

The Potential of Chromium as an Alloying Element

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Despite an international campaign to find viable substitutes for chromium as an alloying element, the indications are that there is really no other element or combination of elements that can replace it. This is due, not only to economic considerations, but also to the unique ability of chromium to confer properties such as passivity and heat resistance. As a result of intensive research efforts to improve the properties of steel for critical applications where enhanced corrosion resistance or high-strength and high-fracture properties are required, it seems that the use of chromium as an alloying element is bound to increase. It is envisaged, not only that the percentage of chromium in alloys will increase, but that new alloys will be developed in which chromium plays a dominant role.

Importance of Chromium as Alloying Element

Apart from the usual elements found in plain carbon steels, chromium is the alloying element that is most frequently used as an alloying additive. Apart from stainless steel, in which chromium is essential, one has to search very hard to find alloy steels in which chromium is absent. Apart from the frequent use of chromium as the only additional element, it is also frequently used in combination with one or more of the alloying elements, Ni, Mo, V, etc. The question that should really be asked is whether it would be at all possible to replace chromium as an alloying element in steel. This is a question that recently received great prominence outside South Africa on strategic grounds. In the case of low-alloy steels, the substitution of chromium is dictated mainly by economic considerations. In a recent publication¹, it was, for example, shown that the 0.4 per cent chromium in a nickel-chromium carburizing steel can be replaced by 0.4 per cent molybdenum. Apart from punitive economic considerations of replacing chromium with molybdenum, it is questionable whether there is really sufficient molybdenum reserves to replace all of the chromium used in low-alloy steels.

In the case of stainless and heat-resistant steels, the question of replacement is quite different and has received comprehensive coverage in the international literature. It turns out that the answer² is an emphatic no! From a practical point of view, there is really no viable alternative alloying element³. At best, it has been found that the chromium content can be decreased from the customary 18 per cent level in SAE type 304 to possibly 9 per cent for use in less severe applications. In order to maintain some form of corrosion resistance, the decrease in chromium content from 18 to 9 per cent has to be compensated for by additions of Mo, Si, Cu, V, N, and Ni. Many of the potential alloying elements of interest are more potent ferrite stabilizers than chromium. In order to maintain an austenitic structure, some alloys in which chromium has been partially substituted require a nickel addition of up to

24 per cent. The results of some of these tests³ are shown in Figure 1, where the influence of the chromium content on the corrosion rate in H₂SO₄ solutions for a wide variety of alloys is plotted. From this graph, the dominant importance of chromium is quite evident. Similarly, the quality of the passivity, as measured by the minimum current density in the passive region in a 10⁻⁴ p.p.m. NaCl solution as shown in Figure 2, is largely influenced by the chromium content of the alloys. Figure 3 shows that the sensitization of stainless steels, which results in intergranular corrosion, is also critically dependent on the chromium content of the steel. Much the same result was found when test panels were exposed to a marine atmosphere, as shown in Figure 4. One of the shortcomings of austenitic stainless steels, such as SAE type 304, is their susceptibility to stress-corrosion cracking (SCC). In the tests referred to above, none of the alternative compositions, when U-bend specimens were evaluated in boiling MgCl₂, was resistant to SCC, and there was no indication that any of the other alloying elements in the leaner chromium alloys conferred better stress-corrosion properties. Apart from the alchemic dream of creating a new super stainless steel without any chromium, there is nothing even to suggest a break-through in this direction.

Instead of initiating research projects to find viable alternatives to chromium as an alloying element, I believe that, because the potential of chromium has not yet been fully exploited, we should concentrate on the optimum usage of chromium. There are various new avenues that should be explored. In many of the new developments, such as the duplex steels, the tendency has been to increase the chromium content rather than to decrease it. The high cost of nickel in austenitic steels has resulted in the development of a whole new generation of ferritic stainless steels in which the use of nickel has been curtailed drastically. Among the new developments, the super-ferritics, which are resistant to SCC, are noteworthy. On the other side of the coin, there is the development of steels

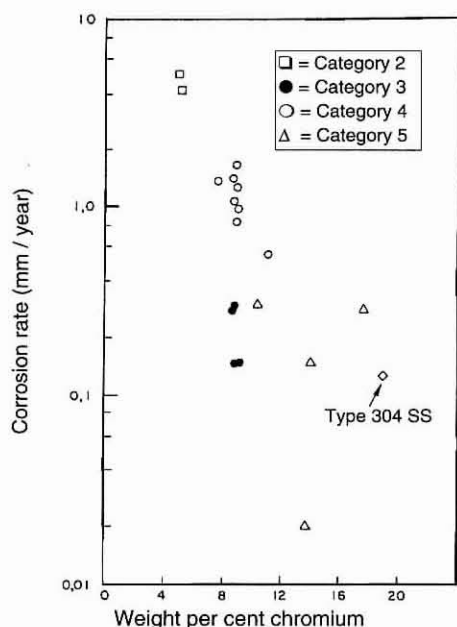


FIGURE 1. The influence of chromium content on estimated corrosion rates in 1.0 NH_2SO_4

Category 2. 24 Ni-5 Cr-Mo alloys
 Category 3. 24 Ni-9 Cr-Mo-Cu-V alloys
 Category 4. 24 Ni-9 Cr-Mo-V-Si alloys
 Category 5. 24 Ni-14 Cr-Mo alloys

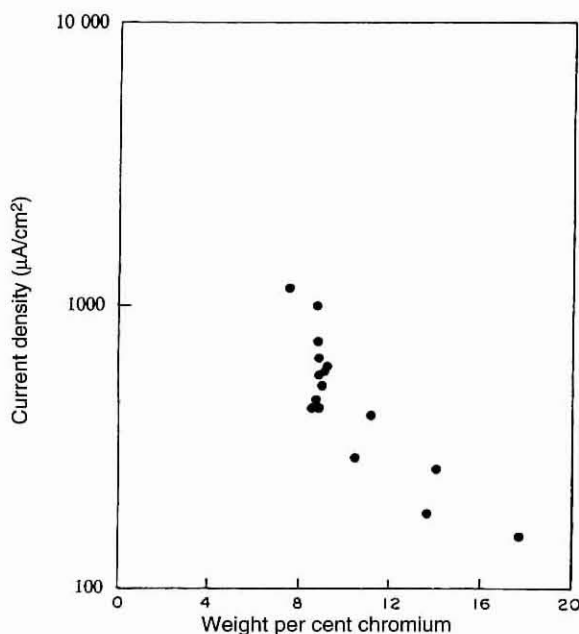


FIGURE 2. The influence of chromium on the minimum current density in the passive region in a 1% NaCl solution³

derived from SAE type 409 steel. Apart from very attractive mechanical properties, these steels have adequate corrosion-resistance properties and satisfactory welding properties. The cost of this type of steel is particularly attractive, and I expect that the last word on this subject has not yet been heard.

Chromium in Low-alloy Steels

The potential of chromium as an alloying element is by no means limited to stainless and heat-resistant steels. Similar

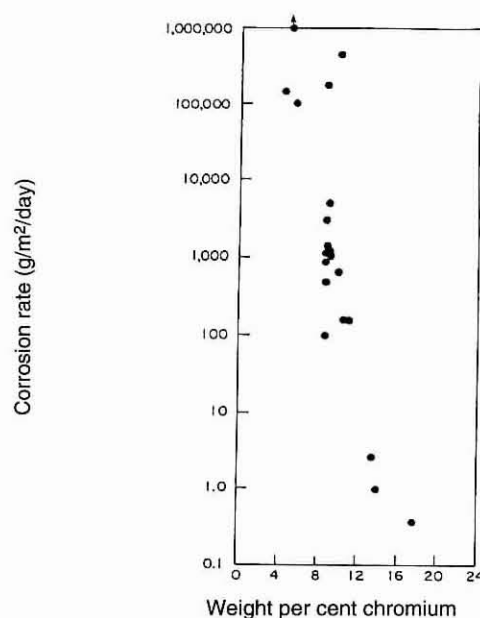


FIGURE 3. The influence of chromium content on the corrosion rates in boiling 25% HNO_3 solution³

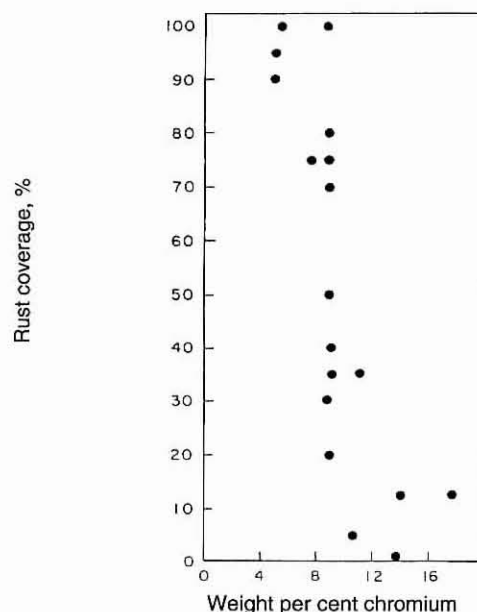


FIGURE 4. The influence of chromium content on rust coverage after 6 months of exposure in a marine environment³

possibilities exist for the use of chromium as an alloying element in low-alloy steels.

In the design of low-alloy steels, one of the main functions of alloying additions is to increase the hardenability. Traditionally, the influence of alloying additions on hardenability can be calculated by use of the empirical Grossman equation⁴, which expresses the influence of alloying elements in terms of multiplying factors:

$$D_1 = D_C \cdot F_{\text{Mn}} \cdot F_{\text{Cr}} \cdot F_{\text{Si}}$$

where D_1 = Ideal critical diameter

D_C = Base diameter

F_X = Multiplying factors that relate the influence of each element addition on hardenability

$$F_X = 1 + a \cdot \%x.$$

This approach implies that there is strong inter-element synergism between the different alloying elements; the addition of twice the amount of a specific alloying element is not as effective as the single equivalent addition of two different alloying elements, which ordinarily is just as effective as the initial alloying element. This synergism has never been explained satisfactorily.

In recent research work at the University of Pretoria^{5,6}, it has been shown that the real inter-element effect operates mainly via the carbide-forming tendency of the individual alloying elements. It has been shown that hardenability can be determined more accurately by the use of the following equation:

$$\log D_1 = \log D_C + K_1 (\% \text{ Mn}) + K_2 (\% \text{ Cr}) + K_3 (\% \text{ Mo}) + K_4 (\% \text{ Ni}) + K_5 (\% \text{ Si}).$$

In this equation, the constants $K_1, K_2 \dots K_5$ can be expressed by a relationship of the type

$$K_i = k_i + n_i \log \% C.$$

The constants were obtained from an analysis of a carefully documented continuous-cooling transformation diagram⁷.

The magnitude of k indicates the effectiveness of the alloying addition in the absence of carbon, whereas the value of n is indicative of an interaction between the alloying element and the carbon in the steel. A high value of n signifies a strong interaction and a hardenability effectiveness that increases with carbon content.

A comparison of the magnitude of the values of k and n for different alloys is shown in Table I.

TABLE I
HARDENABILITY EXPONENTS k AND n

Alloying element	k	n
Si	1,40	0
Ni	1,50	0,016
Mn	2,51	0,150
Cr	4,68	0,56
Mo	7,59	0,92

Table I clearly shows that, as a result of the weak tendency of Si and Ni to form carbides, the values of n for these two elements are negligible. The value of n increases from Ni to Mo approximately in accordance with their carbide-forming tendencies. The values of k , which indicate the effectiveness of alloying element additions in the absence of carbon, similarly increase from a comparatively low value for Si to the highest value for Mo. Whereas it is clear that Mo is the most effective element that can be used to increase hardenability, Table I also indicates that chromium is particularly efficient in improving hardenability. It is certainly much more cost-effective to use chromium than Mo.

High values of k imply that the effectiveness of a particular alloying element increases exponentially with alloy content. Twice the amount of a particular element would therefore be more than twice as effective in increasing hardenability. Figure 5, for example, shows the modified Grossman multiplication factor⁴ for chromium as it is influenced by the carbon content. It is suspected that

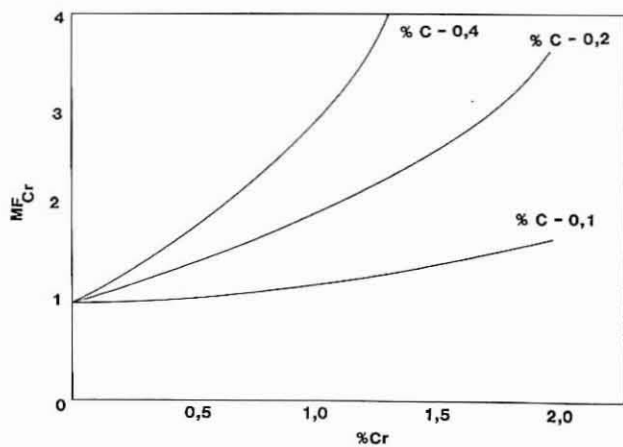


FIGURE 5. The influence of carbon on the hardenability multiplication factor for chromium in low-alloy steels

the Grossman equation has been an important factor in the design of multi-alloy, high-hardenability steels with minimum total alloy content. The implication of the new results on hardenability indicate that the same result can also be obtained when more of a single alloying element is used. A judicious choice of alloying elements can consequently reduce the total cost. It is not suggested that the multi-alloy steels, such as the well-known and respected Cr-Ni-Mo steels, should be replaced by simpler alloys. It is clear, however, that new avenues have now been opened in the design of alloy steels, and it is envisaged that chromium will gain even greater prominence.

Fracture-tough High-strength Stainless Steel

The quest for high-strength steels with high fracture toughness has been the preoccupation of generations of metallurgists. To date, the best that has been achieved in this respect is the development of the high-alloy maraging steel⁸ and the subsequent derivatives. A typical maraging steel may contain 18 per cent Ni, 5 per cent Mo, and 8 per cent Co. The maraging grades of steels are unique in that the hardening mechanism is not based on the presence of carbon as in other steels. The hardening in maraging steels occurs by precipitation in a parent phase, which consists essentially of carbon-free martensite. While the superior mechanical properties of maraging steels are acknowledged, there nevertheless remain the high costs associated with such high-alloy steels and the fact that they are not stainless. The use of chromium in this regard offers a range of attractive possibilities. Many of these developments are fairly new and have not yet been fully exploited.

The use of carbon as a hardening element in conventional high-strength low-alloy (HSLA) steels is to a large extent limited by the brittle nature of the carbides that are formed during tempering. It has long been realized that, for optimum strength and fracture toughness, the carbon content should be reduced as far as practically possible. In the case of HSLA steels, the lower limit for carbon is probably in the vicinity of 0,3 per cent if a viable reserve of hardenability is to be maintained. Lack of sufficient hardenability and the detrimental effects of even small

percentages of upper bainite on fracture toughness are well documented⁸. If much larger amounts of chromium are used than that conventionally used in HSLA steels, high hardenabilities can be realized even in fairly low-carbon steels. This opens up a whole new class of fracture-tough, high-strength stainless steels.

The idea of using high percentages of chromium (4 per cent), together with manganese and/or nickel in low-carbon steels, usually with less than 0.25 per cent carbon, was first developed by Thomas and his co-workers⁹⁻¹¹. The reduction in carbon content results in very favourable combinations of fracture toughness and strength. In Figure 6, the fracture toughness–strength relationship for commercial quenched and tempered steels is shown in comparison with that of 4% Cr steels. The superior properties of 4% Cr steel are partly due to the reduction in carbon content, which results in comparatively tough lath martensite in comparison with higher-carbon steels, where transformation results in brittle, twinned martensite. Fracture toughness is also enhanced by the presence of a thin film of thermally and mechanically stable retained austenite at the lath boundaries. The presence of small amounts of ductile tough austenite, which surround martensite laths, has a crack-arresting effect, and also results in the refinement of the martensite packet size and consequently in an improvement in fracture toughness.

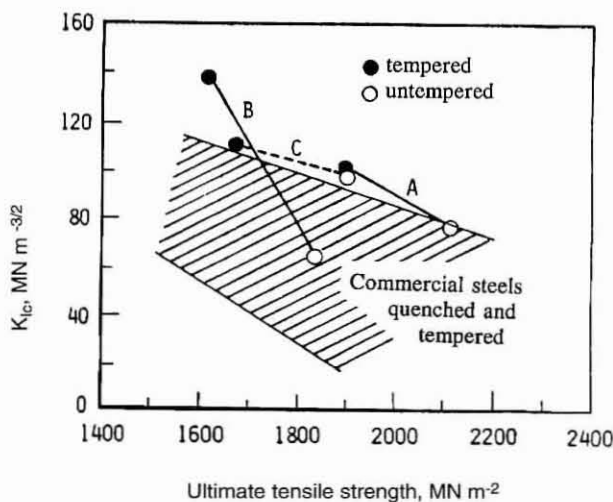


FIGURE 6. Relationship between tensile strength and fracture toughness, K_{IC} , of Fe-C-4Cr steels⁹
 A Fe-0.35 C-Cr
 B Fe-0.25 C-1.93 Mn-4.1 Cr
 C Fe-0.27 C-3.8 Cr-5Ni

In a recent study¹², the same principle was extended to steels that contain from 8 to 12 per cent chromium. On account of the high chromium content, these steels, apart from possessing very favourable mechanical properties, have attractive stainless properties. These alloys are air-hardenable and, after controlled rolling and on-line cooling, develop a very desirable structure of auto-tempered lath martensite, together with films of retained austenite on the lath boundaries, as shown schematically in Figure 7. Subsequent tempering (below 300 °C) results in some softening but also in a concomitant improvement in fracture toughness. At higher tempering temperatures (300 to 450 °C), the interlath-retained austenite films decompose to

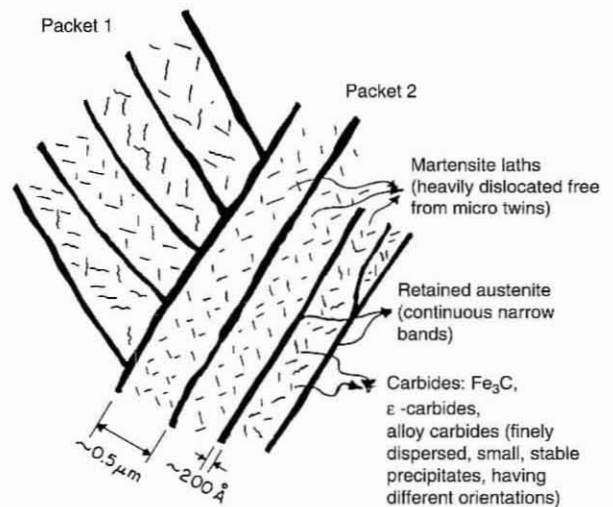


Figure 7. Schematic representation¹¹ of the optimum microstructure of lath martensite steels. The microstructure consists of auto-tempered, dislocated lath martensite with thin films of retained austenite on the lath boundaries



FIGURE 8. Transmission electron microscope (TEM) showing the films of retained austenite (white) surrounding martensite laths (dark)

coarse interlath carbides, resulting in temper martensite embrittlement. Figure 8 shows a transmission electron-microscope micrograph of the austenite films surrounding martensite laths.

The advantage of this type of self-hardening stainless steel is still to be exploited on a commercial scale. The fact that the steel is self-hardening and does not require subsequent tempering should prove cost-effective in applications where wear and corrosion occur together. Ore-handling and ore-dressing equipment is a logical application for this kind of steel. On account of its high strength, the steel may be prone to hydrogen embrittlement. Precipitation of high-chromium carbides in the heat-affected zone (HAZ) during welding will obviously also present a potential corrosion problem.

Iscor (Ltd) has independently developed a steel (designated type 927) that is generically similar to that described above. In addition to chromium, type 927 is also alloyed with some nickel and molybdenum. Hot-rolled plate has a typical Vickers hardness of 500, tensile and yield values of 1500 MPa and 1000 MPa respectively, and Charpy impact-energy values of 60 to 80 J at room temperature. Salt-spray corrosion testing yielded a corrosion rate of 0,1 mm/a in comparison with a value of 0,03 for SAE type 304L. Under comparable circumstances, the corrosion rate of mild steel is 0,8 mm/a.

Conclusion

Whereas it is probably true that there is no other class of material that is so prone to exceptional types of corrosion as stainless steel, it nevertheless remains a metallurgist's dream. Despite the tremendous complexities in the metallurgy of stainless steel, the demand for stainless steel has grown steadily since its first appearance on the market. Although the original composition of 18-8 is still used today, the number of speciality grades has grown spectacularly. Though we still do not fully understand all of the manifestations of passivity, pitting, and SCC, we have learnt to control the incidence of these phenomena. Although there has been a campaign to replace chromium as an alloying element in steel, I believe that a different scenario will develop. New developments will probably result in the use, not only of higher percentages of chromium in steels, but also of larger tonnages of steels that contain chromium as an alloying element.

References

1. Cameron, T.B. (1986). Chromium substitution technology. *J. Metals*, May, p. 18.
2. Bittence, J.C. (1979). Can there be stainless without chromium? *M.E.*, Mar. pp. 28-32.
3. Floreen, S. (1982). Examination of chromium substitution in stainless steels. *Metall. Trans. A.*, vol. 13A, pp. 2003-2013.
4. Grossman, M.A. (1942). *Trans. AIME*, vol. 150, pp. 227-259.
5. Mostert, R.J. (1989). Ph.D. thesis, University of Pretoria.
6. Mostert, R.J., and Van Rooyen, G. T. (1988). *Phase transformations* 87, Lorimar, G.W. (ed.). London, The Institute of Metals, pp. 537-544.
7. Rose, A., and Hougardy, H. *Atlas zur Warmbehandlung der Stähle*, vol. 2, Dusseldorf, Verlag Stahleisen GMBH.
8. Decker, R.F., and Floreen, S. (1965). *Precipitation in iron base alloys*. New York, Gordon & Breach, p. 69.
9. Carlson, M.F., Rao, B.V.N., and Thomas, G. (1979). *Metall. Trans.*, vol. 10A, pp. 1273-1284.
10. Rao, B.V.N., and Thomas, G. (1980). *Metall. Trans.*, vol. 11A, pp. 1273-1284.
11. Sarckaya, M., Steinberg, B.G., and Thomas, G. (1982). *Metall. Trans.*, vol. 13A, pp. 2227-2237.
12. Ramash, R., Kim, N.J., and Thomas, G. (1990). *Metall. Trans.*, vol. 21A, pp. 683-695.

