Stainless Steels Past, Present and Future

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The large and steadily growing family of stainless steels can offer unique combinations of corrosion resistance and properties such as high strength, low temperature toughness, creep strength and formability. Although small in tonnage compared to mild steels, they represent an economically important and steadily growing group of steels finding their way into an increasing number of applications. This review briefly summarises the history of stainless steel development and discusses selected weldability aspects. Examples from ESAB's long history of stainless steel welding are given and some future trends discussed.

Introduction

Iron is one of the most common and one of the most important metals in the earth's crust. It forms the basis of the most widely used group of metallic materials, irons and steels. The success of these metals is due to the fact that they can be manufactured relatively cheaply in large volumes and provide an extensive range of mechanical properties - from moderate strength levels with excellent ductility and toughness to very high strengths with adequate ductility.

Unfortunately, mild and low alloy steels are susceptible to corrosion and require protective coatings to reduce the rate of degradation. In many situations, galvanic protection or painting of a steel surface is impractical. In the United States, in 2000, it was estimated that corrosion costs industry and government agencies $276 billion/year [1]. The benefits of corrosion resistant chromium alloyed stainless steels can, therefore, be easily recognised.

The vast majority of the world's steel is carbon and alloy steel, with the more expensive stainless steels representing a small, but important niche. Of all steel produced, approximately 2% by weight are stainless steels. However, as illustrated in Figure 1, there has been a steady annual growth of about 5-8% for stainless steels [2]. With the ever-growing awareness of environmental issues, the need for easily recyclable materials and life cycle cost considerations, there is no reason to expect anything other than a continuing increase in the use of stainless steels.

"Stainlessness"

"Stainless" is a term coined, early in the development of these steels, for cutlery products. It was adopted as a generic name and, now, covers a wide range of steel types and grades for corrosion or oxidation resistant applications. The minimum chromium content of standard stainless steels is 10.5% [3]. Other alloying elements, particularly nickel, molybdenum and nitrogen, are added to modify their structure and enhance properties such as formability, strength and cryogenic toughness.

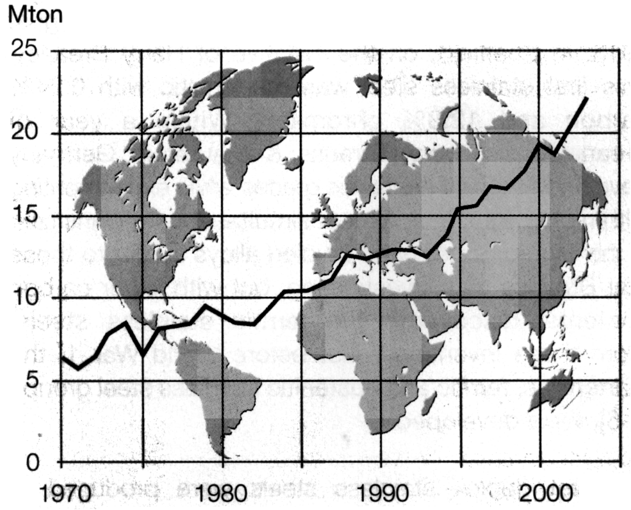

Figure 1. World production of stainless steels. (http://www.jernkontoret.se)

Stainless steels owe their corrosion resistance to the presence of a "passive", chromium-rich, oxide film that forms naturally on the surface. Although extremely thin, 1-5 nanometres (i.e. 1-5 x 10^{-9} m), and invisible, this protective film adheres firmly, and is chemically stable under conditions which provide sufficient oxygen to the surface. Furthermore, the protective oxide film is self-healing provided there is sufficient oxygen available. Therefore, even when the steel is scratched, dented or cut, oxygen from the air immediately combines with the chromium to reform the protective layer [4-5]. As an example, over a period of years, a stainless steel knife can literally be worn away by daily use and by being re-sharpened – but remains stainless.

However, stainless steels cannot be considered to be "indestructible". The passive state can be broken down under certain conditions and corrosion can result. This is why it is important to carefully select the appropriate grade for a particular application. Effects of welding and handling on corrosion resistance also have to be considered.

History

The history of stainless steels dates back almost as long as the history of the covered electrode - invented by the founder of ESAB during the first decade of the last century.

Stainless steel was discovered independently, around 1913, by researchers in Britain and Germany. The first true stainless steel was melted on the 13th August 1913, in Sheffield, on the initiative of Harry Brearley. This first stainless steel was martensitic with 0.24% carbon and 12.8% chromium. Within a year of Brearley's discovery, Strauss & Maurer in Germany developed the first austenitic grades while experimenting with nickel additions. Almost simultaneously, Dansitzen in the United States, who studied alloys similar to those that Brearley was investigating, but with lower carbon contents, discovered the ferritic stainless steels. From these inventions, just before World War 1, the martensitic, ferritic and austenitic stainless steel groups [4-5], were developed.

The first duplex stainless steels were produced in Sweden, around 1930, for applications in the paper industry. However, commercial production of precipitation hardening stainless grades did not take place until after World War 2. New grades with a better weight-to-strength ratio were then required for jet aircraft, which led to the development of the precipitation hardening grades such as 17:4 PH [6-7].

The basic metallurgy of the iron/chromium and iron/chromium/nickel systems was understood by about 1940 and by the 1950's stainless steels became standardised in specifications that have changed little since that time. As these standard grades became accepted, the emphasis changed to finding cheaper mass-production methods, and popularising the use of stainless steel. The next leap in stainless steel development was made possible by the development of the argon-oxygen decarburisation (AOD) process, in the late 1960's. This technique made it possible to produce much cleaner steels with a very low carbon level and well controlled nitrogen content. The introduction of continuous casting in stainless steel production, in the 1970's, has contributed to lower production costs and higher quality.

From the 1970's onwards, the addition of nitrogen and lowering of carbon content made it possible to develop the duplex stainless steels into readily weldable materials. The last two decades have seen the introduction of the "super" stainless steels. Superferritic grades with very low interstitial levels and high chromium and molybdenum contents have superior corrosion resistance compared to standard ferritic grades. However, although these steels have found certain applications, their success has been limited.

The highly alloyed superaustenitic and superduplex stainless steels, with excellent corrosion resistance and better fabricability and weldability than the ferritic steels, have found a more widespread use and are today important engineering alloys. Supermartensitic steel is the most recent contribution to the stainless family [8]. These steels are extremely low in carbon (typically <0.010%) and offer a combination of high strength, adequate corrosion resistance and weldability at a competitive price. Although the use, as is not uncommon with the introduction of new stainless steel grades, have been hampered by some unforeseen corrosion problems, this is still a very interesting material that can be expected to find increasing use in the future.

Welding

Development of new steels inevitably brings new problems in manufacturing and joining. This is particularly true for welding where the desired material properties, carefully produced by the steelmaker, can be radically changed by a process that locally melts and recasts part of the construction. There is definitely a continuing demand for increased productivity in welding, while maintaining the parent material properties.

The history of stainless steel welding on an industrial scale was, until well into the 1950's, more or less that of manual metal arc (MMA) welding. Stainless steel stick electrodes were an early inclusion in ESAB's consumable range and, in the first issue of Svetsaren, in 1936 [9], an application using ESAB OK R3 (18%Cr 10.5%Ni 1.5%Mo) was reported.

Many of today's martensitic, ferritic, austenitic and ferritic-austenitic stainless consumable types were well established more than five decades ago. A common problem with steels and weld metals in those days was the high carbon content which introduced the risk of intergranular corrosion due to precipitation of chromium carbides at grain boundaries [10] (Fig. 2). With the introduction of lower carbon grades, this is rarely a problem, nowadays. The risk of forming intermetallic phases in weld metals was also well researched at an early stage [11, 12]. However, with the introduction

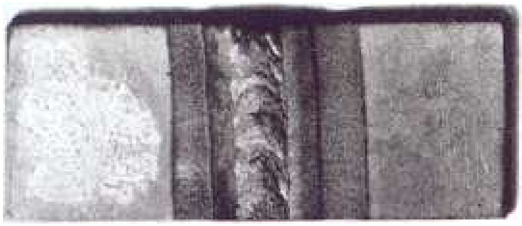

Figure 2. Intergranular corrosion in the heat affected zone of a 18%Cr, 8%Ni steel with 0.10%C as tested in 1944 [10].

of more highly alloyed grades, this is still something that has to be considered when designing welding consumables and selecting welding parameters.

Manual metal arc welding was the dominating welding process into the 1980's and is still significant for welding of stainless steels [13]. Solid wires for semi-automatic welding were introduced into ESAB's consumable range in the 1950's, and submerged arc fluxes and wires and strips were readily available in the early 1960's (Fig. 3). Cored wires have, in the last decades, become an important group of consumables offering advantages in productivity and easier alloy modification than solid wires.

Mechanisation

Although many new fusion and solid state welding techniques have been introduced and are applied in specific applications, none has yet been able to replace conventional fusion welding on a large scale. However, mechanisation and robots have changed the approach to welding with increased productivity and quality.
An example is welding of Francis turbines for hydropower projects. A 67 tonnes turbine runner produced, in 1957 [15], in 13%Cr steel, was assembled using ESAB OK R6 (17.5%Cr, 11.5%Ni, 2.5%Mo) consumables. Joint faces were buttered using a preheat of 250°C, directly followed by a post-weld heat treatment at 680°C. The runner was then assembled (Fig. 4) after machining of joint faces and the final welding was at room temperature by 4-5 welders working, simultaneously, on opposite sides to minimise the risk of deformation. A final stress relieving post-weld heat treatment at 680°C ensured optimum corrosion resistance.

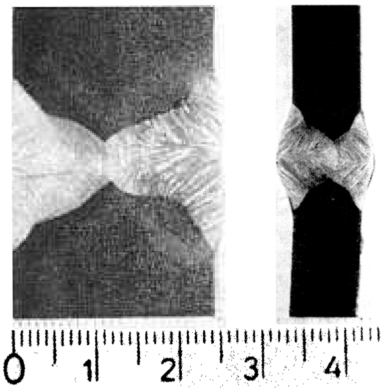

Figure 3. Two examples of submerged arc welds in 8 and 25 mm 18%Cr, 8%Ni austenitic stainless steels from a study in the early 1960's [14].

A more recent project illustrating the trend towards mechanisation is the welding of Francis turbine runners for the world's largest hydroelectric project, the Three Gorges dam in China [16]. Altogether 26 Francis turbines, 10m in diameter and with a weight of 450 tonnes will be installed. The runners are made of solid 410 NiMo type martensitic stainless steel (13% Cr, 4% Ni, 0.5% Mo) castings.

Submerged arc welding (SAW) with two wires (twin-arc) was considered the best method for joining the vanes to the crown and band of the runner. The selection was based both on productivity and weld metal quality criteria and included the development of OK Flux 10.63 to be used in combination with the matching composition filler wire OK Autrod 16.79. The thickness of the vane varies along the 4 m long joint, but it is mainly between 70 and 220 mm. With a typical welding current of 700-800A, and a welding speed of 70 cm/min, some 200-300 weld beads had to be deposited with heat inputs of about 2 kJ/mm for each joint.

Consistent performance and reliability were therefore just as important as deposition rates during welding. The welding head had to follow precisely the approximately 4m long joints with complicated three-dimensional geometry. High-accuracy numerically controlled welding manipulators were, therefore, necessary to obtain all the benefits from a fully mechanised welding process and to achieve the required productivity (Fig. 5).

Future welding processes

Although techniques such as laser and electron beam welding have been available and applied for some time, they have never been able to challenge the more conventional fusion welding processes on a large scale. Economic factors, as well as requirements on joint fit-up, etc, have limited their use. The introduction of friction stir welding quickly had an impact on welding of aluminium alloys. Successful attempts to weld stainless steels have been reported [17], but tool life and welding speed are still major obstacles to a more widespread use.

At present, laser-hybrid welding [18] seems to be the most likely, recently introduced, technique to be used on a large scale. The hybrid technique combines most

Figure 4. Assembly of a 67 tonnes Francis turbine runner in 1957. Manual metal arc welding with ESAB OK R6 consumables was used for buttering of joint faces and for final assembly welding (15).

Figure 5. Mechanised SAW welding of Francis turbine runners for the Chinese Three Gorges hydro-power project [16].

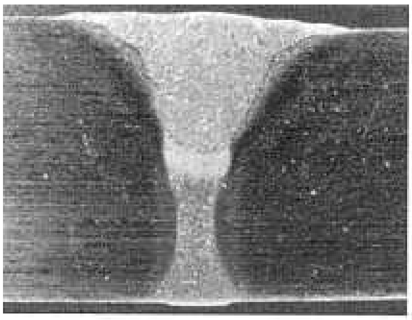

Figure 6. Laser hybrid welding of 11 mm 22%Cr duplex stainless steel. A first laser-hybrid run was combined with a second MIG run to optimise weld properties and bead profile. Addition of a standard 22%Cr 9%Ni 3%Mo (OK Autrod 16.86, Ø 1.0 mm) filler wire was used to ensure sufficient weld metal austenite formation.

on a large scale. The hybrid technique combines most of the best features of laser welding, such as good penetration, with the gap bridging ability of metal inert gas (MIG) welding. When combined, high quality welds can be produced with high productivity, while retaining the option of adding a consumable wire, thereby making it possible to compensate for lack of material and, when needed, to modify the weld metal composition. Figure 6 shows an example of welding 11mm duplex stainless steel with a combination of one laser-hybrid run and a second MIG run. Excellent mechanical properties were achieved, while maintaining proper phase balance in the weld metal and heat affected zone.

Welding consumable development

Although consumable manufacturers must follow the lead of steelmakers in formulating new alloys, there have been significant improvements in consumables design, both in terms of weldability and control of residual elements. Weldability has always been, and will continue to be, an important aspect in stainless steel development. The range of potential applications for a new steel grade is definitely smaller if welding is a problem, or if suitable welding consumables are not available.

ESAB has a history of closely following steel development. Duplex stainless steel consumables have been part of the ESAB range for many decades and considerable effort was put into developing improved consumables as duplex steel development accelerated in the 1970's and 1980's [19]. A recent example of the ambition to stay at the frontier of stainless consumable development is the introduction of matching composition supermartensitic (Fig. 7) metal-cored wires (OK Tubrod 15.53 & 15.55) [20, 21].

A trend in austenitic and duplex stainless steel production (the "super-trend"), for more than two decades, has been the introduction of grades with higher alloy contents to meet the demand for higher corrosion resistance in special applications.

Commonly, Cr- and Mo-contents are increased to improve corrosion resistance although, recently, N and to some extent W, have become important alloying elements. From the consumables point of view, this puts the spotlight on two "old problems": porosity/loss of nitrogen and precipitation of intermetallic phases. A challenge for the future is finding reliable consumable/welding process combinations for alloys, highly alloyed with nitrogen, that produce porosity free welds with matching corrosion resistance and mechanical properties.

The adverse effect on corrosion resistance of segregation during the solidification of stainless steel weld metals, is well known, over-alloying being a well-established practise to counteract this phenomenon. However, as alloying content increases, precipitation of deleterious phases becomes unavoidable, and more structurally stable nickel-based consumables are employed. Currently, the corrosion resistance of the most highly alloyed austenitic grades is difficult to match - even with nickel-based consumables.

An interesting alloy development is the use of modern modelling tools to find new ways around what might seem to be fundamental problems. For example, thermodynamic calculations and experiments have showed that a higher total alloying content can be tolerated in nickel-based weld metal if a combination of W and Mo is used, rather than either of the two elements alone [22]. The explanation is illustrated in Figure 8 showing, that whereas Mo is enriched in interdendritic regions, a corresponding W-depletion occurs, resulting in a more even distribution of alloying elements, better resistance to localised corrosion and less risk of precipitation.

The stainless future

The future certainly looks bright, shiny and non-stained for stainless steels. With greater attention to achieving low long-term maintenance costs, increasing environmental awareness and greater concern with life cycle costs, the market for stainless steel continues to improve. However, the cost, relative to alternative materials, will definitively continue to be an important factor in finding new markets in rapidly developing regions.

It is difficult to identify the major product in stainless steel development since the group is so diversified and applications range from cutlery to critical components in the process industry. It is to be expected that today's standard grades will remain much the same, but will be produced at lower costs. The introduction and increased use of leaner less expensive grades, such as lean duplex and 11-13Cr ferritic-martensitic grades, will contribute to a pressure on price reduction and also to finding new applications where currently, mild steel is used. There is also continuous development of new specialised highly alloyed grades intended for very corrosive environments and high temperatures. Nitrogen is increasing in popularity, being probably the least expensive of all alloying elements, and is likely to be introduced, to a larger extent, in standard grades, in an attempt to improve properties and decrease alloying costs.

In conclusion, the use of stainless steels is expected to continue to grow at a significant rate. Existing grades will be the industry's workhorses, and upgraded versions and new alloys will also be seen. New and existing welding processes are continuously developing and, in particular, laser-hybrid welding can be expected to gain ground in the near future.

Nevertheless, it is likely that, for the foreseeable future, stainless steels will in large part continue to be welded using established arc processes.

Figure 7. Typical microstructure of an all-weld metal deposited with the supermartensitic metal-cored wire OK Tubrod 15.55 (<0.01%C, 12%Cr, 6.5%Ni, 2.5%Mo).

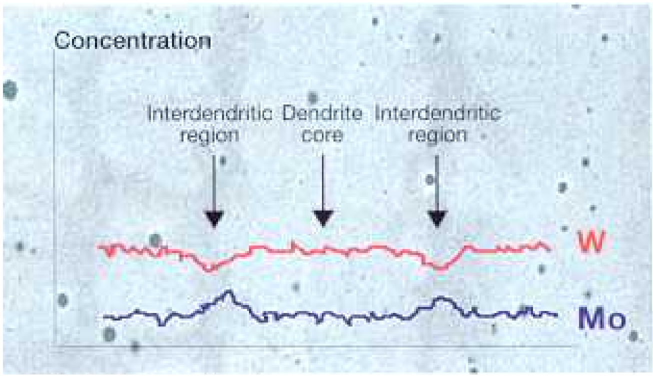

Figure 8. Concentration profiles for W and Mo across dendrites in a Ni-based weld metal. Mo is enriched in interdendritic regions whereas W is depleted resulting in a more even distribution of alloying elements and thereby better corrosion resistance. (Dendrite spacing is approximately 10 µm).

Families of stainless steels

It is fortunate that corrosion resistance can be obtained in an iron-based system simply by the addition of chromium, since, by appropriate adjustment of other alloying elements such as nickel and carbon, a wide range of microstructures can be developed. Hence, stainless steels can offer a remarkable range of mechanical properties and corrosion resistance and are produced in many grades. For example there are more than 150 grades of wrought stainless steel in the latest edition of EN 10088-1 (3).

The five major families of stainless steel are:

- Ferritic stainless steel has properties similar to mild steel but with better corrosion resistance due to the addition of typically 11-17% chromium.
- Martensitic grades can be hardened by quenching and tempering like plain carbon steels. They have moderate corrosion resistance and contain, typically, 11-13% chromium with a higher carbon content than ferritic grades.
- Precipitation hardening stainless steels can be strengthened by heat treatment. Either martensitic or austenitic precipitation hardening structures can be produced.
- Duplex (Austenitic-Ferritic) stainless steels have a mixed structure of austenite and ferrite, hence the term "duplex". Modern grades are alloyed with a combination of nickel and nitrogen to produce a partially austenitic lattice structure and improve corrosion resistance. These steels offer an attractive combination of strength and corrosion resistance.
- Austenitic stainless steels have a nickel content of at least 7%, which makes the steel austenitic and provides ductility, a large scale of service temperature, non-magnetic properties and good weldability. This is the most widely used group of stainless steels used in numerous applications.

“Super”-austenitic or “super”-duplex grades have enhanced pitting and crevice corrosion resistance compared with the ordinary austenitic or duplex types. This is due to further additions of chromium, molybdenum and nitrogen.

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Figure 1 is from:
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Dr. Leif Karlsson joined ESAB's R&D department in 1986, after receiving a Ph.D. in materials science from Chalmers University of Technology. He currently holds a position as Manager Research Projects at ESAB AB in Sweden, focussing on projects dealing with corrosion resistant alloys and high strength steels.