Ferritic Stainless Steel
Metallurgy and corrosion – properties and possibilities

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A few years ago, the nickel-free, ferritic, stainless steel was regarded as a bit of a joke. A poor corrosion resistance combined with poor weldability and poor mechanical properties was not enough to compensate for the low price, and ferritic, stainless steels were only considered useful for making very simple, not-critical parts, such as cheap tea spoons.

However, the unpredictable fluctuations of the nickel price during the last few years have changed this pattern markedly. From 2006 to the middle of 2007, the nickel price increased from 15,000 to 55,000 $/ton, and shortly thereafter, it dropped steeply to 30-35,000 and further on to a minimum of 10,000 $/ton. In the time of writing (July 2012), the price is around 18,000 $/ton.

Due to its very high and fluctuating price, nickel is the price determining element in normal, austenitic stainless steel, and most of the alloy surcharge for an EN 1.4301 steel (= AISI 304) happens to be nickel ("Stainless steel and corrosion", Chapter 4.1). For higher alloyed steel types, this pattern is even more evident. In short, nickel is a pricey and economically unstable element, and a lot could be gained if nickel was by-passed as alloying element. What if one could maintain the corrosion resistance without the nickel?

Stainless Steel With or Without Nickel
("Stainless steel and corrosion", Chapter 3.1 + 4.1)

Fortunately, that scenario is not entirely science-fiction. In most cases, the corrosion resistance depends on molybdenum (Mo) or chromium (Cr), while the main purpose of nickel (Ni) in stainless steel is to stabilize the ductile austenitic phase. Ni owes its presence to mechanical reasons rather than the corrosion resistance, and by cutting down the Ni content, one gets a stainless steel possessing great corrosion resistance at a much lower cost. In short, that is the "secret" of the ferritic stainless steels": High Cr, perhaps Mo and little or none Ni.
<table>
<thead>
<tr>
<th>EN 1.-</th>
<th>Structure</th>
<th>% C</th>
<th>% Cr</th>
<th>% Ni</th>
<th>% Mo</th>
<th>Others</th>
<th>AISI (UNS)</th>
<th>SS</th>
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<tbody>
<tr>
<td>4003</td>
<td>Ferritic</td>
<td>≤ 0,08</td>
<td>10,5-12,5</td>
<td>0,30-1,00</td>
<td>-</td>
<td>N ≤ 0,030</td>
<td>410S</td>
<td>-</td>
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<tr>
<td>4016</td>
<td>Ferritic</td>
<td>≤ 0,03</td>
<td>16,0-18,0</td>
<td>-</td>
<td>-</td>
<td></td>
<td>430</td>
<td>2320</td>
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<tr>
<td>4509</td>
<td>Ferritic</td>
<td>≤ 0,03</td>
<td>17,5-18,5</td>
<td>-</td>
<td>-</td>
<td>Ti 0,10-0,60; Nb 3x(C+N)+0,30-1,00</td>
<td>(UNS 43932)</td>
<td>-</td>
</tr>
<tr>
<td>4512</td>
<td>Ferritic</td>
<td>≤ 0,03</td>
<td>10,5-12,5</td>
<td>-</td>
<td>-</td>
<td>Ti 6x(C+N)–0,65</td>
<td>409</td>
<td>-</td>
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<tr>
<td>4521</td>
<td>Ferritic</td>
<td>≤ 0,025</td>
<td>17,0-20,0</td>
<td>-</td>
<td>1,80-2,50</td>
<td>N ≤ 0,030; Ti 4(C+N)+0,15–0,80</td>
<td>444</td>
<td>2326</td>
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<tr>
<td>4301</td>
<td>Austenitic</td>
<td>≤ 0,07</td>
<td>17,5-19,5</td>
<td>8,00-10,5</td>
<td>-</td>
<td>N ≤ 0,11</td>
<td>304</td>
<td>2333</td>
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<tr>
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<td>Austenitic</td>
<td>≤ 0,030</td>
<td>18,0-20,0</td>
<td>10,0-12,0</td>
<td>-</td>
<td>N ≤ 0,11</td>
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<td>2352</td>
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<tr>
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<td>≤ 0,030</td>
<td>17,5-19,5</td>
<td>8,00-10,5</td>
<td>-</td>
<td>N ≤ 0,11</td>
<td>304L</td>
<td>-</td>
</tr>
<tr>
<td>4401</td>
<td>Austenitic</td>
<td>≤ 0,07</td>
<td>16,5-18,5</td>
<td>10,0-13,0</td>
<td>2,00-2,50</td>
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<tr>
<td>4404</td>
<td>Austenitic</td>
<td>≤ 0,030</td>
<td>16,5-18,5</td>
<td>10,0-13,0</td>
<td>2,00-2,50</td>
<td>N ≤ 0,11</td>
<td>316L</td>
<td>2348</td>
</tr>
</tbody>
</table>

The alloy composition of the most common ferritic steel types compared to the most common austenitic ones. Please note that the Ni content of the five ferrites is close to zero, while the austenites contain at least 8 % Ni.

Pitting corrosion is one of the most commonly observed types of corrosion on stainless steel. The resistance against initiation of pitting increases a lot with increasing Cr, Mo and N in the steel. This pit is from the bottom of a water tank made of 4301.
Pitting Corrosion ("Stainless steel and corrosion", Chapter 6.2)

In most media, local corrosion resistance is dependent upon the contents of Cr and Mo, and while the ferrites of the past usually contained around 12 % Cr and no Mo at all, the ferrites of today are much higher alloyed and the corrosion resistance correspondingly higher. As a result, the ferrites of today are fully capable of competing with the traditional austenites (both "normal" stainless and "acid resistant") with regards to corrosion resistance.

With respect to pitting corrosion, one of the most destructive types of corrosion for stainless steel, the corrosion resistance, is determined by the Pitting Resistance Equivalent (PREN; "Stainless steel and corrosion", Chapter 6.2.6):

\[
\text{PREN} = \%\text{Cr} + 3.3 \times \%\text{Mo} + 16 \times \%\text{N}
\]

Practice has shown that two stainless steel grades with equal PREN numbers posses roughly the same resistance towards initiation of pitting corrosion, and, using the table above, 4301 (5 % Cr, 0 % Mo, 0 % N) has a PREN of 17.5. The ferritic 4509 (5 % Cr, 0 % Mo, 0 % N) has exactly the same PREN, which means that the two types 4301 and 4509 can be expected to perform equally well towards pitting corrosion. In 2008-09, this was confirmed by experiments conducted at the Technical University of Denmark (DTU).

Similarly, the ferritic 4521 (PREN 22.9) can be expected to perform equal to the austenitic 4404 (AISI 316L, PREN 23.1), and, not surprisingly, this was also confirmed by the Technical University of Denmark (DTU). Consequently, for both groups of steel (4301 / 4404), it’s possible to substitute the traditional austenite with the parallel ferrite and maintain the resistance towards pitting corrosion.

The above considerations apply for the initiation of pitting corrosion. Should the corrosion, against all precautions, start, Ni is a beneficial element, and corrosion tends to propagate faster in a Ni-free, ferritic steel than an austenitic steel type. However, this is just an additional argument for choosing stainless steel with care. Quite simply, one has to choose a stainless steel where the corrosion will never initiate. Just choose a steel type with a sufficiently high PREN.
Stress Corrosion Cracking ("Stainless steel and corrosion", Chapter 6.4)

Stress Corrosion Cracking (SCC) is a type of corrosion giving rise to cracks due to a combination of mechanical stress and exposure to certain corrosive media, and it is normally regarded as the most destructive type of corrosion. SCC specifically attacks the austenitic steel types, and in particular the 4301 and 4401/04 groups are vulnerable, particularly in chloride containing media.

As a guideline, SCC is a risk for 4301 at temperatures above only 50-60 °C while the “acid resistant” 4401 class lasts until 100-110 °C. This actually makes the austenitic stainless steel inadequate for a number of technical appliances ranging from reactors and distillation columns to heat exchangers, evaporators and drying equipment.

In such conditions, the ferritic stainless steels possess a tremendous advantage, as chloride induced SCC specifically attacks the austenites – not the ferrites. Consequently, the ferritic types can be used in a lot of applications where the austenitic 4301 and 4401 groups will suffer from SCC.

Chloride-induced, trans-granular SCC in baking oven made of 4301. By using ferritic, stainless steel instead of the traditional austenites, such disasters can be largely avoided – and money can be saved in the process.
General Corrosion ("Stainless steel and corrosion", Chapter 6.1)

General corrosion is a type of corrosion, which takes place in either very strong acids or very strong alkalines. In these media, the austenites are normally slightly more resistant than the ferritic alternatives, so for handling extreme pH media it is safer to stick to the traditional austenites.

Mechanical Properties ("Stainless steel and corrosion", Chapter 3.1 + 3.3)

Mechanically, the differences in between the austenitic and ferritic types are more evident. Measured by HRC, Rp0.2 or Rm, most ferrites equal the austenitic steel types. However, ferritics possess slightly higher yield strength (Rp0.2) and slightly lower tensile strength (Rm), although the difference is not great. By experience, the slightly lower Rm, means that cutting and drilling is easier in the ferrites than the similar austenites.

Sketches of stress-strain curves for five different groups of stainless steel. The martensites are generally the hardest, the ferrites and austenites the softest. Please note that the austenite curve stretches much further to the right (right to the dotted circle) than the other ones. This is due to the very high "elongation" of the austenites, an important property during deep drawing or stretch forming.
As a rule, the mechanical properties of stainless ferrites are comparable to high strength carbon steels, and a major difference in between the stainless ferrites and the austenites is the elongation, i.e. the possible deformation until breakage. For the austenitic 4301 or 4401 groups, the minimum elongation is around 40-45 % (and often > 50 %) meaning that these steel types may be stretched and deformed very much, before they break.

In contrast, the ferritic types posses a minimum elongation of 18-20 % which means that they are much less useful in the case of mechanical deformation, such as pure stretch forming. On the positive side, ferritics are more suitable for deep drawing, and alloys like 4016 are widely used in i.e. England and Italy for catering purposes. However, do not expect to be able to make a very complicated double kitchen sink from a ferritic stainless steel. In such a case, the traditional, chewing-gum-like 4301 is better.

Another notable difference is the mechanical properties at very low and very high temperatures, notch toughness (AV) and creep, respectively. At very low temperatures, the ferrites may become brittle. This effect is seen as a sudden decrease in notch toughness ("Stainless steel and corrosion", Chapter 3.3.3), however, for most applications down to, say, ±20 °C, problems are rarely observed. The risk of brittleness is influenced by the thickness of the sheets, possible welds and the size/direction of the forces, plus whether the forces are static or dynamic.

At very high temperatures (7-800 °C or more), the ferrites are worse at maintaining their mechanical strength. On the other hand, the ferrites are not bad at all with regards to scaling and high-temperature corrosion. The reason for this is the thermal elongation of the oxide layer which is closer to that of the ferrites than the austenites. The risk of cracks in the oxide layer is therefore smaller for the ferrites than for the austenites which possess a thermal elongation which is 60 % higher. In general, the ferrites are better at cyclic temperature changes, while the austenites are superior at constant temperature.

Finally, at long-term exposure to temperatures in between approx. 400 and 550 °C, the ferrites may suffer from "475° brittleness". Similar phenomena are known from duplex steel grades in the same temperature range, and, as a whole, ferrites are therefore a bit less adequate at extreme temperatures than the traditional austenites, although we recommend that each case is evaluated separately.
Magnetically, the ferritic stainless steels resemble mild steel. All ferritic stainless steels are strongly magnetic while the nickel containing austenites are either non-magnetic or, in the case of cold working, slightly magnetic.

Also with respect to thermal properties, the ferritic stainless steels are closer to the carbon steels than the austenites. The thermal elongation of the ferrites is about 30-35 % lower than that of the austenitic types thereby reducing the risk of deformation during welding or subsequent operation. This is particularly important if the equipment is to be made from both stainless steel and mild steel, as the thermal tension in between the mild steel, and the austenitic steel is larger than in between the mild steel and the ferrites.

With regard to wear, stainless steel against stainless steel has a nasty habit of adhesive wear. This risk may be reduced by choosing two different types of stainless steel (i.e. with two different grain structures). A ferrite against an austenite is a better wear combination than austenite against austenite, although still inferior to well-known combinations as, say, bronze against stainless steel.
Welding of Ferritic Stainless Steel ("Stainless steel and corrosion", Chapter 10.1.11)

In contrast to previous teachings, it is perfectly possible to weld ferritic stainless steel, although they are less foolproof than the austenites. The lack of Ni increases the risk of grain growth and the formation of unwanted phases as a result of the heating. Such effects may cause brittleness and reduced corrosion resistance, and therefore, one has to be more careful when welding the ferrites as compared with the austenites, in particular with regard to the heat input. The thicker the steel, the more important it is to keep the heat input low in order to avoid unwanted side effects.

This said, the present-day ferritic steels are much easier to weld than the past generations of steel. This is due to the fact that the higher alloyed ferrites are “stabilized” by adding titanium (Ti) and/or niobium (Nb), both of which stabilize against grain growth during welding. It is essential to employ stabilizers in sufficient quantities, e.g. Ti and/or Nb, both strong carbide formers and blocking grain growth. Thereby, chromium carbides are unable to form during the thermal cycles of welding.

Unstabilized ferritic grades, such as 4016, can therefore be susceptible to intergranular corrosion in the HAZ, due to chromium carbide formation. In addition, brittle phases may be formed adjacent to the weld seam, and for these reasons, the non-stabilized types, such as 4003 and 4016, are not recommended for welding without a subsequent heat treatment ("Stainless steel and corrosion", Chapter 10.1.11).

A sad case of welding 4016 (2 mm). 4016 is not stabilized and may form brittle phases in the weld seam or the HAZ which, in turn, may cause fracture.
4509, 4521 and 4526 and the low-alloyed 4512 (10.5-12.5 Cr, 0 Mo) can be welded (TIG or MIG) by using filler metal type 4430 (20 Cr, 2.5-3.0 Mo) or similar types. In the case of 4512 and 4509, the lower alloyed “308L” (18-21 Cr, 10-12 Ni, 0 Mo) may be used, although the 4430 provides a better corrosion resistance.

Up to 1-1½ mm thickness, welding can be done with no filler metal at all. No particular problems should occur when welding ferrites (4509, 4521) and austenites (4301, 4401 groups) together. Recommended filler metal for the 4301/4509 is 309L (22-24 Cr, 12-15 Ni, 0 Mo), whereas the molybdenum alloyed 4430 is preferred when welding the 4404/4521.

An important difference in between the ferrites and the austenites is the use of purge gas. For TIG, welding of ferritic stainless steel, argon (Ar) or argon-helium (< 20 % He) is recommended, while former gas (N2 + H2) should not be used due to the risk of grain growth and brittleness. For MIG welding, Ar + 2 % CO2 is recommended; higher content of CO2 may give rise to carbide formation (sensitization).

A short summary on welding ferritic grades is given below:

- Filler metal: AISI 308 (18-21 Cr, 10-12 Ni, 0 Mo = slightly higher than 304L) is normal. Alternatively, acid resistant AISI 316LSi/EN 1.4430 (20 Cr, 2.5-3.0 Mo = higher 316L).
- Low heat input recommended due to the risk of grain growth (temp. above 1150 ºC).
- 4509 (and 4521) may be welded together with the austenitic grades 4301/4401. Filler metal: 316LSi/4430 – or AISI 309L (22-24 Cr, 12-15 Ni, 0 Mo) for 4509/4301.
- N2 and H2 must be avoided in the purge gas due to the risk of brittle, non-ductile phases. Instead, pure argon (Ar) is recommended.
- Max 2% CO2 to avoid sensitization (carbide formation).

With regards to the risk of corrosion implied by welding two different grades together, the rule of the thumb says that as long as both steel grades stay passive, the risk of galvanic coupling in between the two parts is minimal. The environment should therefore be adjusted to fit the “weakest” part.

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Chemical Surface Treatment ("Stainless steel and corrosion", Chapter 12)

In contrast to the information given by the literature in the last millennium (before 2000!), ferritic stainless steels can be subject to a chemical surface treatment. The higher alloyed ones, such as 4509, 4521 and 4526, can be pickled, passivated and even electro polished, although it is recommended to be more careful than with the austenitic types. The reason for this extra care is the fact that ferrites are generally more sensitive towards very strong acids than are the parallel austenites.

When performing a pickling process, one should take care that the ferrites are etched rather quickly when exposed to strong acids, and one should make sure that a relatively mild pickle is used. This is just one of a number of reasons why the heat tinting should be kept at a low level during the welding of ferritic steel types ("Stainless steel and corrosion", Chapter 12.1.1 & 12.1.5).

Electro polishing of ferritic stainless steels is possible as well, however, in these extreme acids (50 to 70 % sulfuric and phosphoric acids at temperatures around 60 °C), the ferrites are more sensitive than the austenites and it’s hard to obtain the same mirror-bright surface. If a mirror-like surface is required, the austenites are better.

Passivation may be carried out with a pure nitric acid. The lowest alloyed ferrites, such as 4003 and 4512, can neither be pickled nor electro polished, and passivation should only be done with a di-chromate inhibited nitric acid.
Food Appliances and Nickel Problems ("Stainless steel and corrosion", Chapter 6.9)

Without any problems, ferritic stainless steel may be used in most applications where the austenitic steels are, at present, the state of the art. This includes the food industry, and the ferritic 4016 is widely used for catering purposes in England and Italy, and the higher alloyed 4509, 4521 and 4526 may easily be used for more demanding purposes within the same business.

A particular advantage with the ferritic steel types is the absence of nickel and with a Ni content of zero, the risk of Ni leaking into the media is equally zero. In contrast, the 4301 and 4404 contain 8 and 10 % Ni, respectively, which (mostly by corrosion) may be leaked into the media. At present, there are no rules and regulations with regard to the use of nickel free steel types in the food industry. However, should this ever be the case, it does not hurt to be ahead of time.
Supply, Dimensions and Prices (“Stainless steel and corrosion”, Chapter 9)

The most important ferritic stainless steels are the 4509, the “acid resistant” 4521 and the very popular 4016. They are all available as sheets (various surfaces) and pipes; however, in all cases, the thickness hardly ever exceeds 3 mm, apart from hot-rolled sheets. In any case, the supply time for any ferritic stainless steel may be longer than for the similar austenites, and despite the increasing production and demand it will take a few years until the supply of the ferrites exceeds that of the austenites.

The prices depend upon the steel type, the dimensions, and, of course, the fluctuations in the alloy surcharge. In particular, this is dependent upon the nickel content, for which reason the economical advantage of using the ferrites more or less follows the development in the nickel prices. The higher the nickel price, the larger the economical advantage by switching to ferrites.

An additional advantage is the price stability. The prices of the ferrites is not affected by the lability of the nickel price and it’s therefore less “risky” to stock large piles of ferrite than austenite. The risk of losses is much reduced and future planning is made a lot easier.
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Advantages, Disadvantages and Possible Applications

The ferrites are less ductile than the austenites (making cold forming a bit more complicated), and the welding process is somewhat more sensitive than that of the traditional austenites. In addition, the reduced supply is bound to have a negative effect, but the ferrites are nevertheless extremely useful. With regard to manufacturing and corrosion, a list of possible pros and cons are, among others, given below:

<table>
<thead>
<tr>
<th>Pros</th>
<th>Ulemper</th>
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<tbody>
<tr>
<td>Comparable local corrosion resistance (PREN4509 = PREN4301)</td>
<td>Lower pitting corrosion resistance when the corrosion has already begun</td>
</tr>
<tr>
<td>Excellent resistance towards SSC; much better than the austenites</td>
<td>Lower resistance towards general corrosion</td>
</tr>
<tr>
<td>Good corrosion resistance towards general and intergranular corrosion</td>
<td>Slightly higher risk of crevice corrosion; increased focus on design is necessary</td>
</tr>
<tr>
<td>Pickling, passivation and electro polishing possible</td>
<td>Welding parameters are more critical</td>
</tr>
<tr>
<td>No risk of Ni leakage to food</td>
<td>Low notch toughness for thicknesses above 3 mm</td>
</tr>
<tr>
<td>Low thermal expansion, approx. 2/3 of that of the austenites</td>
<td>Lower elongation = less suitable for pure stretch-forming</td>
</tr>
<tr>
<td>High thermal conductivity, approx. 50 % better than for the austenites</td>
<td>Reduced toughness at very low (cryogenic) temperatures</td>
</tr>
<tr>
<td>Less prone to spring-back during bending</td>
<td>Britteness at long-term exposure to temperatures around 475 °C</td>
</tr>
<tr>
<td>Slightly easier to cut / punch than the chewing gum-like austenites</td>
<td>Magnetic (sometimes a disadvantage)</td>
</tr>
<tr>
<td>Magnetic (sometimes an advantage)</td>
<td>Lower availability, in particular thick dimensions; better planning required</td>
</tr>
<tr>
<td>Lower and less volatile price</td>
<td></td>
</tr>
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</table>
All in all, the ferrites are expected to possess the greatest potential within the following fields:

- Thin sheets – preferably max. 2 mm
- Simple geometries
- Simple manufacturing with no complicated processes (bending, stretch forming or welding)
- Large material costs (large quantities = large savings!)
- Hot specimens with a risk of stress corrosion cracking

On a global scale, one of the major consumers of ferritic stainless steel is the automotive industry of Europe and the USA, however, also within building construction and the manufacturing of household equipment, mail boxes, signs, white goods and catering equipment, there is a large need for the comparatively cheap and quite corrosion resistant stainless steel alloys. In particular the high-alloyed, weldable ferrites (such as 4509, 4510 and 4521) are bound to replace a major part of the classic 4301 and 4401 grades. For applications where pitting corrosion is the determining factor, it is frequently possible to switch from austenite to ferrite without compromising the corrosion resistance.

Above water (cool conditions), pitting corrosion is the main problem, and in many cases, 4301 can be substituted with 4509 – and 4404 with 4521. Such substitutions are quite common in i.e. the catering business, however, it ought to be even more common, such as for lamps, signboards and furniture. Ferritic 4509 is the normal choice indoor, whereas 4521 is a potential winner for outdoor applications, where 4401 is too expensive, and where 4301 is not good enough.

One of the major advantages of ferritic stainless steel is observed at slightly elevated temperatures. Already at 60-70 ºC and above (for the 4301 class) and 100-110 ºC (for the acid resistant 4401 class), stress corrosion cracking becomes the dominant type of corrosion (RS&K, kapitel 6.4), however, unlike the traditional austenites, the ferrites are not particularly prone to such disasters. For that reason, ferrites are highly relevant for exhaust pipe systems, baking ovens and heat exchangers. In such conditions, the ferrites hold a significant advantage to the austenites and by substituting into ferrite, one obtains an increased corrosion resistance and a lower price. Not a bad combination!

A final remark should be said regarding the option of replacing hot-dip galvanized steel with ferrites stainless steel. The combination of a, at present, comparatively high price of the galvanized steel and a rather low price for the ferritic stainless steel has ensured that it’s sometimes possible to substitute the galvanized steel with a proper ferrite.

Jumping into the stainless world, one gets a steel which, pound by pound, is still a bit more expensive than the galvanized, however, one may save a bit on the weight and end up with a competitive product. It certainly doesn't harm that stainless steel looks incredibly nice. For indoor use, 4509 is often the standard grade, while 4521 is necessary for outdoor applications.

All references are with regards to “Stainless Steel and Corrosion” (Claus Qvist Jessen, Damstahl a/s, October 2011). The book can be ordered through www.damstahl.dk.