# Handbook of Stainless Steel

## Preface

The world consumption of stainless steels has shown a more or less constant increase of 6 % per annum since the middle of the 20th century. The rapidly increasing number of applications has led to a need among engineers, designers and materials specifiers for an introduction to stainless steel which provides basic and readable information. This need will at least partly be fulfilled by the present handbook. The handbook is also aimed to be useful to students by providing a complement to the general and often limited information on stainless steels in the existing student literature.

The reader will become acquainted with the commodity stainless steel grades and also introduced to the most common specialty steels, e.g. the modern weldable duplex grades with reduced alloying content and increased strength. The handbook gives a broad view of the properties of different types of stainless steels, their production and physical metallurgy, applications of stainless steels and fabrication techniques. It also reflects the rapidly increasing use of stainless steels in load bearing constructions, such as bridges and buildings, where the low maintenance costs, high recycling ratio and thus low environmental impact and carbon footprint contributes to a sustainable society.

This handbook has been written by a group of specialists at Outokumpu, with each person contributing their special competence. It can act as an introduction to the other stainless steel handbooks produced by Outokumpu, such as the Welding Handbook, the Corrosion Handbook and the handbook Machining of Stainless, in which more in depth knowledge is presented.

It is our hope that after reading the handbook you should have a reasonably clear picture of the variety and the versatility of the most important available stainless steels on the market today, keeping in mind the constantly on-going development work within Outokumpu and elsewhere. We have strived to provide technical objective knowledge and not to include subjective marketing.

Espoo, October 2013

Mika Seitovirta

Chief Executive Officer
Outokumpu

# Read this note

This handbook provides a guide to the history, production, performance and use of stainless steel. The information herein is intended to facilitate understanding of the properties of the different types of stainless steels available from Outokumpu. It is, however, well known that the performance of stainless steel in service can be profoundly affected by minor changes in the environment or use. Accordingly Outokumpu Oyj makes no representation or warranties, expressed or implied, and have no liability, compensatory or consequential, for the performance of any stainless steel in any individual application that may be made based on the information provided in this handbook. See also the disclaimer on page 89.

# Contents

# Introduction

Iron and the most common iron alloy, steel, are from a corrosion viewpoint relatively poor materials since they rust in air, corrode in acids and scale in high temperature furnace atmospheres. In spite of this there is a group of iron-base alloys, the iron-chromium (Fe-Cr) alloys, often with nickel (Ni) additions, known as stainless steels, which "do not rust in sea water", "are resistant to concentrated acids" and which "do not scale at temperatures up to 1100 °C".

It is this largely unique universal usefulness, in combination with good mechanical properties and manufacturing characteristics, which gives the stainless steels their raison d'être and makes them indispensable for the designer. The usage of stainless steel is small compared with that of carbon steels but exhibits a steady growth, Figure 1:1. Stainless steels as a group are perhaps more heterogeneous than the constructional steels, and their properties are in many cases relatively unfamiliar to the designer. To take full advantage of these materials requires an increased understanding of their basic properties, so the following chapters aim to give an overall picture of the "stainless world" and what it can offer.

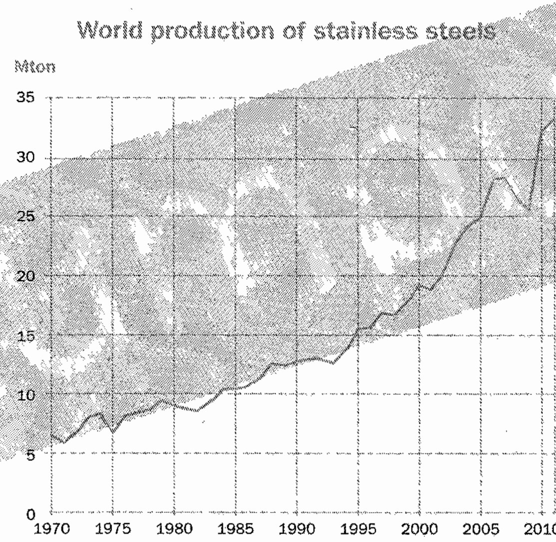


Figure 1:1. World stainless steel production 1970-2010.

## Use of stainless steel

Steel is unquestionably the primary industrial constructional material.

The dominant product form for stainless steels is cold rolled sheet, Figure 1:2. The other products individually form only a third or less of the total amount of cold rolled sheet.

Usage is dominated by a few major areas: consumer products, equipment for the oil and gas industry, the chemical process industry and the food and beverage industry. Figure 1:3 shows how the use of stainless steel is divided between the various applications.

The most widely used stainless grades are the austenitic Cr-Ni 18-8 type steels, i.e. EN 1.4301/1.4307, which form more than 50 % of the global production of stainless steel. The next most widely used grades are the ferritic Cr-steels such as 1.4512 and 1.4016, followed by the molybdenum-alloyed Cr-Ni-Mo austenitic steels 1.4401/1.4404. Together these grades make up over 80 % of the total tonnage of stainless steels. The remaining part contains other austenitic grades like high performance austenitic grades as well as duplex and martensitic grades.

## How it all started

Scientists and industrial developers from three countries; France, Germany and the UK, were involved in the development of stainless steel. The French mineralogist Berthier reported as early as 1821 about Cr-steels resistance to acid attack. The situation was for some time obscured by the famous English metallurgist Robert Hadfield who reported in 1892 that Cr was not beneficial for the corrosion resistance. He based this statement on tests in 50 % sulphuric acid. Had he used seawater or nitric acid in his tests he would have been the discoverer of stainless steels. In 1911 Monnartz published a thorough article on Fe-Cr-alloys and specially their acid-resistance and pointed out that the results from traditional testing with sulphuric acid could not be generalised. He was also the first to point out the beneficial effect of Mo on the corrosion resistance of Cr-steel.

In an attempt by Krupp in Germany to find a suitable material for thermocouple tubes Pasel, Strauss and Maurer investigated Cr- and Cr-Ni-steels. They stated that steels with high contents of Cr or Cr-Ni could be stored for months in humid and aggressive environment without rusting. The first patent claim for a ferritic or martensitic 14 Cr steel (V1M) and an austenitic 20 Cr, 7 Ni steel (V2A) was filed in 1912.

At the same time in Sheffield, England, Brearley was experimenting with 12–14 % Cr steels and observed that they did not etch in normal etching acids. He also noticed that Cr steels resisted corrosion much better in the hardened than in the annealed condition. Brearley saw commercial possibilities of this material in cutlery and gave non-rusting steel the name Stainless Steel. In 1916 he was granted patents in the USA and a number of European countries.

Parallel with the work in England and Germany, Becket was working in Niagara Falls, USA, to find a cheap and scaling-resistant material for troughs for pusher-type furnaces that were run at temperatures up to 1200 °C. He found that at least 20 % chromium was necessary to achieve resistance to oxidation or scaling. This was the starting point of the development of heat-resisting steels.

In Sweden the interest was increased after the Baltic exhibition in Malmö in 1914 where stainless steels from Krupp were presented. This lead to investing in a Rennerfeldt furnace in Avesta and the production rapidly increased in the early 1920's. This was not least due to the recruitment of Bo Kalling in 1923 from the company Ferrolegeringar in Vargön and the first commercial chromium steel 393 was produced in March/April 1924. In April 1925 18-8 type steel (Avesta 832) was produced and in the following year a Mo alloyed grade was produced. The very first stainless steel produced in Sweden was made in Långshyttan by Kloster AB; a 15 % Cr steel in 1921. However, it was not until after World War II that the development in process metallurgy lead to the growth and widespread use of the modern stainless steels.

The production stainless steel in Krefeldt, Germany, followed after October 17, 1912, when the firm of Fried Krupp, in Essen, applied for a patent for the "manufacture of objects requiring high resistance to corrosion ..." with the German patent office in Berlin. Krupp Thyssen Nirosta GmbH (KTN) was formed in 1995 by combining the stainless flat-rolled activities of the Krupp and Thyssen groups. Outokumpu today comprise stainless production sites in Finland, Sweden, Germany (KTN), UK, Mexico (Mexinox founded in 1976), US, and China, and is the leading stainless producer in the world.

In Tornio, Finland, the stainless steel production started in 1976 and has after strong expansion emerged to be one of the world's largest production sites of stainless steel.

Duplex stainless steels were first developed in Avesta in 1930 with two main target properties – heat resistance and acid resistance, the latter with a composition of 26Cr–5Ni–1Mo. These grades were however not weldable due to the high ferrite content formed in the heat affected zone. This was mastered in the 1970's by the addition of nitrogen which together with a more austenitic alloying led to the modern duplex grades exemplified by the Sandvik SAF 2205 and not least by the German Krupp Südwestfalen FALC223. The 2205 grade was a great success and is still the workhorse of the duplex grades today.

## Where does science stand today?

With the advent of the AOD (Argon Oxygen Decarburisation) process in the 1970's, a new development ensued since the process allowed high accuracy in the control of nitrogen and carbon. The

Product forms

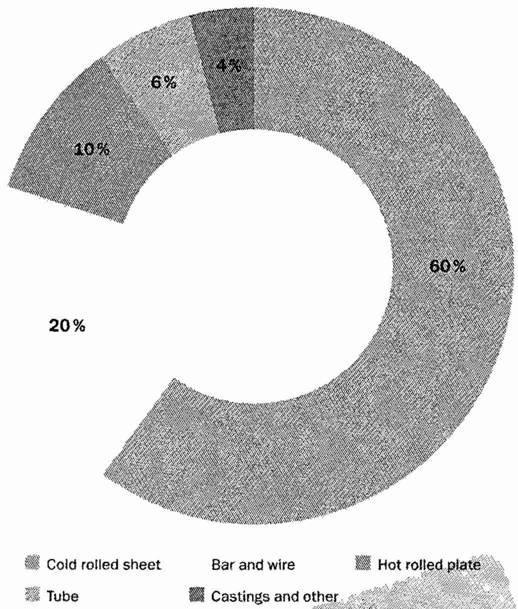


Figure 1:2. Use of stainless steel in the industrialised world, divided into various product forms. Ref.: Leffler Béla.

Application categories

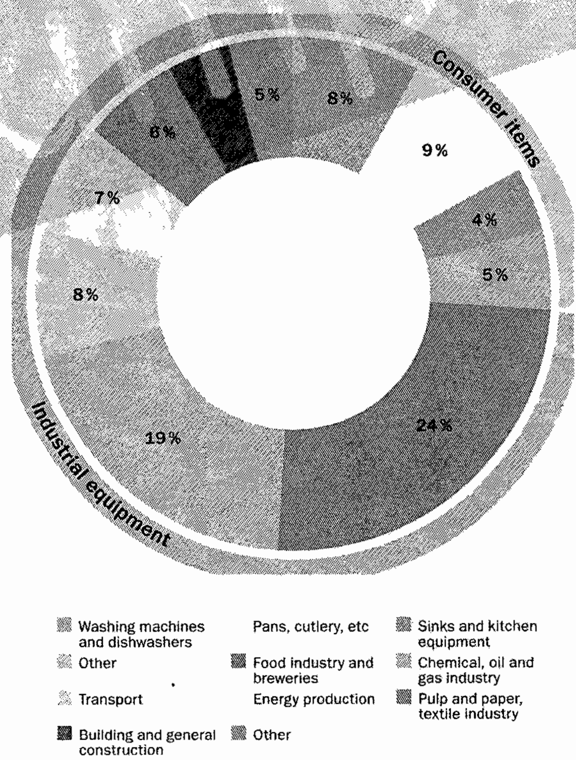


Figure 1:3. Use of stainless steel in the industrialised world, divided into various application categories. Ref.: Leffler Béla.

carbon content could be significantly reduced and the old problem of intergranular attack could be more or less eliminated since the precipitation of chromium carbides could be avoided with normal welding procedures. The favourable effect of nitrogen in terms of delaying the precipitation of sigma-phase was discovered and nitrogen was introduced in a number of highly alloyed stainless steels. Higher contents of Mo and Cr could now be added without the detrimental effects of sigma-phase. The mechanisms were discussed and the argument of "increased austenite stability" was frequently forwarded. This lead to research efforts at the Royal Institute of Technology (KTH) in Stockholm, Sweden, where the effect of nitrogen in terms of phase equilibria in the Fe-Cr-Ni-Mo system was studied and the nitrogen effect could be rationalized. The results were added to the evolving thermodynamic database Thermo-Calc which became the primary alloy development tool in the stainless steel area, particular for duplex stainless steels. This development is on-going and the coupling of critical experiments and thermodynamic calculations has led to a decrease in lead times in product development by a factor of 5–10, in addition to the increased understanding of alloying element effects in general. The laborious experimental mapping can then be replaced by simulations, both in terms of equilibria and kinetics of phase transformations.

The IDS (InterDendritic Solidification) program package, a dedicated thermodynamic-kinetic-empirical tool has been developed to simulate complex solidification phenomena in casting of e. g. stainless steels. The predictions include phase transformations from melt down to room temperature. The model was developed in the Laboratory of Metallurgy, Helsinki University of Technology, Finland.

The thermodynamic databases were, and still are, strongly dependent on accurate experimental data which was collected in temperature regions where equilibrium could be expected. In order to understand the lower temperature reactions, ab-initio or first principles calculations are now being used. No experimental information is needed and the results are truly predictions. Walter Kohn was awarded Nobel prize in 1998 for the density functional theory, DFT, which is the basic building block for this approach. Advanced calculations can contribute to the understanding of atomic movement and preferred positioning in metallic microstructures, and hence new insights into hardening due to martensite formation and cold deformation, and physical properties like anisotropy of elastic modulus. This technique will not within reasonable future replace the thermodynamic databases but will have an increasingly important role as a complement.

Two examples of the application of different types of modelling to stainless steels are given in Figures 1:4 and 1:5.

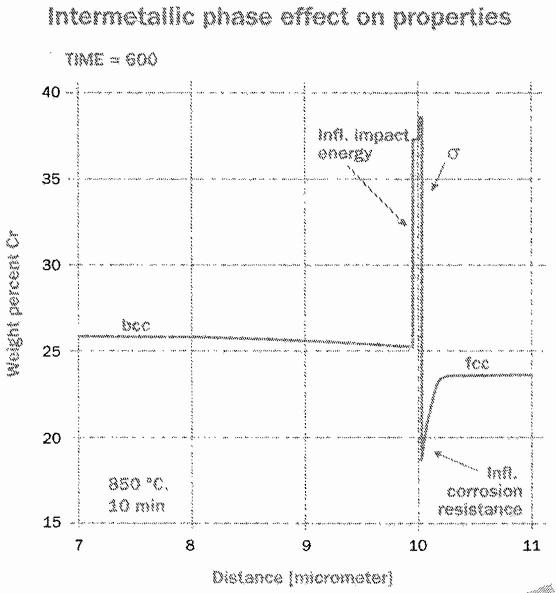


Figure 1:4. Calculated chromium profile, simulating growth of sigma-phase in a duplex stainless steel, using the kinetic Dictra program in the Thermo-Calc database system. The rapid growth of sigma-phase into the ferrite explains the effect on impact energy and the chromium depletion adjacent to sigma phase on the austenite side explains the detrimental effect on corrosion resistance.

Figure 1:5. Calculated stress-assisted martensitic microstructure evolution under uni-axial tensile loading of a stainless steel. Snapshot taken at three different time steps.

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# Stainless steel categories and grades

Over the years, ever since the start of the development of stainless steels, the number of grades have increased rapidly. Tables 2:1 and 2:2 show most of the stainless steel grades, together with their chemical compositions, that are produced by Outokumpu today. There are a large number of stainless steels with widely varying chemical compositions and at least at some time all of these grades have been sufficiently attractive to merit the trouble of standardisation. For more information see the standards EN 10088-1, ASTM A240 and ISO 15510. In view of this 'jungle' of different steel grades, a broader overview is helpful, and in Table 2:3 and 2:4, the stainless steel designations according to different standards are shown.

Since the microstructure has a decisive effect on properties, stainless steels have traditionally been divided into categories depending on their microstructure at room temperature. This gives a rough division in terms of both composition and properties. Typical microstructures are seen in Figures 2:1 to 2:4.

The Outokumpu stainless steels can be divided into four main groups: ferritic, martensitic and precipitation hardening, duplex (ferritic-austenitic) and austenitic stainless steels. The different categories of stainless steel are suited for different applications, and a number of examples are given in Figures 2:5 to 2:9.

## Ferritic stainless steel

The standard ferritic grades are alloyed with chromium (11.2–19 %), but with no, or very small addition of nickel. As nickel is one of the most expensive alloying elements and has demonstrated high price volatility, the low nickel content of the ferritic grades make them more price stable compared to grades with high nickel content. Molybdenum is added to some grades to improve the corrosion resistance, while alloying with niobium and/or titanium improves the weldability.

The ferritic grades, also referred to as Cr-steels, are magnetic due to the ferritic microstructure.

### Ferritic high temperature grades

There are also high temperature ferritic grades with increased resistance to high temperatures (800–1150 °C). These are mainly used in applications with sulphurous atmospheres (as sulphur may react with nickel in austenitic grades) and/or at low tensile loads. These grades are typically alloyed with more carbon compared to standard ferritic grades, in order to increase the creep strength, and with silicon and aluminium to improve the resistance to oxidation.

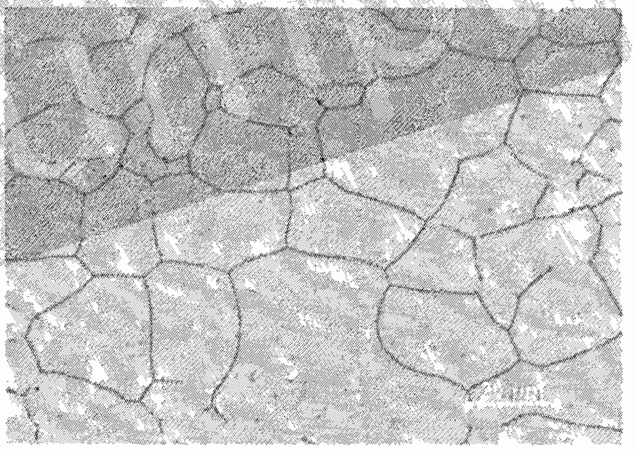

Figure 2:1. Ferritic microstructure showing equiaxed grains. Some presence of small inclusions and Ti(CN) can be observed.

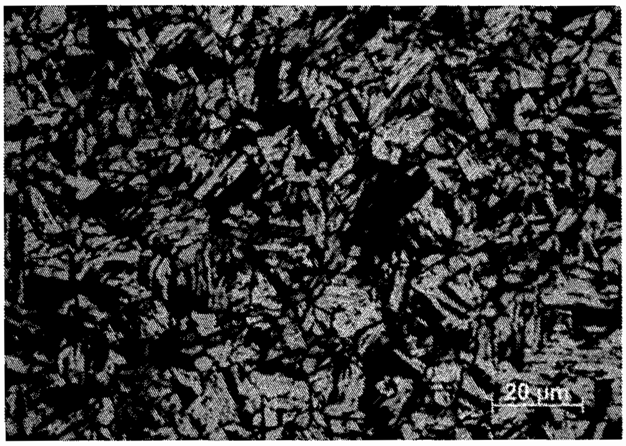


Figure 2:2. Martensitic microstructure showing fine-scale martesnite which has formed within the prior austenite grains. Smaller dark carbides can also be observed.

# Martensitic and precipitation hardening stainless steel

The martensitic grades are the smallest group of stainless steel. To improve the strength and hardenability of the martensitic grades they have higher carbon content compared to other grades, and nitrogen is sometimes added to further improve the strength. These grades contain no or rather small amounts of nickel, and molybdenum is seldom added. By adding some nickel and reducing the carbon content the rather poor weldability of martensitic grades can be improved. Sometimes sulphur is added to improve the machinability. The martensitic grades are magnetic and hardenable.

The precipitation hardening grades are hardened by a special mechanism involving the formation of precipitates within the microstructure. Also these grades are magnetic.

# Duplex stainless steel

Duplex grades have a ferritic-austenitic microstructure, with a phase balance of approximately 50 % ferrite and 50 % austenite. Duplex grades combine many of the beneficial properties of ferritic and austenitic stainless steels. The duplex microstructure also contributes to the high strength and high resistance to stress corrosion cracking. Characteristic for the duplex stainless steels is high chromium content (20.1–25.4 %), but rather low nickel content (1.4–7 %) compared to the austenitic grades. The low nickel content of the duplex grades makes them more price stable. Molybdenum (0.3–4 %) and nitrogen are added to improve the corrosion resistance and balance the microstructure. Nitrogen also increases the strength. Manganese is added to some grades, as partial replacement of nickel, but also to increase the solubility of nitrogen in the material.

The duplex grades LDX 2101® and 2304 are sometimes referred to as lean duplex grades. The duplex grade 2205 is sometimes referred to as 22Cr duplex and grades 2507 and 4501 as 25Cr superduplex grades. The duplex grades are magnetic due to the ferrite content.

Recently a new group of duplex grades with better formability has been introduced, the so called FDX-grades.

# Austenitic stainless steel

The austenitic grades are the largest group of stainless steels, and can be divided into five sub-groups, Cr-Mn grades, Cr-Ni grades, Cr-Ni-Mo grades, high performance austenitic grades and high temperature austenitic grades. The austenitic grades have good to excellent corrosion resistance, good formability and weldability. Their good impact strength at low temperatures is often exploited in cryogenic applications. The austenitic grades are non-magnetic in the solution annealed condition due to the austenitic microstructure. Cold working increases their strength and certain grades are therefore supplied in the temper rolled condition and may then be magnetic due to the presence of some martensite.

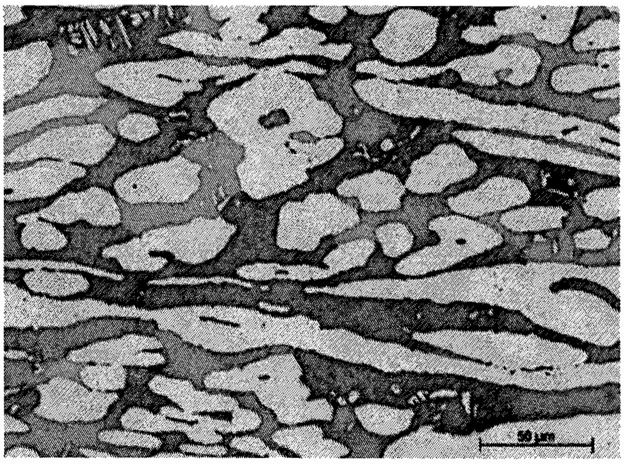

Figure 2:3. Duplex microstructure showing an elongated lamella structure of darker etched ferritic regions and brighter austenitic regions.

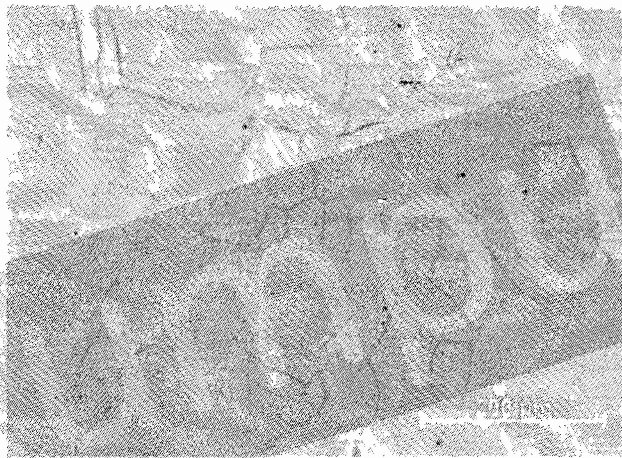
Figure 2:4. Austenitic microstructure showing equiaxed grains and characteristic annealing twins. Normal presence of small inclusions can be observed.

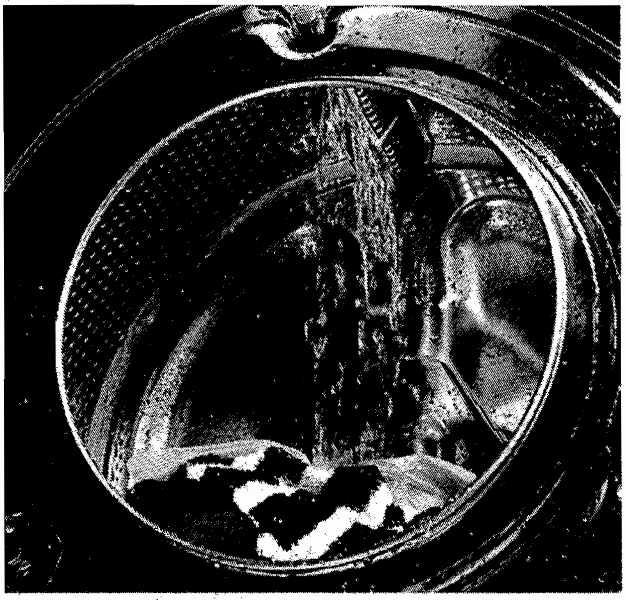
Figure 2:5. Ferritic stainless steel is commonly used for e.g. washing machine drums.