

# History and development of ferritic stainless steels

by M.B. Cortie\*

## SYNOPSIS

An account is given of the development of ferritic stainless steels since their discovery in the early years of this century. The alloys became very widely used in the 1950s, the market during that decade being driven strongly by a demand for automobile trim made of ferritic stainless steel. The production of ferritic stainless steel declined as a proportion of the total at the end of the 1950s as consumer preferences changed. However, the market is now growing strongly again, this time driven by a demand for oxidation-resistant alloys for motor-vehicle exhaust systems. The tonnages produced, applications, and market shares of the various alloys are discussed and compared. Trends in world stainless-steel production, product forms, technological development, and usage are examined.

## SAMEVATTING

Daar word verslag gedoen oor die ontwikkeling van ferritiese vlekrye staal sedert hul ontdekking gedurende die beginjare van hierdie eeu. Die legerings is in die vyftigerjare baie algemeen gebruik en die mark is gedurende daardie dekade sterk gestimuleer deur 'n vraag na motorversierings wat van ferritiese vlekrye staal gemaak is. Die produksie van ferritiese vlekrye staal het teen die einde van die vyftigerjare as 'n verhouding van die totaal afgeneem namate verbruikers se voorkeure verander het. Die mark groei egter tans weer sterk, hierdie keer as gevolg van 'n vraag na oksidasiebestande legerings vir motorvoertuie se uitlaatstelsels. Die tonnemaat geproduseer, aanwendings en marktaandeel van die verskillende legerings word bespreek en vergelyk. Tendense in die wereldproduksie van vlekrye staal, produkvorms, tegnologiese ontwikkelings en gebruike word ondersoek.

## INTRODUCTION

Ferritic stainless steels are one of five different kinds of stainless steel, the others being austenitic, martensitic, duplex, and precipitation-hardening stainless steels. The austenitic stainless steels currently constitute more than 70 per cent of the total tonnage of stainless steels produced worldwide, but the ferritic stainless steels are the second most-important group, making up about 25 per cent of the total. About 65 per cent of the austenitic stainless steels produced are the 18-8 alloys typified by AISI types 301 and 304 and their variations. It is not surprising, therefore, that the austenitic stainless steels receive the most attention from industrialists and the authors of metallurgical textbooks. While reviews or discussions of the ferritic stainless steels have appeared in the past<sup>1-10</sup>, these have often been in journals or books of limited circulation. An exception may be the reasonably accessible review written by Demo in 1977<sup>6,11,12</sup>, although it emphasizes the various mechanisms of embrittlement and does not address other issues comprehensively. In addition, each of the publications cited has been rendered somewhat dated by the developments of the past decade. Finally, most of the published information has been dedicated purely to the technological aspects of these alloys, and the overall development of these materials seems not to have been addressed in print recently.

Ferritic stainless steels are, by definition, iron-based alloys containing more than 11 per cent chromium and consisting largely of the body-centred-cubic ferrite phase. Some grades also contain up to 2 per cent nickel and 4 per cent molybdenum. While ferritic stainless steels containing up to 40 per cent chromium can be formulated in principle<sup>13</sup>,

there have been no commercially available wrought alloys containing more than 30 per cent chromium. Ferritic stainless steels are significantly cheaper than austenitic stainless steels (Table I). The reason for the smaller share of the market held by the ferritic alloys is that most of them possess poorer resistance to general and localized corrosive attack than the austenitic alloys, and generally have poorer weldability and toughness at ambient temperatures. On the other hand, ferritic stainless steels have excellent resistance to chloride stress-corrosion cracking (a common occurrence given the abundance of chloride ions on the Earth's surface).

Although there are dozens of designations for ferritic stainless steels, only a few kinds are produced in large quantities. An examination of the varieties on the market at present indicates that they can be divided into three groups: 12 per cent Cr alloys, 17 per cent Cr alloys and, of lesser economic importance, super-ferritic alloys. Most engineers around the world identify individual alloys in these groups by their tradenames or by a label containing their AISI-equivalent number. German DIN specifications and the old Soviet system are used to a lesser extent. The AISI system is used in Table II, which lists the more significant compositions, as well as the amount of each alloy manufactured in the USA in 1989 as an example, where available. Although the usage of the alloys differs slightly elsewhere, these figures can be considered to be reasonably representative of world trends. Table III lists some of the newer ferritic stainless steels, which are still generally known by their

**Table I**  
Prices of cold-rolled stainless-steel sheet in the USA in February 1993<sup>14</sup>

Alloy	Description	Microstructure	US\$ / kg
Type 304	Utility austenitic	100% austenite	2,59
Type 316	Quality austenitic	95% austenite	3,38
Type 409	Low-cost ferritic	100% ferrite	1,55
Type 430	Utility ferritic	100% ferrite	1,58

\* Mintek, Private Bag X3015, 2125 Randburg, Transvaal.

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tradenames. It should be noted that the compositions given in each table are indicative only, and should not be regarded as complete in all regards.

## HISTORY

There is a measure of confusion regarding the actual discoverer of stainless steels, and some authorities give this honour to Brearley<sup>18,19</sup>. However, the resistance to corrosion of iron-chromium alloys had been noted as early as 1838, and several researchers during the nineteenth century commented on the phenomenon (see for example, discussions of this topic by Zappfe<sup>20</sup> and Streicher<sup>18,21</sup>). Between 1902 and 1910, Guillet, in his laboratory in France, manufactured the first samples of alloys with compositions similar to those of modern stainless steels<sup>20</sup>. Among his alloys was a 17 per cent Cr steel containing 0,13 per cent carbon. This could conceivably be considered to be the first ferritic stainless steel. It is interesting to note that Monartz and Borchers took out a patent in Germany in 1911 on corrosion-resistant alloys containing between 30 and 40 per cent chromium and 2 to 3 per cent molybdenum<sup>18</sup>. Today this represents a range of composition considered to be on the leading edge of the development of ferritic stainless steels, although it has not yet been commercialized.

However, Brearley could certainly be considered to have been the first to recognize the commercial significance of the iron-chromium alloys. Although his first efforts concerned martensitic stainless steels<sup>19,22</sup>, the first industrial cast of ferritic stainless steel, with a composition of about 12 per cent chromium with 0,07 per cent carbon, was made in June 1920 by the Sheffield firm of Brown Bayley<sup>19</sup>. This

composition corresponds to what would now be known as type 409 ferritic stainless steel.

The concept of ferritic stainless steels, i.e. stainless steels with a ferritic rather than a martensitic microstructure, was rapidly established in the 1920s, but the compositions manufactured were generally used only in heat-resisting applications. This was on account of the fact that there was no cheap way at the time to reduce the carbon content to below 0,10 per cent without losing chromium in large amounts to the slag. As will be seen later, the corrosion resistance and mechanical properties depend closely on the carbon and nitrogen contents, and these properties of the early grades were therefore poor. Nevertheless, these early ferritic alloys found a market, and by the 1940s the 17 per cent Cr ferritic alloy had been standardized in the USA and Britain, and was being used for coinage in Italy<sup>23</sup>. At least 6 per cent of the stainless steel manufactured in the USA in 1942 was in one of the standard ferritic grades, while about 20 per cent was martensitic<sup>24</sup>. The state-of-the-art in ferritic stainless steels in 1951 was summarized in an excellent review paper by Thielsch<sup>1</sup>.

Use of the ferritics rose rapidly after World War II, driven largely by the extensive use of these grades in trim for motor vehicles. The severe shortage of nickel as a result of the Korean War was an additional, but temporary, factor encouraging ferritic manufacture, and in 1953, a year of severe nickel shortage, nearly as much type 430 was produced in the USA as all the austenitic grades put together<sup>24</sup>. Usage in automobile trim ensured that the ferritics remained popular even after the nickel shortage had ended. In 1957, about 25 per cent of the stainless steel manufactured in the USA was ferritic, and this proportion has been approximately maintained in the USA and the rest of the world ever since. This statistic is considered later in greater detail.

The extensive application of type 430 as automobile trim in the 1950s revealed that the corrosion resistance of this grade was not totally satisfactory, particularly in coastal regions, or where salt was used to de-ice roads. Improved versions of the 17 per cent chromium alloy with either a molybdenum addition (type 434) or a combination of molybdenum and stabilizing elements (type 436 and, later, type 444) were introduced in the USA, but had already been in use in Europe in the 1940s<sup>1</sup>. These grades have very much better corrosion resistance, but at a higher price. They are not yet manufactured in South Africa. An account of the history of automobile trim, and further details of the alloys used in the USA, can be found in the *Handbook of Stainless Steels*<sup>25</sup>.

It was well known that the corrosion resistance of the ferritics in non-reducing environments depended in a large measure on the chromium content, but the poor mechanical properties of the early ferritics, particularly those with higher chromium contents, discouraged further development. Binder and Spendelow<sup>26</sup> and Hochmann *et al.*<sup>7</sup> finally proved that the problem was due to interstitial content rather than to chromium content *per se*, but the technology available at that time was not able to produce alloys of the required purity. The introduction of vacuum-induction melting on an industrial scale changed this, and the French manufacturer Creusot Loire manufactured small tonnages of an alloy containing 30 per cent chromium in the late 1960s, reportedly on a 'semi-commercial' basis<sup>7</sup>. This may

Table II

Standard grades of ferritic stainless steel manufactured in the USA<sup>15-17</sup>  
(compositions in mass per cent)

Alloy	Cr	C	Other*	Output, t
405	11,5-14,5	0,08	0,6Ni and 0,1-0,3Al	1 514
409	10,5-11,75	0,08	Up to 0,5Ni and 0,75Ti	278 217
430	16,0-18,0	0,12	Up to 0,75Ni	62 670
434	16,0-18,0	0,12	1Mo and up to 0,75Ti	19 962
436	16,0-18,0	0,12	1Mo and Nb+Ti to 0,7	11 554
439	17,0-19,0	0,07	Up to 0,5Ni and 1,1Ti	13 236
444	17,5-19,5	0,025	1Ni, 2Mo and Ti+Nb to 0,8	< 2000
446	23-27	0,2	0,25N, up to 1,5Mn, 0,6Ni	< 2000

\* These alloys may also contain up to 1 per cent each of Mn and Si

Table III

Some of the better-known proprietary grades of ferritic stainless steel

Alloy	Cr	C	Mn	Si	Ni	Mo	Other
3CR12	12	0,035	1	0,5	0,5	0	Ti 0,3
3CR12L	12	0,020	1	0,4	0,1	0	Ti + Nb to 0,8
F12N	11	0,060	0,8	0,4	0,8	0	N 0,02
E-Brite	26	0,010	0,4	0,4	0,5	1	Cu, Nb to 0,2
Monit	25	0,025	1	0,75	4	4	Ti + Nb to 0,8
Sea-cure	26	0,025	1	1	2,5	3	Ti + Nb to 0,8
AL29-4-2	29	0,010	0,3	0,2	2	4	Cu 0,15
AL29-4C	29	0,025	1	0,75	0,5	4	Ti + Nb to 0,8

have been the first industrial example of what are now called 'super-ferritics'. However, the alloy proved not to be commercially viable.

Up to that stage, stainless steels had mostly been produced by the basic electric-arc process<sup>2,27,28</sup>, which typically produced a steel with a carbon content of 0,05 per cent, although a carbon level of 0,03 per cent could be attained by the use of low-carbon charge materials<sup>8</sup>. In the late 1960s, the concept of electron-beam refining was developed, and the Air Reduction Company, later called Airco Vacuum Metals, was established to manufacture a ferritic stainless steel known as E-Brite 26-1, which contained less than 100 ppm of total carbon and nitrogen<sup>29-31</sup>. E-Brite (now often called just 26-1) enjoyed a modest success on account of its exceptional corrosion resistance in aggressive chloride-containing media. It was also extremely tough and ductile, and full-size (10 mm) Charpy specimens of the alloy were able to stop the hammer of a 350 J testing machine at room temperature. However, electron-beam refining is not a cheap process, and Airco later licensed the product to Allegheny-Ludlum<sup>32</sup>, who then manufactured this alloy using vacuum-induction technology<sup>21,33</sup>.

In the meantime, conventional process technology had been developing steadily. The chief improvements were argon-oxygen decarburization (AOD), which was introduced by Union Carbide in 1968<sup>8,27</sup>, continuous casting and, to a lesser extent but especially in Japan, the vacuum oxygen decarburization process (VOD)<sup>34,35</sup>. The AOD technique can bring the carbon-plus-nitrogen content down to 0,016 per cent, whereas the VOD can bring it to less than 0,004 per cent<sup>34</sup>. It has become routine by such techniques to manufacture ferritic stainless steels containing only about 0,025 per cent carbon, but in either case a further decrease in carbon content is governed by thermodynamic considerations (including the chromium content) and requires higher temperatures<sup>27</sup> or an acceptance of greater losses of chromium. The other major improvement, continuous casting, not only increases the throughput, but also reduces the amount of unavoidable scrap by at least 10 per cent and improves the surface quality<sup>27</sup>.

The 1970s also saw an ongoing effort in the USA, Germany, France, and, later, Japan to develop low-interstitial high-chromium super-ferritic alloys containing molybdenum, an initiative championed by M.A. Streicher of the Du Pont company, which resulted ultimately in the introduction of the alloys AL29-4-2 and AL29-4C in the USA, Shomac River S30-2 in Japan<sup>8,21,36-38</sup>, and Usinor Chatillon's UNS S44735<sup>39</sup>. AL29-4-2 is prepared by vacuum-induction melting from pure raw materials, whereas AL29-4C is made by AOD and is thus much cheaper. AL29-4C also has better resistance to stress-corrosion cracking than AL29-4-2<sup>8,40</sup>. Shomac River S30-2 was available from Kawasaki Steel<sup>38</sup> and, like Usinor's UNS S44735, was manufactured by a variation of the VOD process<sup>38,39</sup>.

The development of the utility alloys containing 11 or 12 per cent chromium was guided by a different set of objectives. These alloys, unlike the super-ferritics, were not intended to compete with austenitic stainless steels, but rather with ordinary low-alloy and carbon steels. The most successful of these alloys so far is the alloy 3CR12, originally developed and patented by Middelburg Steel & Alloys in the 1970s<sup>41</sup>. There were originally two versions of

the alloy: 3CR12Ni, which contained about 1,3 per cent nickel, and 3CR12 with about 0,6 per cent. The former alloy was found to exhibit superplasticity at elevated temperatures but was not commercialized. A considerable tonnage of the second alloy was placed into service before it was replaced with a low-carbon, titanium-free version, also denoted 3CR12. Several other manufacturers are now producing alloys with compositions, and, in some cases, names similar to 3CR12. The reader is referred to the literature for further details of the history and development of this alloy<sup>42,43</sup>.

The new processing technologies encouraged the development of several variations in the basic 17 per cent chromium ferritic stainless steel. Besides the molybdenum addition mentioned previously, producers around the world have experimented with small additions of elements such as niobium, titanium, copper, aluminium, and zirconium. These alloys are generally regarded as proprietary variations of the basic type 430 composition, and are discussed in more detail in a later section.

Several important changes have taken place between the situation described by Thielsch in 1951<sup>1</sup> and that prevailing today; these include the dramatic decrease in the contents of interstitial elements, the introduction of niobium-stabilized grades, the wider use of molybdenum-containing grades, the introduction of super-ferritic grades, the introduction of welding technologies that facilitated the welding of alloys with more than 14 per cent chromium, the rise in importance of 12 per cent chromium alloys, the decline in importance of high-carbon high-chromium heat-resisting alloys and martensitic stainless steels in general, and a vastly improved understanding of the ductile-to-brittle transition phenomenon.

## CURRENT STATUS

### World Production of Stainless Steel

Growth in the consumption of stainless steel has consistently exceeded economic growth in the world, and was especially rapid in the mid-1980s<sup>44,45</sup>. Figure 1 shows the growth in stainless-steel production in the market-economy countries since 1950, and reflects the INCO estimates of stainless-steel production in the market economies<sup>44</sup>. These figures have previously excluded the People's Republic of China, the USSR, and the other Eastern Bloc countries. Pariser has estimated that Eastern Europe produced 1,575 Mt of stainless steel in 1989, mostly in the former USSR<sup>46</sup>. The production of stainless steel shows considerable year-by-year variations. The strong growth of stainless steel was abetted by a decline in the real price of stainless steel of about 50 per cent between 1967 and 1983, whereas that of carbon steel and aluminium increased by around 20 per cent over the same period<sup>27,47</sup>.

Encouraged by the rapid growth in the late 1980s, manufacturers around the world have installed, or plan to install, considerable amounts of new capacity, amounting to an increase of about 20 per cent in cold-rolled products<sup>44</sup>. The first half of the 1990s is therefore generally expected to be characterized by considerable over-capacity in the industry<sup>44</sup>. The best strategy for the producers under these conditions may be to concentrate strongly and co-operatively on expanding the market, rather than on cutting prices.

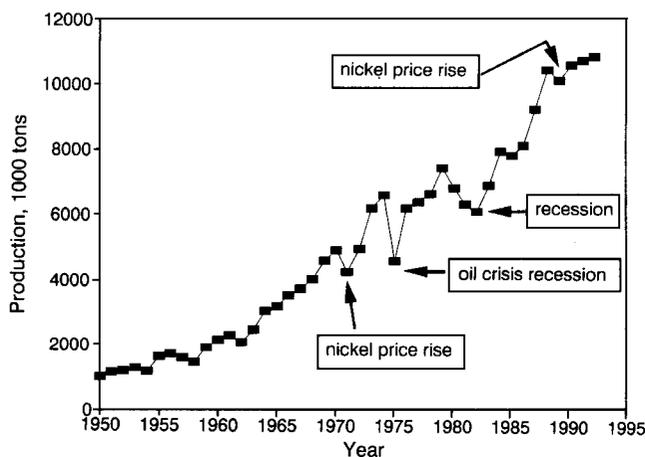


Figure 1—Growth in world stainless-steel production (market economy countries) from 1950 to the present

### Forms of Product

Stainless steel is manufactured in a very wide range of forms: plate, sheet, bar, tube, section, etc. However, cold-rolled sheet and strip constitute the largest part of the market. The situation in 1989 is shown in Figure 2 for some regions for which statistics are available. Cold-rolled products constituted between 53 and 64 per cent of the total, depending on the region<sup>44</sup>. In contrast to this, only 25 per cent of the former USSR's stainless-steel output was cold rolled in 1989<sup>48</sup>. Virtually all of this cold-rolled product is produced on Sendzimir mills, and the number of these mills in each country controls the production of this group of products<sup>44</sup>.

Determining the fraction of the cold-rolled flat products that is ferritic is less easy. However, figures are available for some countries in terms of international trade statistics<sup>44</sup>. The export of cold-rolled stainless steel from those countries for which a distinction was made between ferritic/martensitic and austenitic stainless steels in official trade statistics is shown in Table IV, which supports statements made<sup>49</sup> that most stainless steel produced around the world is consumed in the country of production, with a much lower proportion—less than 20 per cent—entering international trade. (The corresponding figures for the USA

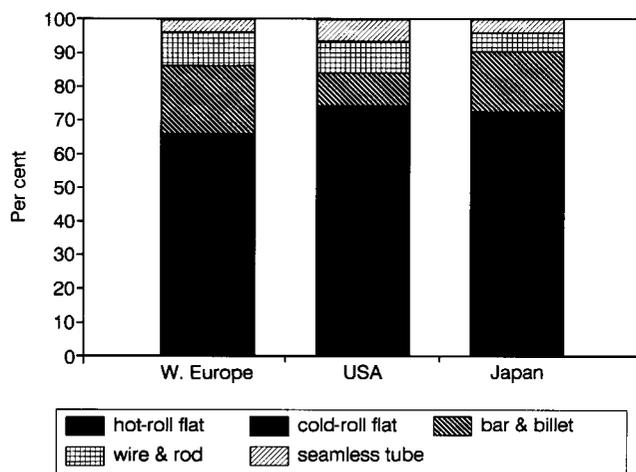


Figure 2—Consumption of stainless steel by product shape for Western Europe, Japan, and the USA in 1989

were not available. However, that country exports less than 5 per cent of its stainless steel<sup>50</sup>, and the inclusion of its data would not have made much difference to the global trend.) Overall, about 30 per cent of the cold-rolled material traded internationally in 1989 appears to have been ferritic or martensitic. The figures also indicate that the large French producer, Ugine, has made a significant commitment to ferritic stainless steels.

Most ferritic stainless steels are supplied as sheet on account of the poor weldability and toughness of most ferritic plate. However, 12 mm plate in type 444 is available from some producers<sup>51</sup>, and the 12 per cent Cr alloy, 3CR12, is available in up to 25 mm plate on account of its unusually good overall toughness and weldability<sup>52</sup>.

### The 12 Per Cent Chromium Alloys

The better-known ferritic alloys that contain about 12 per cent Cr include types 405 and 409, Crucible E-4, 3CR12 and its clones, and the alloy F12 from Ugine<sup>8,11,53-55</sup>.

Type 405 has been used for trays and linings in petroleum-distillation columns<sup>56</sup> but is not a widely produced material. Type 409, on the other hand, has achieved great prominence on the basis of its use in motor-vehicle exhaust systems in the USA, and the tonnage produced in the USA is now second only to that of type 304<sup>57</sup>. However, localized corrosion of type 409 mufflers (silencers) may still occur as a result of the condensation of exhaust gases<sup>58</sup>, and some Japanese motor manufacturers prefer a 17 per cent Cr alloy<sup>34,59,60</sup>. The great prominence of type 409 has encouraged the development of some proprietary variations especially intended for automobile exhausts. Some existing and proposed examples include Allegheny-Ludlum's AL466<sup>61</sup>, BSC's HyForm 409<sup>62</sup>, Nippon Steel's YUS409D<sup>35</sup>, and a 15 per cent Cr grade stabilized with combinations of Zr, Nb, and Al<sup>63</sup>. A minor application of type 409 is in cheap kitchen implements, such as large spoons.

Crucible's E4 was intended as a general-purpose corrosion-resistant steel, but it does not seem to have captured a significant share of the market. The South African alloy 3CR12 has, however, found widespread application in conditions where a modest resistance to corrosion is required, and the alloy, or copies of it, is now manufactured by producers in the UK, Germany, France, Spain, and Australia<sup>53-55,64-66</sup>. Current applications include coal-handling equipment, hot-well boiler tanks, switchgear cubicles, hopper cars, and equipment in the food-processing industries<sup>54,55,67</sup>. Approximately 220 kt of the alloy type is already in service, and production around the world is

Table IV  
Proportion of cold-rolled non-austenitic stainless-steel exports

Country	Total exported, kt	Ferritic, %
Belgium	98,4	1,3
France	188,9	59,4
Germany,W.	285,6	34,6
Italy	64,7	12,8
Spain	93,8	17,6
Sweden	101,2	7,0
UK	83,4	10,1
Japan	225,0	36,4

expanding<sup>54</sup>. Although originally titanium-stabilized and containing 0,5 per cent nickel, this alloy in its latest version contains neither titanium nor significant quantities of nickel<sup>68</sup>, and can be manufactured without a separate annealing step between hot and cold reduction provided that use is made of an insulated hood to control the temperature after hot work<sup>54,66</sup>. Maxwell<sup>54</sup> and others have predicted that the usage of dual-phase 12 per cent Cr alloys will continue to grow, and this would be especially true if a carbon-steel producer were to invest in the additional equipment required to produce 3CR12 or a similar alloy.

### The 17 Per Cent Chromium Alloys

The closest example of a general-purpose ferritic stainless steel is type 430, which, along with the other 17 per cent chromium ferritics, is, or has been, used in many aesthetic and functional applications such as architectural building panels, automotive trim and hubcaps, cooking utensils (especially the cheaper forks and spoons), kitchen sinks (especially in Japan and France), appliances, and refrigeration and water tubing. Some less well-known uses include a 0,3 mm cold-rolled cladding for insulated chilled-water pipelines in gold mines and, recently, in the exhaust manifolds of some cars<sup>34,60,69</sup>.

The basic type 430 composition has been the target of considerable alloy development around the world and, as mentioned previously, is available in several variations. An addition of 0,1 per cent aluminium, for example, is reputed to enhance the plastic strain ratio,  $r$ , of material that must be continuously annealed after hot rolling, and is available from Nippon Steel in Japan<sup>70</sup>. Titanium ('type 439') or zirconium additions<sup>59</sup> are able to stabilize the carbon and nitrogen, but the resulting carbo-nitride precipitates are relatively large (of the order of 10  $\mu\text{m}$ ). These precipitates are exposed on the surface of the sheet as a result of mechanical reduction, and are a source of unwelcome surface defects<sup>66,71</sup>. Niobium additions are also able to tie up the carbon and nitrogen, and do not have the disadvantage of causing surface defects. Niobium-stabilized variations are available from several manufacturers. Copper additions (of the order of 0,4 per cent) are reputed to improve the corrosion resistance of the 17 per cent Cr stainless steels<sup>71,72</sup>, and the simultaneous addition of niobium and copper recently found favour with some producers, such as Brazil's Acesita<sup>73</sup> and Nippon Steel<sup>74</sup>.

The corrosion resistance of the basic 17 per cent Cr alloy can be much improved if it is stabilized and alloyed with 1 or 2 per cent molybdenum. This has produced a variety of related alloys such as types 434, 436, 439, and 444. Types 434 and 436 have better resistance to corrosion in industrial and rural atmospheres than type 430, and are used for exterior vehicle trim, while type 430 is now used for trim inside vehicles<sup>3,25</sup>. Type 444, the most highly alloyed of the family, is widely recommended for applications where the austenitic stainless steels types 304 and 316 fail by stress-corrosion cracking, and is used in the food-processing industry, for solar-heater installations, and for heat exchangers, as well as for hot-water geysers currently manufactured in Japan and, previously, Scandinavia<sup>34,47,51,67</sup>. (It appears that the duplex alloy 2304 has replaced type 444 in hot-water heaters in Sweden<sup>75</sup>.)

### The Super-ferritic Alloys

The super-ferritic stainless steels, i.e. those containing more than about 25 per cent chromium and less than 0,05 per cent carbon, were originally designed for service in hot chloride solutions, such as those found in the cooling circuits of power stations located on the coast. Besides possessing good resistance to pitting (on account of their high chromium and molybdenum contents), these alloys also have good resistance to crevice corrosion and stress-corrosion cracking<sup>8,37,40,76</sup>. They also have excellent resistance to general corrosion in oxidizing and moderately reducing environments, to organic acids, and to caustic soda solutions<sup>37,38,40</sup>.

Alloys such as Crucible's Sea-Cure, Allegheny-Ludlum's AL29-4-2 and AL29-4C, and Kawasaki's S30-2 are examples. However, these alloys must compete in these applications with the super-austenitic alloys such as Avesta's 254SMO or Allegheny's AL-6X<sup>47</sup>. Although they cost more, the super-austenitic alloys are apparently easier and cheaper to fabricate, and less susceptible to brittle fracture. Nevertheless, it was reported in 1985 that the super-ferritics had largely displaced the super-austenitics from coastal power-station applications in North America<sup>47</sup>, and the dual Ti- and Nb-stabilized alloy AL29-4C appears to be particularly popular nowadays for this application<sup>40</sup>. Other applications for AL29-4C include geothermal-energy plants, and it is claimed to have the best overall resistance of all the stainless steels to corrosion in seawater<sup>40</sup>. It has recently been reported that SUS447J1, a Fe-29%Cr-4%Mo type alloy, will be used extensively on the new Kansai International Airport being constructed in Osaka Bay in Japan<sup>77</sup>. While the use of super-ferritics in condenser tubing has apparently not grown much, the greatest single use of AL29-4C at present is said to be in high-efficiency domestic heating furnaces<sup>40,78</sup>. About 25 kt of AL29-4C is currently produced per year.

E-Brite appears to have found a wide range of niches in chemical-process plant and in food processing, and is regarded as especially resistant to attack by sodium hydroxide solutions<sup>32</sup>. Although AL29-4-2 has comparable or better resistance to reducing acids than even super-austenitic alloys<sup>37</sup>, the 2 per cent nickel content is regarded as deleterious for resistance to stress-corrosion cracking. Both E-Brite and AL29-4-2 are reportedly being produced in only small quantities, mainly as repeat orders for clients already using the materials.

The excellent resistance of the super-ferritic alloys to chloride solutions and oxidizing acids (such as nitric acid) should be weighed up against their generally poor performance (29-4-2 excepted) in reducing acids such as dilute sulphuric acid solutions<sup>32</sup>. In addition, a reasonable resistance to intergranular corrosion in weldments is achieved only if the amount of free carbon and nitrogen is limited to less than about 200 ppm<sup>36</sup>. Although AL29-4C costs less in bulk than the super-austenitics, it takes twice as long to weld into tubing because it needs more shielding<sup>78</sup>. The price of the finished product is therefore similar.

### FUTURE PROSPECTS

#### The Pros and Cons of Ferritic Stainless Steels

The arguments for and against the use of ferritic stainless steels are presented as objectively as possible in the following section.

A few of the negative features of ferritic stainless steels include a relatively poorer general corrosion resistance than the austenitic grades (unless they contain molybdenum and are stabilized), poorer toughness and weldability in plate form, and a tendency to form ridges on the surface of sheet after drawing<sup>3,5,6,28,38,39,79,80</sup>. In addition, these alloys are not as easy to manufacture as the common austenitic alloys<sup>4</sup>. A problem sometimes experienced by steelmakers is brittle cracking of as-cast slabs, or cracking as a result of grinding<sup>54,81,82</sup>.

An advantage that the ferritics enjoy over the austenitic grades is a virtual immunity to chloride-induced stress-corrosion cracking. This has, for example, made the super-ferritic alloys a material of choice for desalination plants and the cooling circuits of coastal power stations<sup>40,47</sup>, and type 444 a material of choice for moderately corrosive applications where the austenitics exhibit stress-corrosion cracking<sup>51</sup>. Other advantages include their lower price, their stable pricing structure, their easier machinability, and their better deep-drawing properties. These last-named properties are particularly apparent when the plastic strain ratio parameter,  $r$ , is compared with that of austenitic grades: between 1 and 1,7 versus 0,8 to 1.

The better thermal conductivity of the ferritics (about  $21 \text{ W}\cdot\text{m}^{-1}\text{K}^{-1}$  at room temperature, compared with about  $15 \text{ W}\cdot\text{m}^{-1}\text{K}^{-1}$  for most austenitics<sup>83</sup>) is often also considered to be an advantage, and has occasionally led to substitution of a ferritic for an austenitic on this ground alone<sup>51</sup>. In a similar vein, the lower thermal expansion of the ferritics compared with the austenitics is considered to be an advantage in automobile exhaust systems, and would probably justify their use even if the prices were similar. The two types of material have a very slight, but noticeable, difference in colour, and this has some minor economic implications. For example, austenitics are sometimes regarded as 'too yellow' for automotive trim, and may even be chromium-plated so that their colour matches that of the ferritics<sup>25</sup>. On the other hand, the slightly yellow colour of the austenitics is usually regarded as desirable in cutlery and tableware. The bluish colour of the ferritics<sup>23</sup> has been given as a negative property with regard to their use in coinage, but might actually offer benefits in terms of coin-detection devices.

The ferritics are magnetic, which leads to their use in selected niche applications where a magnetic material with good corrosion resistance is required. Examples of this include the hub of a 'stiffy' diskette, Figure 3, and some coinage. On the other hand, there is a widespread belief among less-sophisticated users that magnetic stainless steels are either inferior to non-magnetic ones, or not even stainless steels at all. This factor is claimed to be responsible for a proportion of the resistance to ferritics in the Asian market<sup>5,84,85</sup>.

### Local and World Trends

#### Production of Stainless Steel

From 1950 to 1992, the consumption of stainless steel increased steadily at an overall average annual rate of 6 per cent. (The figure of 3 per cent is often quoted, but seems to be an under-estimate, since 1008 kt in 1950 increasing to 10 500 kt in 1990 gives an annual growth rate of 6 per cent when worked through the compound-interest formula.)

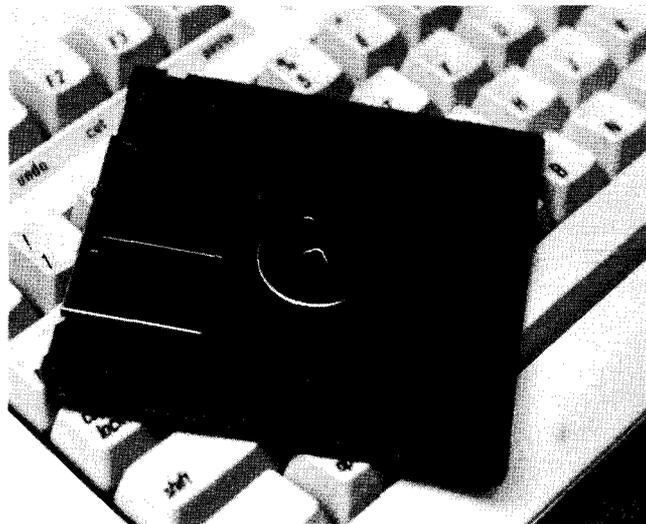


Figure 3—The hub of this computer diskette is made from a ferritic stainless steel selected for its corrosion resistance and magnetic properties

This is considerably faster than the growth in the world economy over the same period. Of particular interest is the proportion of world production held by the USA, which declined from 63 per cent in 1957 to 20 per cent in 1987. The difference is due to increased production in Europe and a dramatic increase in Japan. Japan became the world's largest producer of stainless steel in 1976<sup>86</sup>. However, countries like Japan and the USA appear to be losing their share of the international market, presumably to producers in Europe and developing countries. The trend for Japan is evident in Figure 4, which shows that exports from Japan declined even while the total production continued to increase. The latest data available indicate that production in 1991 increased by 7,3 per cent in Japan (compared with the previous year) and decreased by 7,7 per cent in the USA<sup>87</sup>.

There was a movement towards the replacement of the chromium in stainless steels during the 1970s and 1980s, but the substitution programme was guided more by politi-

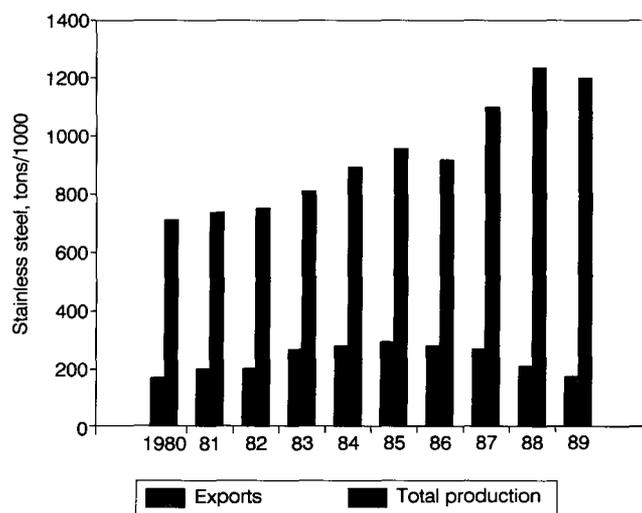


Figure 4—Japanese stainless-steel production and exports (after Kai<sup>34</sup>)

cal than by technological considerations. The alternative austenitic alloys generally contained more than 10 per cent nickel, or were based on the Fe–Al–Mn system. The corrosion resistance and mechanical properties of all the proposed substitutes are poor<sup>88</sup>, and there seems little likelihood at present that they will have any significant effect on the growth of the stainless-steel market.

### The Proportion of Ferritic Stainless Steel

The share of the total production held by ferritic stainless steels (as opposed to martensitic grades) peaked at about 40 per cent in the early 1950s, declined to about 20 per cent at the start of the 1960s, and has recovered very slightly since then to about 28 per cent. A slightly greater proportion of Japanese stainless steel used to be non-austenitic than in the USA, but it can be seen from Figure 5 that the situation is now reversed. The data for this graph were extracted from several sources, including the current and previous editions of *Metal Statistics*<sup>17</sup> and *World Stainless Steel Statistics*<sup>44</sup>. The change is the result of a great increase in the production of the 12 per cent Cr grades in the USA. There is usually some confusion in these figures because some sources refer only to ferritic stainless steels, and others to all non-austenitic (or 'nickel-free') stainless steels. The difference between the two figures is due to the production of martensitic grades, as well as of non-standard, unlisted ferritic grades.

As shown by Table IV, France exports a considerable proportion of its stainless steel as ferritics; indeed, it is said that about 60 per cent of all French production is ferritic<sup>89</sup>. On the other hand, developing nations appear to concentrate on austenitic grades; for example, South Korea's 365 kt of stainless steel manufactured in 1990 was only 7 per cent ferritic and 5 per cent martensitic<sup>90</sup>.

The data available indicate that ferritic stainless steels are not generally considered (France excepted) by the fabrication industry to be an alternative to the 300-series. If they had been, the production of ferritic stainless steels would have increased significantly during the more recent nickel-price excursions<sup>91</sup>. This has not happened, and the effect of these price excursions seems to be mostly to suppress the demand for austenitic stainless steel.

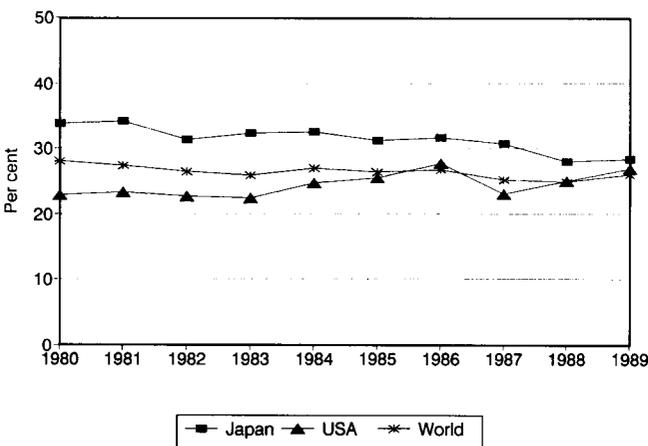


Figure 5—Proportion of non-austenitic stainless steel in Japan, the USA, and the world

### Changes in Usage Patterns

Conditions within the ferritic steels themselves have been anything but static. Figure 6 shows the proportion of non-austenitic stainless steels manufactured in the USA since 1960, as well as the share of the total held by the 12 per cent chromium ferritic stainless steels, the 17 per cent chromium ferritic stainless steels, and the ferritic stainless steels overall. Data for this figure were obtained from various editions of *Metal Statistics*<sup>17</sup>. While the proportion of non-austenitic stainless steel has remained approximately constant since 1960, the proportion of *standard* ferritic stainless steels has risen from a low of about 10 per cent to a high of about 22 per cent. However, the 17 per cent chromium grades have lost a share of the market in the USA, but their share has been mostly made up by the large increase in the production of 12 per cent chromium grades.

However, this is not a case of 12 per cent chromium grades replacing the 17 per cent chromium grades. The former had been used only for some parts of motor-vehicle exhaust systems in the USA up to 1970. In that year, the USA passed the Federal Clean Air Act, which required the introduction of catalytic converters. These are relatively high-priced components, and type 409 was used in order to provide a long life at the converter's high operating temperatures. Type 430 had, however, been popular for automobile trim (as in beading along the edges of windows and doors, and in bumpers/fenders), and had its heyday in the 1950s and 1960s during the period when it was fashionable for American cars to be decorated with lots of 'chrome'. This fashion is now in considerable decline worldwide, and the latest luxury cars have virtually no exterior trim.

The first 12 per cent chromium automobile muffler (silencer) was apparently manufactured in 1960 for a demonstration Ford Thunderbird<sup>69</sup>. The AISI began to report type 409 as a separate production grade only in 1977, so that type 409 production before that time is reported in the 'all other' category. This category reported no production immediately after type 409 was placed in its own category, indicating strongly that it was, at that time, mostly materials of 409 composition. Accordingly, the statistical trends reported here have been made on the assumption that 'all other' was type 409 from 1968 to 1976. The increased share

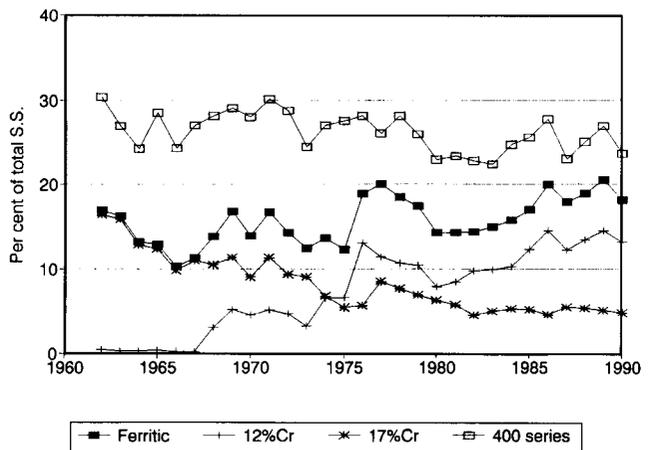
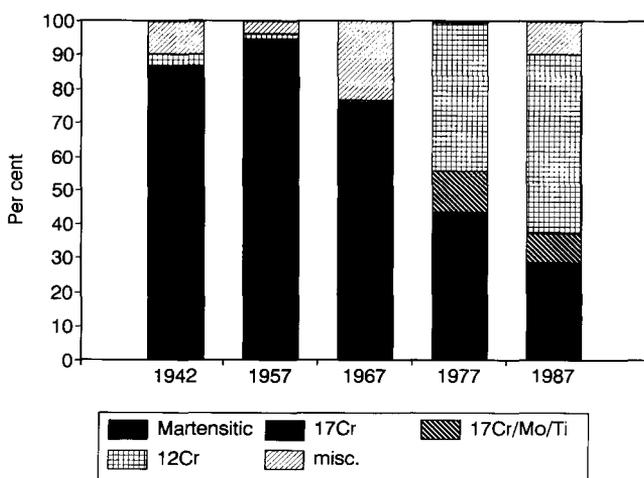


Figure 6—Changes in the usage of non-austenitic stainless steel in the USA from 1960 to the present

of the non-austenitic stainless steels captured by the standard ferritic grades was at the expense of the martensitic stainless steels. This trend is seen more clearly when examined over a longer time span. Figure 7 shows the changes in proportion of the non-austenitic alloys manufactured in the USA in the years 1942, 1957, 1967, 1977, and 1987. The post-war surge in the production of the 17 per cent chromium ferritics can be deduced from a comparison of the columns for 1942 and 1957, but the market share of the 17 per cent chromium steels declined after that. In particular, the usage of standard type 430 has been reduced, with the more highly alloyed variations such as types 434 and 436 taking nearly as much of the market as type 430 itself. The increase in usage of the 12 per cent chromium steels after 1970 is also evident.

As far as the overall trends in usage are concerned, the most noticeable development in the past 20 years has been a resurgence in the use of ferritics in motor vehicles. Although their use in trim seems unlikely to regain the 1950s' prominence, their use in exhaust systems has grown rapidly. In particular, type 409, or hot-dipped aluminium-coated type 409, has virtually displaced the use of aluminized mild steel in mufflers (silencers) in Japan and the United States<sup>34</sup>. (However, this is not yet true of South Africa and other developing countries.) Type 409 is now the second-most popular grade of stainless steel as a result. The remarkable rise in use of type 409 will continue. Type 409 exhaust systems are becoming the norm in Europe and Japan<sup>67</sup>. Legislation in the European Community will require that all new cars in Western Europe carry catalytic converters by 1993, and about half of these will be in ferritic stainless-steel containers. This is expected to increase the European market for ferritic stainless steels from 80 kt (1990) to more than 250 kt by the end of the decade<sup>92</sup>. The Japanese market for ferritic stainless steel for automobile exhausts is said to be already about 300 kt per annum<sup>92</sup>.

The 12 per cent chromium alloys are still susceptible to some localized corrosion in exhaust-gas condensates<sup>58</sup>, and there may be some competition here in future from the 17 per cent chromium alloys<sup>34,60</sup>. Usage of the 12 per cent chromium alloys has spread to exhaust manifolds<sup>57,93</sup>,



**Figure 7—Breakdown of the non-austenitic stainless steels manufactured in the USA for the years 1942, 1957, 1967, 1977, and 1987**

although it is said<sup>34,69</sup> that US and Japanese manufacturers are now more interested in 17 per cent chromium manifolds as a substitute for cast iron. (Of course, austenitic or even duplex manifolds are also possible substitutes for cast iron on account of their higher strength-to-mass ratio and better oxidation resistance.) The widespread use of ferritics for exhaust manifolds, if widely implemented, would make quite an impression on the industry. Proprietary grades developed especially for motor-vehicle manifolds include Allegheny's type 439 and type 441<sup>69</sup>.

Although catalytic converters are not yet required for South African automobiles, there are now several companies in this country either engaged in, or planning to engage in, the production of automobile catalytic systems for export. The consumption of type 409 for this application alone is expected to amount to over 2 kt in 1993, but it can be expected that a market for several kilotonnes per annum will eventually be created.

A new application of heat-resisting ferritics is as a catalyst support in automobile catalytic converters. Ceramic supports are currently used in most cars with catalysts. (Porsche is a notable exception in the USA, and Porsche and some other high-performance vehicles already use a stainless-steel substrate<sup>93</sup>.) However, 50 µm foil in the alloys consisting of Fe-20%Cr-5%Al + REM (rare-earth metal) offers notable advantages, and it appears that this will become the norm for catalyst substrates in future<sup>34,60,78</sup>. In particular, the stainless-steel substrates are less sensitive to vibration and shock, and they not only heat up faster but are also less affected by thermal cycling. Interest in this topic is keen at the moment, as attested to by patents registered from time to time, for example by VDM in Germany<sup>94</sup>. While alloys to which yttrium has been added are superior, those containing lanthanum and cerium are cheaper<sup>95,96</sup>. Allegheny-Ludlum, Kawasaki Steel, and VDM Nickel-Technologie are among the companies that already manufacture strip or foil for auto-catalyst substrates<sup>78,95,96</sup>.

Overall, an increased consumption of stainless steel in motor vehicles seems certain. For example, although the mass of an average US automobile declined from 1533 kg to 1273 kg between 1979 and 1991, the amount of stainless steel in it rose from 12 to 17 kg over the same period<sup>97</sup>. This is, however, still less than the 20 kg used in the mid-1950s<sup>25</sup>! It has been predicted that the use of stainless steels in the average US motor car will increase further to 45 kg in 1995<sup>93</sup>. Much of this increase will be in the form of ferritic stainless steels<sup>60</sup>.

Niche applications for specially tailored grades continue to emerge. For example, hubs of 'stiffy' diskettes, mentioned earlier, must be magnetic, resistant to corrosion, of high strength, and easy to form. Nisshin Steel in Japan now manufactures 50 t per month of a 17 per cent chromium ferrite-martensite grade developed for this purpose<sup>98</sup>. A danger of niche applications is that the material can be displaced by a single technological development. Type 409 is especially vulnerable in this regard, but the principle applies to other ferritics as well. For example, AL29-4C has found a niche in heat exchangers for home furnaces, but could be displaced by recent German attempts to commercialize a ceramic unit for the same application<sup>99</sup>.

The experience with type 409 indicates that a single mass-production niche can have a large effect on the market. There are some other future possibilities for such develop-

ments, and several are, or have been, under consideration. Thus, although 12 per cent chromium steels have proved to be unsuitable for municipal water-reticulation schemes<sup>100</sup>, they would give excellent performance as reinforcing bar in concrete structures subjected to corrosive conditions<sup>101</sup>. A successful implementation in, for example, road bridges in the USA and Europe, would have marked market implications.

### Impact of Novel Processing Technologies

The introduction of the AOD process provided a cheap method of reducing the interstitial content of ferritics. Metallurgical thinking on the subject of ferritics has consequently undergone a paradigm change, and there are now a host of alloys available that were previously inconceivable, even in the 1960s.

Another change has involved annealing practice. Ferritic stainless steels were previously always batch-annealed (or 'box-annealed'), but there has been an increasing tendency since 1985 to use a continuous annealing process. The change has not been painless, and the new process has brought its own share of problems, such as a greater tendency towards 'gold dusting' and roping. New variations of the basic type 17 per cent chromium alloy have now been developed in order to cope with these.

Other processing technologies may also affect the future production and usage of the ferritics. For example, several manufacturers have commissioned pilot or semi-commercial thin-strip casting plants<sup>82,102</sup>. Allegheny-Ludlum Corporation have made no secret of their hopes for their 'Coilcast' facility, which is currently being built in collaboration with Voest-Alpine<sup>102</sup>. The existing unit at Allegheny can apparently cast stainless steel directly to a strip 700 mm wide and 1 mm thick in amounts of up to 4.5 t at a time<sup>47</sup>, but the new facility (to be operational in mid-1993) will apparently cast 18 t coils of up to 1200 mm in width and down to 3 mm in thickness<sup>102</sup>. This is similar in scale to the more conventional production technologies. Krupp Stahl and VDM operate experimental thin-strip casters in Germany, and these can cast a 3 t coil of 700 mm width at 30 m/s<sup>103</sup>. Nippon Steel have a similar unit<sup>103</sup> as well as, with Mitsubishi Heavy Industries, a caster that can reportedly produce 9 t coils of strip with a width of up to 800 mm<sup>104</sup>. Other manufacturers such as Thyssen Stahl<sup>103</sup> operate smaller pilot-scale installations. Some further details are available in a paper by Ueda<sup>105</sup>. These and other installations are expected to eventually cast usable sheet and strip directly, and it is hoped that, when scaled up, they will reduce operational and capital costs by about 75 per cent<sup>93</sup>. An examination of the available literature on these units, taken in combination with what can be gleaned from plant visits and discussions, indicates that attention is focused at present on the casting of austenitic grades such as type 304. However, attention may ultimately turn to ferritics as well. As an example, a ferritic product that has been mentioned as a future possibility is the Fe-20Cr-5Al material required for the new stainless-steel substrates for exhaust catalysts.

While commercial thin-strip casting may lie some years in the future, Nucor has already produced a trial quantity of type 409 plate using its thin-slab caster. This equipment is normally used at Nucor to manufacture low-alloy steels, and it is not yet clear whether the stainless material will find favour with all customers<sup>106</sup>.

As for electron-beam refining and other 'cold hearth' technologies, it seems that their use in the manufacture of stainless-steel in the 1970s was premature. The extremely high energy consumption and capital costs of these technologies have apparently rendered them unsuitable for the production of ferritic stainless steel, although they continue to find favour in the production of metals such as titanium, refractory metals, and nickel-based super-alloys for aerospace applications<sup>107</sup>. Another technology that was previously predicted for stainless steels was that of rapid solidification. However, this has not yet been of any commercial significance. Vacuum-induction melting remains in use as a means of producing ultra-pure ferritic alloys such as E-Brite and AL29-4-2, but these alloys are expensive as a result.

There is continued interest around the world in the direct manufacture of stainless steel<sup>34,108,109</sup>. In this concept, chromite ore is combined with scrap iron and other raw materials to produce stainless steel. It is interesting to note that the direct reduction of stainless steel was discussed in this *Journal* (under its former name) as early as 1936<sup>110</sup>. While companies such as Kawasaki Steel and NKK in Japan are known to be involved in some development work using LD converters, it is said that most of their chromium is still added as ferrochromium.

The weldability of ferritic alloys is reasonable to poor. While construction and many fabrications are performed using techniques such as TIG or MIG, and tube-mills often employ high-frequency resistance welding, it is now also possible to use laser welding equipment in selected mass-production lines. The manufacture of welded tubing, for example, seems to be one such industry, and Sumitomo Metals now apparently manufactures ferritic stainless-steel tubing with a 6 kW carbon dioxide laser<sup>111</sup>, while Nippon Steel weld type 444 tubing using a 5 kW carbon dioxide laser at their Hikari Works<sup>112</sup>. It is possible that laser welding will spread further through the industry, and this would have the benefit of improving the corrosion resistance and mechanical reliability of welded tube. Super-ferritic tube in alloys such as AL29-4C might benefit from the use of laser welding, since it has been said that the high cost of welded tube reduces much of the price advantage over the super-austenitics.

### Prognosis for Ferritic Stainless Steels

The ferritics are still perceived by the market as materials with their own particular market niches and applications. For example, the consumption of ferritic stainless steel during the recent increase in the nickel price scarcely altered, although that of the austenitic grades decreased. This is apparently a reflection of the fact that the austenitic grades find their major application in capital goods, whereas the ferritics are used more in consumer goods. This, according to Fassinotti<sup>91</sup>, explains why the production of austenitic grades varies more severely with economic climate than that of the ferritic grades.

The future of the ferritics is naturally tied up with that of stainless steels in general. It has been indicated that the trend in the growth of stainless-steel production shows no sign of levelling off, and the alloys have by no means reached the 'mature' portion of the development cycle<sup>113</sup>. The potential for increased stainless-steel production may also be deduced from Table V, which compares the con-

sumption of stainless steel in various countries. Opportunities for increased stainless-steel utilization abound, even in the developed countries. More than 50 per cent of the USA's cooking ware is still made of aluminium<sup>114</sup>, for example, despite the fact that stainless steel, including ferritic stainless steel, performs better.

The evidence suggests that the market for ferritics will be maintained, driven by economics (lifetime costing), improved manufacturing technology, and the future development of the Eastern European, Pacific Rim, and South American regions. The 17 per cent chromium grades may never replace the austenitics, but will continue, nevertheless, to hold their own share of the market. The production of the 12 per cent chromium alloys will continue to grow strongly, but an extremely rapid expansion of these products, especially the 3CR12-type alloys, is possible if they are produced by a carbon-steel producer. In that case, the resulting economies of scale would ensure that they captured a large slice of the steel, as opposed to the stainless-steel market, and significant growth would be possible. Consumption of all the alloys in thin-sheet form can be expected to grow. The volatility of the austenitic grades and the large amount of competition in the austenitic market suggest that it would be prudent for the more advanced manufacturers of stainless steel to maintain a share of the ferritic market.

### CONCLUSIONS

- (1) Ferritic stainless steels hold approximately 25 per cent of the total stainless-steel market, and this fraction has been increasing slowly since 1960.
- (2) The use of grades containing 12 per cent chromium has increased rapidly, especially in automobile catalytic converters, and should continue to do so for several years.
- (3) Consumption of the plain 17 per cent chromium grade has declined, but this has been partially compensated for by an increase in the consumption of stabilized and molybdenum-alloyed 17 per cent chromium materials.
- (4) Production of the super-ferritic grades remains small, and the most widely used material in this category seems to be Allegheny-Ludlum's AL29-4C.
- (5) The onset of stainless-steel substrates for catalytic converters should have significant market implications for stainless-steel producers.
- (6) It is too early to say whether thin-strip casting and direct stainless-steel manufacture will have much effect on ferritic (as opposed to austenitic) stainless steels.

**Table V**

Consumption of stainless steel in various countries<sup>115,116</sup>

Country	Consumption kg per capita
Japan	18
Sweden	18
Germany	12
USA	6
UK	5
Czechoslovakia	5
Former USSR	2.6
Peoples Republic of China	0.2

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## Metallurgical industry to play greater role in education\*

Leading representatives of the metallurgical industry have shown their commitment to education by agreeing to join an advisory board set up by the Department of Metallurgy and Materials Engineering at the University of the Witwatersrand. The board has been established to improve communication and collaboration with industry on all aspects of the Department's teaching and research work.

The Engineering Faculty is represented on the board by Professor Hurman Eric, Head of the Department of Metallurgy and Materials Engineering, and Professor Roy Adams, Dean of the Engineering Faculty. Senior staff members in the Department will also participate in board proceedings.

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The other members of the board are Dr Alan Haines, Chief Executive; Minerals Technology at Genmin (Chairman); Richard Beck, Chief Consulting Metallurgist at Gold Fields of South Africa; David Deuchar, Deputy Technical Director at Anglo American Corporation; Ludi Nel, Group Manager: Research and Development at Iscor; and Dr Nic Barcza, Vice President of Mintek.

The advisory board will meet twice annually. 'Through this medium, the Department of Metallurgy and Materials Engineering will keep industry informed on its activities, and the members of the board will in turn guide us on how best to tailor our teaching and research to the requirements of the industry', says Professor Eric.