomposition in alloy E3, are illustrated by a comparison of the Charpy V-notch impact toughness of alloys E2 and E3. Subsize Charpy specimens (5 mm) were solution treated at 1000 °C and tested at room temperature. The impact energies for alloys E2 and E3 were 15 J and 47 J respectively.

Tempering response of alloy E3

Charpy V-notch impact energies were measured for alloy E3 after it was solution treated at 1000 °C for 2 hours (air-cooling), followed by soaking at 500, 600, 700, and 800 °C for 2 hours (oil-quenching to room temperature). In each case, sub-size specimens (7.5 mm) machined in the longitudinal-transverse orientation were tested. The impact results, together with the Vickers hardness measurements, are given in Figure 8.

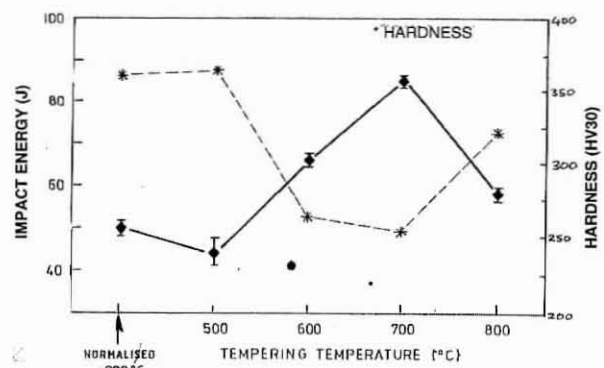


FIGURE 8. Hardness and impact properties of alloy E3 as a function of heat treatment

The microstructure of alloy E3 was examined after the various heat treatments in an attempt to explain the associated impact results. As indicated in Figure 6, the solution treated condition consists of residual δ -ferrite (primary ferrite) in a martensitic matrix. Tempering at 500 °C leads to very little change in the microstructure, and this is reflected by the very slight change in impact energy and hardness compared with the solution treated condition. After heating at 600 °C, considerable tempering of the martensite occurs, and this is indicated by a notable drop in hardness and an appreciable increase in impact energy. Soaking at 700 °C

leads to a further marked increase in impact energy, but only a slight reduction in hardness compared with the 600 °C condition. The microstructure in this condition, as reproduced in Figure 9, indicates primary ferrite, which is mostly unaffected, whereas the original martensite has decomposed substantially to form secondary ferrite and new austenite (transformed to martensite during cooling to room temperature). Thus, the microstructure can be described as primary ferrite (δ -ferrite) in a matrix consisting of a fine lamellar mixture of secondary ferrite and new martensite. In addition, as shown by energy-dispersive X-ray spectroscopy analysis of this microstructure, there is a partitioning of chromium and nickel between the new martensite and the secondary ferrite. The results presented in Table II indicate that the growing austenite phase has become enriched in nickel, whereas chromium has been rejected to the residual tempered martensite (termed secondary ferrite due to the rapid loss in tetragonality associated with the low content of interstitial elements). Similar lamellar structures have been observed during the tempering of a 0,024 C–16 Cr–1,5 Mo–5Ni stainless steel². After heat treatment at 800 °C, a fine woven structure of secondary ferrite and martensite is again evident in the original martensite regions, although in this case a greater proportion of new martensite is formed. This gives rise to a lowering in impact energy and a corresponding rise in hardness.

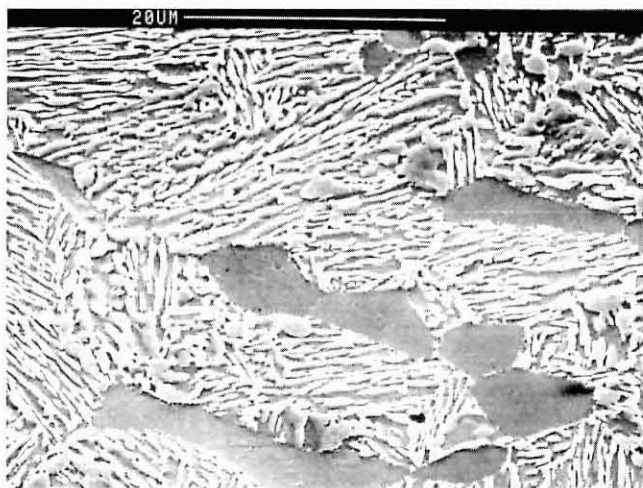


FIGURE 9. Lamellar ferrite–martensite structure evident in alloy E3 after 2 hours at 700 °C
Dark areas = ferrite, light areas = martensite

TABLE II
ELEMENT PARTITIONING* DURING THE HEAT TREATMENT
OF ALLOY E3 AT 700 °C FOR 2 HOURS

Element	Primary ferrite	Secondary ferrite	Martensite
Cr	18,7	15,2	14,6
Ni	1,9	2,5	3,7

*The values are given in wt per cent, and are reliable only for comparative purposes because of the use of a standardless analytical routine

Mechanical properties of E3 and AISI alloys

The hardness, tensile, and Charpy V-notch impact properties of alloy E3 were compared with those of AISI alloys 430, 431, and 304 in various microstructural conditions. The AISI alloys were chosen in view of their similarity to

alloy E3 in chromium content. The results for the various heat-treated conditions are shown in Table III. With the exception of AISI 304, alloy E3 has by far the best combination of tensile strength and impact toughness in the 1000 °C solution-treated condition. The impact toughness of AISI 430 and 431 can be improved by sub-critical annealing or tempering operations, as indicated by the as-received and laboratory-tempered properties.

TABLE III
MECHANICAL PROPERTIES OF STEEL ALLOYS IN
VARIOUS HEAT-TREATED CONDITIONS

Alloy	0,2% MPa	UTS MPa	Charpy 7,5 mm, J	Elong. %	HV ₃₀	Condition
Alloy E3	760	990	63	19	337	1000 °C 2 h, air-cooled
Alloy E3	621	821	85	19	293	700 °C 2 h
AISI 430	475	530	30	27	195	As-received
AISI 430	407	690	2	16	253	1000 °C 1 h, oil-quenched
AISI 431	693	820	37	24	277	As-received
AISI 431	1 245	1 731	8	8	557	1000 °C 1 h, oil-quenched
AISI 431	665	900	55	21	305	700 °C 2 h, air-cooled
AISI 304	230	695	188	71	160	As-received
AISI 304	234	688	289	70	158	1040 °C 1 h, oil-quenched

Discussion

The microstructural behaviour of the experimental alloys (E1 to E3) can be related to their compositions. The marked difference in the transformation behaviour of alloy E3 can be attributed to both the absence of titanium and the higher nickel content. The removal of titanium reduces the chromium equivalent and increases the effective carbon content, while an increase in nickel content also increases the austenitizing ability of the steel. It would seem that sizable nickel additions to the titanium-stabilized alloys, E1 and E2, are required in order to provide advanced δ -ferrite decomposition. In view of the substantial chromium content and the low carbon levels (0,03 wt per cent), it is probably not necessary to stabilize these alloys. Certainly, the absence of titanium would lead to a lower nickel requirement, which would undoubtedly reduce the cost.

Examination of the microstructure of alloy E3 showed that transformation-induced grain refinement relies on the extent to which the δ -ferrite decomposes to austenite. An advanced state of decomposition, as a result of Widmanstätten-type growth of austenite into ferrite, leads to a high degree of refinement of the large-grained δ -ferrite structure formed either during solidification or during reheating (e.g. in welding operations). The good impact toughness of alloy E3 in the solution-treated condition can be explained by its combination of fine grain structure (15 to 25 μ m), low content of interstitial elements, and substantial amounts of tough, nickel-containing martensite. The marked improvement in impact toughness after heat treatment at 700 °C is provided by the resistance to crack initiation and propagation of the lamellar ferrite–martensite microstructure. Previous work concerning *in situ* observations of tensile fracture in lamellar dual-phase structures demonstrated that martensite lamellae possess good ductility and can sustain a certain degree of plastic deformation³. Consequently, propagating cracks may be blunted by the retardation effect of the lamellar structure. The nickel content in the lamellar martensite phase is enriched as a result

of element partitioning during heat treatment, and this further toughens this phase.

It is of little surprise, then, that the impact toughness of AISI 430 and 431 should be much inferior to that of alloy E3 in the solution-treated condition. The mostly single-phase ferritic nature of AISI 430 after solution treatment gives rise to the notch sensitivity associated with the dissolution of chromium, as well as the dissolution of interstitial elements, in ferrite. In addition, small amounts of austenite form at ferrite grain boundaries at 1000 °C (transformed to martensite during cooling), and the presence of this martensite leads to further embrittlement. Sub-critical annealing improves this situation by tempering the martensite and coarsening precipitates within the ferrite grains. In the case of AISI 431, the high content of interstitial elements (mostly carbon) dissolved in the martensite, as manifested by the high hardness ($HV_{30}=557$), causes considerable embrittlement of the martensite. Once again this situation can be remedied by tempering. However, the fact that AISI 430 and 431 are both very sensitive to heat treatment as compared with alloy E3 leads to the possibility of a much more universal application of an alloy such as E3, particularly in view of its tendency to have much better weldability. Alloy E3 demonstrates an excellent combination of mechanical properties when heated at 700 °C.

Furthermore, the fact that this alloy is hardenable by heating at 800 °C, with acceptable loss in impact toughness, makes it more versatile in its application. The potential displayed by such a microstructure demonstrates the ability to bridge the gap between the mechanical properties of ferritic stainless steels (AISI 430) and austenitic stainless steels (AISI 304), with minimal additional cost in view of the relatively low nickel additions (2,5 wt per cent) when compared with conventional austenitic steels (8 to 10 wt per cent).

One disappointing feature of alloy E4 is its limited elongation to fracture during tensile testing. In order to elaborate on this observation, interrupted tensile testing was performed on alloy E3 in the solution-treated condition. The gauge surface of the specimen was polished and etched, and the microstructure was observed in the scanning electron microscope after loading to strain intervals in the range 0,02 to 0,15. After each particular loading sequence, the specimen was removed from the tensile grips and examined by secondary electron imaging. The specimen was then reassembled in the tester and loaded to a higher strain interval. Observations show that, although the first evidence of deformation occurs within the ferrite grains in the form of slip lines at a strain of approximately 0,02 to 0,03, the ferrite very rapidly becomes constrained, and subsequent strain is partitioned to the martensite matrix. This arises due to the island-type morphology of the ferrite in a martensite matrix. In view of the limited ductility of the martensite, necking and void formation occur within the martensite, and a low fracture strain results. Unfortunately, the island-type morphology is a consequence of the advanced δ -ferrite decomposition, which is necessary to suitably refine the grain structure.

Variations in Nitrogen and Nickel Contents

Although the microstructure and properties of alloy E3 present a promising alternative steel composition, the addition of even limited amounts of nickel is questionable in terms

of maintaining low cost. The prospect of alternative alloying therefore needs to be investigated, both in terms of establishing a more clear understanding of the contribution of nickel to the toughness of the martensite, and as a substitute for nickel in terms of lowering the cost. Since the objective so far had been to refine the grain structure, the optimum phase balance in terms of a ferrite–martensite microstructure would have to be maintained. Therefore, the nickel would need to be replaced with a suitably potent austenite-forming element. To this end, it was decided to investigate the effects of reducing the nickel content, whilst increasing the nitrogen content to maintain a desirable ferrite–martensite phase balance, on the tensile and impact properties of duplex stainless steels containing 16 wt per cent chromium.

Experimental

The composition of two alloys containing reduced nickel levels, as well as that of the alloy low in interstitial elements and containing 2,5 wt per cent nickel, are given in Table IV. The alloys were laboratory cast into 5 kg ingots (50 mm thick) and were hot-rolled to plate thicknesses in the range 6 to 8 mm. The final reduction was terminated at approximately 850 °C.

TABLE IV
COMPOSITION OF ALLOYS E4 TO E6 (IN WT PER CENT)

Alloy	C	N	S	P	Mn	Si	Cr	Ni
E4	0,050	0,121	0,01	0,02	0,9	0,6	16,9	0,52
E5	0,026	0,116	0,01	0,01	0,9	0,3	15,7	1,12
E6	0,020	0,010	0,01	0,02	1,1	0,5	16,4	2,55

Microstructural analysis

The microstructures of alloys E4 and E5 in the solution-treated condition (1000 °C for 1 hour) are shown in Figures 10 and 11. Both alloys display two-phase ferrite–martensite microstructures, although the phase balances are somewhat different. Alloy E4 (0,5 wt per cent nickel) contains 64 per cent martensite, whereas alloy E5 (1,1 wt per cent nickel) has a martensite content equal to 89 vol. per cent. This can be contrasted with the martensite in alloys E3 and E6, which amounts to approximately 75 to 80 vol. per cent. In all cases, the extent of δ -ferrite decomposition has been successful in refining the grain size, but what is important is

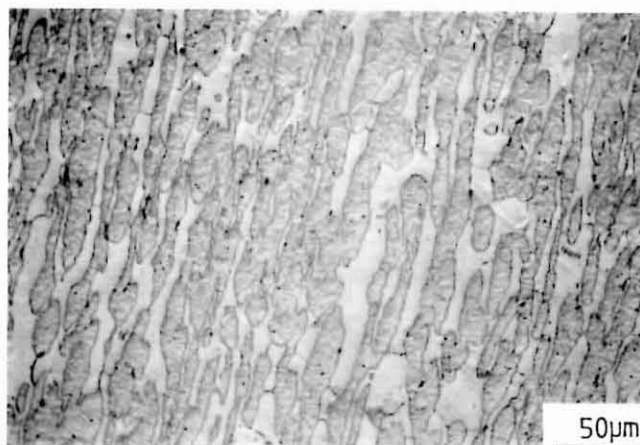


FIGURE 10. Ferrite–martensite microstructure of alloy E4 (solution-treated). Lighter areas = ferrite



FIGURE 11. Alloy E5 exhibits residual δ -ferrite stringers in a martensitic matrix (solution-treated)

the behaviour of the microstructure during heat treatment and the quality of the resulting mechanical properties.

The effect of heat treatment for 1 hour at various temperatures on the hardness of alloys E4 to E6 is shown in Figures 12 to 14. The results indicate the tempering characteristics of the starting solution-treated (1000 °C) microstructure in each case. Alloys E4, E5, and E6 show minima in hardness at 800, 700, and 650 °C respectively. In addition, the variation between the maximum (solution-treated condition) and the minimum hardness is the smallest for the alloy having the highest nickel content (alloy E6). This suggests that the

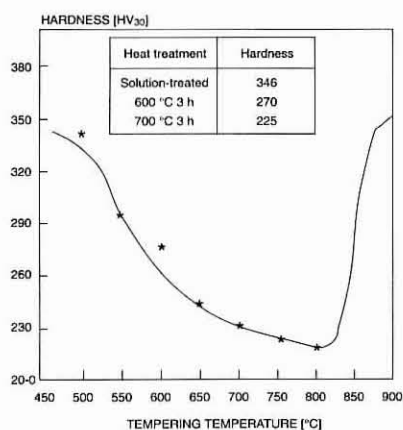


FIGURE 12. Hardness as a function of heat-treatment temperature (soak time = 1 h) for alloy E4. Additional values are inset

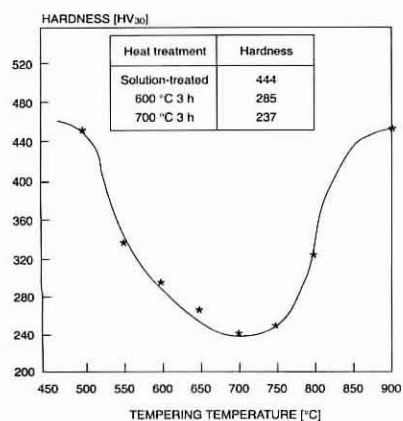


FIGURE 13. Hardness as a function of temperature (soak time = 1 h) for alloy E5. Additional values are inset

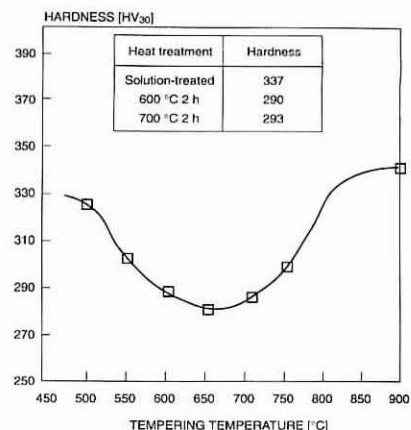


FIGURE 14. Hardness as a function of temperature (soak time = 1 h) for alloy E6. Additional values are inset

tempering kinetics of the nickel-rich martensite (alloy E6) are more sluggish when compared with the alloys containing lower nickel levels. The principal reason for the retarded tempering is the strong tendency for substitutional elements such as nickel to lower the A_{c1} temperature.

Examination of the alloys after heat treatment indicates obvious differences in the tempered microstructures for the various compositions. As discussed earlier, the primary ferrite in the 2.5 wt per cent nickel alloy (low in interstitial elements) shows very little, if any, modification during the tempering treatments. The martensite softens appreciably at 600 °C, and at 700 °C (over-tempering) the original martensitic regions are transformed to a lamellar mixture containing secondary ferrite and new martensite. However, in the case of the alloys high in nitrogen (E4 and E5), very noticeable precipitation occurs during tempering. This is manifested by both inter- and intra-granular precipitation associated with both the ferrite and the martensite phases.

The tempering of alloy E4 at 500 °C leads to fine grain-boundary precipitation, as well as fine interlath precipitation within the martensite. No precipitation occurs within the ferrite grains. After 1 hour at 600 °C, blocky-type precipitates are in evidence on most δ -ferrite grain boundaries, but there is still no clear evidence (as observed in the scanning electron microscope) of precipitation within the ferrite grains. Soaking at 700 °C for 1 hour results in further coarsen-

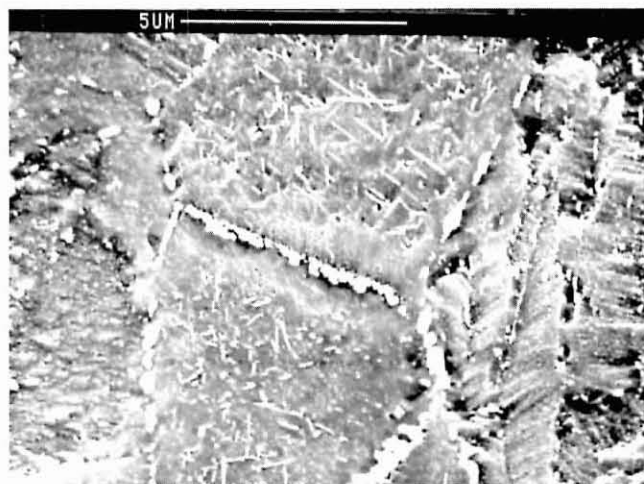


FIGURE 15. Extensive grain-boundary precipitation and precipitation of acicular Cr_2N within the ferrite phase (700 °C)

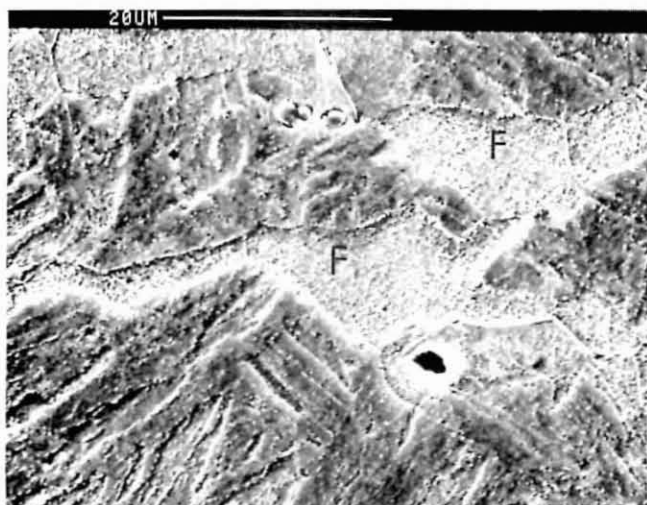


FIGURE 16. Dense precipitation of Cr_2N within the ferrite phase (alloy E5 at 700 °C)

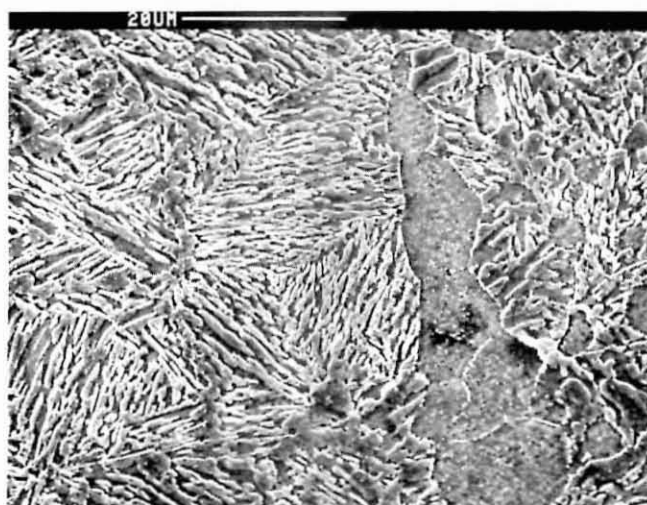


FIGURE 17. Lamellar ferrite-martensite structure developed in alloy E5 at 800 °C

ing of grain-boundary precipitates and in the appearance of a dense distribution of fine acicular precipitates within the δ -ferrite grains (Figure 15). In fact, these fine acicular precipitates were noted in the ferrite grains adjacent to the ferrite-martensite interface after only 8 minutes at 700 °C. The initial heterogeneous precipitation is more than likely due to preferential precipitation on dislocations produced in the ferrite as a result of the expansion accompanying the martensitic transformation. Electron-beam analysis (transmission electron microscope) of the acicular precipitates indicates a composition consistent with Cr_2N . The microstructure of alloy E5 demonstrates tempering characteristics similar to those of E4. Fine intergranular and interlath precipitation occurs at 500 °C, and these precipitates tend to coarsen at 600 °C.

Tempering at 700 °C once again leads to a high concentration of acicular Cr_2N precipitates within the δ -ferrite grains (Figure 16), whereas soaking at 800 °C produces a lamellar ferrite-martensite mixture within the original martensitic regions (Figure 17). This lamellar structure is similar to that produced in the 2.5 wt per cent nickel alloys soaked at 700 °C. However, there is still some precipitation within the primary δ -ferrite grains.

Mechanical properties

The hardness, tensile, and Charpy V-notch impact properties of alloys E4 to E6 as a function of heat-treatment condition are listed in Table V. In all cases, the solution-treated condition represents a 1 hour soak at 1000 °C. Both alloys E4 and E5 exhibit very poor impact toughness when tested in the solution-treated condition. This should be compared with the attractive impact energy of alloy E6 in the same heat-treated condition. Tempering, or in some cases over-tempering, leads to an improvement in the impact properties of all the alloys. As one would expect, the tensile strength and hardness decrease after tempering, although the extent of the reduction is much greater for alloys E4 and E5.

TABLE V
MECHANICAL PROPERTIES OF STEEL ALLOYS E4 TO E6 IN
VARIOUS HEAT-TREATED CONDITIONS

Alloy	0.2% MPa	UTS MPa	Charpy 7.5 mm, J	Elong. %	HV ₃₀	Condition
E4	707	1200	3	14	346	Solution-treated
E4	644	810	37	20	283	600 °C 1h
E4	524	705	56	28	229	700 °C 1h
E5	976	1309	5	14	444	Solution-treated
E5	861	937	32	18	295	600 °C 1h
E5	630	750	72	24	242	700 °C 1h
E5	668	923	38	22	326	800 °C 1h
E6	759	990	63	19	337	Solution-treated
E6	621	821	85	19	293	700 °C 1h

Discussion

The reduction in nickel content, while increasing the nitrogen level, was successful in maintaining a duplex ferrite-martensite microstructure in alloys E4 and E5. As discussed earlier, the duplex structure arises from the δ -ferrite decomposition, which is necessary in order to refine the overall grain size. The extent of the δ -ferrite decomposition, however, is quite different for E4 and E5, but this can be expected in terms of the similar nitrogen levels yet different nickel contents. The result is a coarser ferrite grain size (up to 120 μm in length) in alloy E4 as opposed to a very fine ferrite grain size (7 to 10 μm) in alloy E5. It would be expected that these ferrite grain sizes would affect the mechanical properties differently, but the strength and toughness of the individual phases are also important in governing the response to deformation.

Despite the lower volume fraction of martensite in alloy E4 compared with E6, the hardness of the solution-treated microstructure is greater in the former alloy. This illustrates the greater influence of the interstitial nitrogen on the hardness of the martensite. Alloy E5 has the highest hardness in view of the much higher martensite content provided by the 1.1 wt per cent nickel addition. During tempering of alloys E4 and E5 at 600 °C, and to a larger extent at 700 °C, considerable precipitation occurs at grain boundaries and at martensite interlath boundaries, giving rise to numerous carbide, nitride, and carbonitride precipitates of various stoichiometry. The notable appearance of acicular Cr_2N within the primary ferrite after soaking at 700 °C illustrates the relatively high nitrogen content in the primary ferrite as a con-

sequence of solution treatment. Thus, the presence of appreciable amounts of interstitial elements very finely dispersed within the ferrite after solution treatment would be expected to play an important role in determining the mechanical properties.

The very low impact toughness of alloys E4 and E5 in the solution-treated condition can therefore be explained by both the interstitial content of the ferrite phase and the high hardness of the martensite phase. The presence of interstitial nitrogen in the ferrite phase dramatically impedes the movement of dislocations, and in most cases leads to transgranular brittle fracture⁴. This fracture mode in the ferrite phase was dominant in both these alloys during impact fracture of the solution-treated specimens. Although the brittle fracture of the ferrite phase is expected to lower the impact toughness drastically, there are indications that the predominantly interstitially alloyed martensite, in the case of alloys E4 and E5, is notably less tough than the high nickel-containing martensite in alloy E6. This can once again be explained by the resistance provided by the interstitial elements to dislocation motion, as well as the increased tetragonality associated with a high interstitial martensite. The combination of a high interstitial content within the ferrite phase and a martensite of high hardness gives rise to low energy fracture during impact loading. The limited ductility is also expressed by the poor elongation to fracture during tensile testing.

Tempering of alloys E4 and E5 improves the impact toughness significantly, despite the high concentration of inter- and intra-granular precipitates. The optimum impact toughness is achieved in both alloys when the Cr₂N concentration within the ferrite grains is highest (tempering at 700 °C), and therefore the deleterious effects of a high concentration of precipitates are offset by the greater mobility of dislocations through the lower interstitial *bcc* lattice. Softening of the martensite phase obviously also allows easier dislocation movement, and a greater amount of ductility was observed in both the ferrite and the tempered martensite phases during the examination of the fracture surfaces. Unlike the situation with alloy E6, however, where the formation of a lamellar ferrite-martensite phase improves the impact toughness (700 °C), the formation of the lamellar phase in alloy E5 at 800 °C leads to a reduction in impact properties compared with the values obtained for this alloy at 700 °C. In alloy E6 (and alloy E3), the high impact resistance is attributed to the crack-blunting effect of the lamellar composite phase, which contains 'tough', nickel-enriched martensite. The fact that the impact toughness is not improved by the lamellar phase in alloy E5 is due to the lower nickel and higher content of interstitial elements in the martensite fraction. This leads to brittle fracture of the martensite lamellae, which has an adverse effect on the toughness of the alloy.

Summary

Attempts at refining the grain structure of ferritic steels containing 16 to 17 wt per cent chromium showed that nickel additions of about 2.5 wt per cent are required to sufficiently refine the grain size of the high-temperature phase. The composition gives rise to an advanced $\delta \rightarrow \gamma$ transformation, which leads to the formation of a duplex ferrite-martensite microstructure at room temperature. Comparison of this duplex structure with that of alloys containing much smaller volumes of martensite (i.e. alloys that have undergone much less advanced $\delta \rightarrow \gamma$ transformation) showed that more desirable properties are obtained from the finer-grained alloys high in martensite. In addition, the duplex structure can be heat-treated to form a lamellar composite phase that possesses optimum toughness.

The reduction in nickel content, together with an increase in the nitrogen level to maintain the ferrite-martensite balance, led to a drastic lowering in mechanical properties. Although the grain size can still be considered to be refined, the high interstitial content in both the ferrite and the martensite phases was notably deleterious to the fracture properties. The impact toughness of these alloys can be improved by heat treatment, but there are indications that they would not be suitable for welding. In addition, the low toughness offered by the martensite rich in interstitial elements highlighted the benefits derived from nickel-rich martensite.

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