



Microstructure and Properties of Modern P/M Super Duplex Stainless Steels

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Doctoral Thesis

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Cover pictures:

Main: microstructure of heat affected zone of welded Duplok 27 after soaking treatment at 1020 °C for 1 h and controlled cooling to 570 °C with a cooling rate of 5 °C/min.

Inset: morphology of copper-rich precipitates in Duplok 27 soaked at 1020 °C for 1 h and controlled cooling with a cooling rate of 20 °C/min. TEM micrograph.

***Моим бесконечно любящим
родителям***

To my endlessly loving parents

Olena Smuk

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ABSTRACT

Precipitation of intermetallic secondary phases in duplex stainless steels is a well-known weakness of modern highly alloyed steel grades. Even relatively small amounts of these phases can severely deteriorate the mechanical and corrosion properties, the properties the duplex stainless steels are famous for. The problem can be handled by an appropriate heat treatment. However, finding and following the optimal treatment routine is challenging for modern industry often dealing with voluminous components and a careful separate study is required for each steel grade.

Precipitation kinetics of secondary phases was studied in modern conventional duplex and super duplex stainless steels and in similar grades manufactured by powder metallurgy (P/M) technology by hot isostatic pressing (HIP). This study is a part of a large research program on modern industrial duplex stainless steels, which has been carried out at the Laboratory of Engineering Materials, Helsinki University of Technology for about a decade. Extended collection of data was obtained on the microstructure, precipitation properties, mechanical and corrosion properties of Duplok 27, a novel grade of super duplex stainless steel designed and manufactured by Metso Oyj by P/M-HIP technology for the needs of the pulp and paper industry. Special attention was paid to the role of copper alloying.

Optimal regimes of heat treatments, which take into account the size of the components and the capabilities of the modern industrial heat treatment equipment, were studied. It was found that the regime optimal for the material could hardly be achieved for a component because of the limitations of heat transfer in a massive component.

Thermodynamic calculations with the Thermo-Calc software and TCFE3 database for steels and iron-based alloys showed that copper alloying has beneficial effect on the properties of duplex stainless steels. Copper decreases the high-temperature limit of precipitation of the harmful intermetallic sigma and chi phases and reduces the amount of precipitated chi phase. Copper precipitates as particles of FCC phase containing in addition to copper small amounts of some other elements, such as molybdenum and iron. The particles serve as pinning points for dislocations. This results in beneficial effect on tensile mechanical properties, which is, however, quite small due to the large size and the low volume fraction of the particles formed at high temperature during industrial heat treatment.

Internal friction method was applied to studying the precipitation kinetics of secondary phases and hydrogen effects in duplex stainless steels for the first time. TTT diagram was supplemented with the region of precipitation of secondary austenite. Diffusion coefficients of hydrogen were determined separately for the ferrite and austenite phases in conventional and P/M super duplex stainless steel.

Keywords: duplex stainless steel, powder metallurgy (P/M), hot isostatic pressing (HIP), secondary phase, precipitation kinetics, copper, mechanical properties, corrosion resistance properties, internal friction, hydrogen, thermodynamic calculations, Thermo-Calc

PREFACE

The experimental part of the work on this thesis was carried out in the Laboratory of Engineering Materials, Helsinki University of Technology in co-operation with Metso Oyj. Thermodynamic calculations were performed at the Department of Materials Science and Engineering, Ceramics Division of Royal Institute of Technology, Stockholm, Sweden, where the work was finished.

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LIST OF PUBLICATIONS

- Publication I** **Smuk, O., Jagodzinski, Yu., Tarasenko, O., Smuk, S., and Hänninen, H., 1999**, *Internal friction study of decomposition kinetics of SAF 2507 type duplex stainless steel*, Scripta Materialia, vol. **40**, No. 3, pp. 321-326.
- Publication II** **Smuk, O., Nenonen, P., Hänninen, H., and Liimatainen, 2000**, *Effects of copper on precipitation of secondary phases in duplex stainless steels*, Proc. of Int. Conf. "EUROMAT 2000" (held Tours, France, Nov. 7-9, 2000), eds. D. Miannay, P. Costa, et al., Elsevier, vol. **2**, pp. 841-846.
- Publication III** **Yagodzinsky, Yu., Smuk, O., Tarasenko, O., Smuk, S., and Hänninen, H., 2000**, *Study of hydrogen diffusion in SAF 2507 superduplex stainless steel by internal friction method*, Proceedings of 6th International Conference&Expo "DUPLEX 2000" (held Venice, Italy, Oct. 17-20, 2000), Associazione Italiana di Metallurgia, pp. 143-152.
- Publication IV** **Smuk, O., Nenonen, P., and Hänninen, H., 2000**, *Study of the mechanisms of the secondary phase precipitation in P/M-HIP superduplex stainless steels*, Proceedings of 6th International Conference&Expo "DUPLEX 2000" (held Venice, Italy, Oct. 17-20, 2000), Associazione Italiana di Metallurgia, pp. 395-404.
- Publication V** **Smuk, O., Nenonen, P., Hänninen, H. and Liimatainen, J., 2004**, *Microstructures of a P/M-HIP super duplex stainless steel forming in industrial heat treatments*, Article accepted for publication in *Metallurgical and Materials Transactions*, 2004.
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- Publication VII** **Smuk, O., Selleby, M. and Bergman, B., 2004**, *The effect of copper on secondary phase precipitation in duplex stainless steel – a thermodynamic calculations approach*, Article submitted to Zeitschrift für Metallkunde.

THE AUTHOR'S SHARE OF THE WORK

Publication I	Planning of the experiment, preparation of the samples, evaluation of the results, partly writing.
Publication II	Formulation of the task, planning of the experiment, preparation of the samples, evaluation of the results and analysis, writing, oral presentation at the conference.
Publication III	Planning of the experiment, preparation of the samples, optical and scanning electron microscopy, evaluation of the results.
Publication IV	Formulation of the task, planning of the experiment, preparation of the samples, optical microscopy, evaluation of the results and analysis, writing, presentation at the conference.
Publication V	Planning of the experiment, preparation of the samples, optical microscopy, partly instrumentation, evaluation of the results and analysis, partly writing.
Publication VI	Formulation of the task, planning the experiment, preparation of the samples, optical microscopy, evaluation of the results, theoretical estimations and analysis, writing.
Publication VII	Formulation of the task, planning the experiment, preparation of the samples, optical microscopy, partly mechanical testing, corrosion resistance testing, evaluation of the results and analysis, writing.
Publication VIII	Formulation of the task, planning the experiment, carrying out the calculations, evaluation of the results and analysis, writing.

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When you are a Bear of Very Little Brain, and you Think of Things, you find sometimes that a Thing which seemed very Thingish inside you is quite different when it gets out into the open and has other people looking at it.

A. A. Milne, Winnie-the-Pooh

1. INTRODUCTION

Duplex stainless steels (DSS) have been a well-established class of stainless steels for more than 70 years. One of the earliest references to the duplex structure is from 1927 [BAIN and GRIFFITH 1927]. In France the first duplex steel grade was produced by a mistake in alloying. The properties, however, appeared to be so attractive that in the early 1930s Avesta (Sweden) promoted the first commercial duplex stainless steel mainly intended for the pulp and paper industry. France and Finland started their own production quickly. These countries still hold the leading positions in production and R&D of duplex stainless steels.

The early types of duplex stainless steels were 25 Cr – 5 Ni – 1.5 Mo with carbon in the range of 0.08-0.10, all in wt. %. Offering sometimes even better performance than austenitic stainless steels, DSS had lower nickel content. Alloying with nitrogen was not used at that time and the ferrite content was usually rather high. The chemical compositions of the duplex stainless steel grades progressed rapidly. Molybdenum and copper were used as alloying elements because of the beneficial effects of these elements on corrosion and mechanical properties.

In the 1940s it became clear that the ferrite phase in the duplex stainless steels provides protection against chloride-induced stress corrosion cracking. Duplex stainless steels were used as the solution to the problem of stress corrosion cracking of austenitic stainless steels in chloride environments. The nickel shortage in 1950s stimulated development of high chromium – low nickel stainless steels, as well as alloying with nitrogen. Nitrogen was supposed to reduce the content of expensive nickel in stabilizing the austenitic phase even more and to provide additional strengthening. Then, due to progress in steelmaking it was possible to reduce the carbon content to 0.03 wt. % in duplex stainless steels to avoid intergranular corrosion. However, welding problems were still present. In the 22 Cr-type steels the microstructure of the heat-affected zone after welding was nearly ferritic, which continued to cause corrosion problems.

In the 1970s a breakthrough in steelmaking was achieved, which allowed to control the contents of C, S, O and residual elements on low levels without severe cost penalties. Also, nitrogen could be added in larger quantities without significant cost increase. The effects of nitrogen became better understood, as well as better thermal treatment procedures were developed. All this resulted in duplex stainless steels with better properties and, at the same time, reduced steelmaking costs.

In the beginning of 1980s there was a real jump in activity in the production, as well as in the research and development of duplex stainless steels. The fields of application of duplex stainless steels increased greatly. The nickel supply was no longer considered as a problem and the higher alloyed grades called super duplex stainless steels came back to favor, however, with higher risk of precipitation of unwanted secondary phases. Development of

computer technology and calculation/simulation methods contributed also to the development of new duplex stainless steels. At the Royal Institute of Technology methods of thermodynamic calculations were developed and the computing software Thermo-Calc has become a must-have instrument in the duplex stainless steel development.

Nowadays, the consumption of duplex stainless steels in industry increases by some 10 to 20 % annually. Not only the volumes but also the fields of application extend greatly requiring more sophisticated and more precise alloying, more complex and more precise thermomechanical treatment and welding. New grades, new treatments, new environments, new welding conditions – all this sets great challenge for researchers in physical metallurgy and materials science of duplex stainless steels.

2. MOTIVATION AND THE AIM OF THE RESEARCH

The present work started at Helsinki University of Technology in mid 1990s. All the main features of the behavior of duplex stainless steels had been well established by that time. However, duplex and super duplex stainless steels are very complex systems, which are very sensitive to even minor changes in the composition and/or manufacturing technology. Heat treatment becomes of primary importance when it comes to the top performance of duplex stainless steel components. The comprehensive detailed heat treatment procedure needs to be carefully determined for every particular grade for every particular application.

In addition to the conventional way of steelmaking – casting and forging – powder metallurgical method was successfully applied to the manufacturing of duplex stainless steels. Powder metallurgy (P/M) technology has several important advantages as compared to the conventional one. By making a deliberate mixture of selected powders special alloy compositions can be achieved, which otherwise are impossible to produce. P/M technology allows production of components with complex shape, which would otherwise require substantial amount of machining and/or welding. The thermal treatment during production and the microstructures of wrought and P/M duplex stainless steel are different and in principle different performance of wrought and P/M grades with the same nominal chemical composition can be expected.

It should be mentioned that the largest part of the studies on DSS including those on the microstructure and precipitation kinetics was performed on wrought conventional grades so far. Only very few studies dealing with direct comparison of P/M-HIP versus wrought DSS can be found in literature [HÄMÄLÄINEN et al. 1994, PERDRISSET et al. 1994].

A remarkable recent progress in the production techniques and understanding of the metallurgy has led the development of DSS towards higher alloying with chromium, molybdenum and even nickel. The phase equilibrium in these alloys has become even more complex and the precipitation behavior of DSS can attain new features in the presence of new alloying elements.

To summarize, for achieving the desired mechanical and corrosion resistance properties of DSS, a precise knowledge of the precipitation kinetics of secondary phases, the morphology of the precipitates and effects of the alloying elements on different properties is needed. A complicated chemical composition and the production technology route make each grade of DSS a unique object for a study.

The aim of the present work was to study the main features of phase precipitation in modern P/M duplex and super duplex stainless steels as compared to the conventional grades. One of the tasks was to study the effects of copper on the properties of modern high-alloyed P/M duplex stainless steels. The main task was, however, to apply the produced knowledge and collected data to find the optimal thermal treatment for large components manufactured by P/M-HIP technology from an industrial duplex stainless steel and determining the microstructure and mechanical and corrosion resistance properties of the material in the obtained state.

In the first part of the research, several duplex and super duplex stainless steels produced by the conventional and P/M technologies with similar chemical compositions were selected for the study in order to establish the main features of the precipitation behavior of P/M grades. Careful investigation of the precipitation behavior of selected P/M super duplex stainless steels was carried out. At the second stage, a complex industrial heat treatment resulting in the best performance of large components manufactured from a modern super duplex stainless steel was determined. The role of copper was systematically investigated and its effects on mechanical and corrosion resistance properties were evaluated.

In the study some additional issues were touched upon, namely the application of the internal friction method to the duplex stainless steel research and the hydrogen behavior in duplex stainless steels. The problem of hydrogen embrittlement and hydrogen enhanced localized plasticity is important in some applications of austenitic stainless steels and can become important in duplex stainless steels in welding, as well as in some applications, such as chemical and marine industry.

The study was supplemented with Thermodynamic calculations with Thermo-Calc software and the steel database TCFE3 at Royal Institute of Technology in Stockholm. The goal of the calculations was to investigate whether the experimental results can be reproduced using available thermodynamic descriptions and to analyze the behavior of the materials under conditions not studied experimentally.

3. MODERN VIEWS ON MICROSTRUCTURE, PROPERTIES AND APPLICATIONS OF DUPLEX STAINLESS STEELS

3.1. General background and applications of duplex stainless steels

Duplex stainless steels (DSS) can be defined as a class of alloys with ferritic-austenitic microstructure, either main constituent phase of which is stainless, i.e., contains more than 13 wt. % Cr. The constituents are present in approximately equally large separate volumes, in contrary to two-phase alloys, in which one phase appears in the form of small precipitates.

The volume fraction ratio of the phase constituents is usually around 50:50, but it can be deliberately varied in rather wide range by appropriate chemical composition selection. Austenite content can be increased up to 55 and even 60 vol. %. The following reasons for this can be mentioned [LAITINEN and HÄNNINEN 1996]:

- Austenite-stabilizing elements allow better control of the microstructure in the heat-affected zone formed during welding.
- Environmentally assisted cracking occurs in the ferritic phase of the duplex alloy, and ductile austenite matrix retards efficiently the propagation of crack.
- The ferritic phase can become brittle during long term service at elevated temperature. Due to the inherently tough and unaffected austenitic phase the alloy can maintain relatively high impact toughness.

Duplex stainless steels were originally created as a low-nickel alternative to austenitic stainless steels in some applications. Modern super duplex stainless steels reveal a clear trend to higher alloying. Nickel content has also increased from 4 to about 7 wt. % in modern super duplex stainless steels. As compared to the austenitic stainless steels, DSS reveal several clear advantages, such as higher mechanical strength and superior resistance to corrosion. Advantages of DSS against austenitic stainless steels can be extended by using them in environments, where standard austenitic stainless steels are inappropriate due to stress corrosion cracking.

This beneficial behavior of the duplex stainless steels arises from the partitioning of alloying elements between the phases. The austenitic phase appears to be cathodically protected by the ferritic phase, which is usually mechanically stronger in commercial DSS with low interstitial content of nitrogen. Recently grown interest to DSS is related to the high resistance of newly developed super duplex steels to chloride-induced stress corrosion, which appears to be a major problem in marine and petrochemical applications.

Table 1. Contents (in wt. %) of main alloying elements of austenitic and duplex stainless steel grades. The PREN value = [%Cr]+3.3[%Mo]+16[%N] is most commonly used to compare the corrosion resistance (pitting and crevice) of the stainless steels [CHARLES 2000].

Stainless steel grades	Ni	Cr	Mo	N	PREN
AISI 316L	11.5	17.0	2.0	-	> 23
AISI 316LN	11.5	17.0	2.2	0.12	> 26
AISI 317L	13.0	18.5	3.2	0.08	> 30
AISI 317LN	13.0	18.5	3.2	0.12	> 30
Duplex 32304 – UR 35N	4.2	23.0	0.2	0.10	> 24
Duplex 32205 – UR 45N Mo	5.8	22.0	3.1	0.17	> 36
Duplex 322750 – CLI/SAF2507	7.0	25.0	3.5	0.25	> 40
Duplex 32550/32520 – UR52N+ (+1.5Cu)	7.0	25.0	3.5	0.25	> 40
Duplex 32760 – UR76N(+0.7Cu, +0.8 W)	7.0	25.0	3.5	0.22	> 40

On the other hand, the presence of the austenitic phase in the DSS increases significantly the impact toughness of the alloys as compared to that of the ferritic stainless steels. After appropriate heat treatment super DSS reveal the value of 230 J and higher, which can be considered as a very high value for this class of steels.

Wide application of duplex stainless steels was restricted for a long time because of difficulties in working, e.g., hot cracking during forging, and, especially, welding. Progress in the steelmaking techniques and better understanding of the metallurgy and phase balance at high temperatures allowed to improve forging and hot rolling. The great improvements in weldability were also achieved by increasing the nitrogen content in the steel and further development of the welding methods.

The excellent exploitation properties of DSS determine the field of their applications. Duplex and super duplex stainless steels are used in chemical, petrochemical, pulp and paper industry segments, in power generation and oil and gas production (on- and off shore) for different tubing, pumps, heaters and coolers, bleaching equipment, and even in architecture, e.g. the New Big Arch in Paris La Défense.

3.2. Chemical compositions of DSS

Chemical compositions, as well as thermomechanical treatments of modern DSS are usually selected to produce a desired volume fraction of the ferrite constituent. Chemical composition is used for the classification of DSS by calculating pitting resistance equivalent PRE, sometimes also called PREN since it takes into account the nitrogen content [NILSSON 1992]:

$$\text{PREN} = [\text{wt.\% Cr}] + 3.3 \cdot [\text{wt.\% Mo}] + 16 \cdot [\text{wt.\% N}] \quad (1)$$

NILSSON (1992) identifies four different types of DSS:

- Low alloyed: Low-cost essentially molybdenum-free DSS of the type 23Cr – 4Ni – 0.1N designed to replace AISI 304 and 316 where improved resistance to stress corrosion cracking is required. Often used for construction purposes. PREN \approx 25;
- Medium alloyed: DSS of the type 22Cr – 5Ni – 3Mo – 0.17N with the corrosion resistance lying between that of AISI 316 and 6 wt.% Mo + N superaustenitic grades. PREN = 30-35;
- High alloyed: DSS containing 25 wt.% Cr with varying contents of molybdenum and nitrogen, additions of copper and tungsten. Used for demanding applications. PREN value range 35-39;
- Super DSS: DSS of the type 25Cr – 7Ni – 3.7Mo – 0.27N with the PREN value greater than 40. Include special alloys for extremely aggressive environments, among others.

Sometimes the third and the fourth types of DSS are merged as a single group.

The contents of the main alloying elements (those included in the formula for calculating PREN) for some most common wrought duplex stainless steels are listed in Table 2.

An important feature of duplex stainless steels is the partitioning of the alloying elements between the constituent phases. This partitioning accounts for many peculiarities in mechanical and corrosion properties of duplex stainless steels. The ferritic phase is enriched in δ -stabilizing elements (Cr, Mo, Si), and the austenitic phase in γ -stabilizing elements (Ni, N, Cu, Mn). The distribution of the alloying elements between the phases is described by the partition coefficient, the ratio of the content of an element in ferrite in wt. % to that in austenite. CHARLES 1991 listed partition coefficients for some wrought DSS. Table 3 gives the partition coefficients for some P/M-HIP DSS [HÄMÄLÄINEN et al. 1994]. Little variation of the coefficients between the alloys (except for nitrogen) was explained by the fact that the limits of solubility were not exceeded. Nitrogen, in turn, has very low solubility in the ferritic phase and resides almost completely in the austenite constituent of DSS. A comparison of wrought versus P/M-HIP DSS did not reveal any significant difference in the values of partition coefficients [LAITINEN 1995].

Table 2. Chemical compositions in wt. % of some most common wrought duplex stainless steel grades arranged with ascending PREN value [NILSSON 1992].

Tradename	Producer	Standard	Cr	Mo	Ni	N	Other elements	PREN
SAF 2304	Sandvik, Avesta	UNS S 32304	23	0.2	4.0	0.10		25
UR 35N	Creusot-Loire	UNS S 32304	23	0.2	4.0	0.10		25
UR 45N	Creusot-Loire	UNS S 31803	22	3.0	5.3	0.17		35
SAF 2205	Sandvik, Avesta	UNS S 31803	22	3.0	5.3	0.17		35
FALC 223	Krupp Stahl	UNS S 31803	22	3.0	5.3	0.17		35
DP 3	Sumitomo	UNS S 31260	25	3.0	6.5	0.16	0.5 Cu, 0.3 W	37
UR 52N	Creusot-Loire	UNS S 32550	25	3.0	6.5	0.18	1.6 Cu	38
Zeron 100	Weir	UNS S 32760	25	3.6	7.0	0.25	0.7 Cu, 0.7 W	41
UR 52N+	Creusot-Loire	UNS S 32550	25	3.8	6.0	0.26	1.5 Cu	42
SAF 2507	Sandvik, Avesta	UNS S 32750	25	3.8	7.0	0.27		42

Table 3. Content of the main alloying elements in the ferrite (δ) and austenite (γ) phases and partition coefficients (δ/γ) in some P/M-HIP duplex stainless steels [HÄMÄLÄINEN et al. 1994]

	DUPLOK 22			DUPLOK 27			DUPLOK 27HS		
	δ	γ	δ/γ	δ	γ	δ/γ	δ	γ	δ/γ
N	0.06	0.27	-	<0.03	0.32	-	<0.03	0.39	-
Cr	26.0	22.0	1.18	30.0	26.8	1.12	29.7	25.0	1.19
Mo	3.4	2.2	1.55	3.5	2.3	1.52	4.7	3.0	1.57
Ni	4.6	7.0	0.66	6.8	10.4	0.65	6.4	8.9	0.72
Cu	0.1	0.2	-	2.0	3.0	0.67	1.8	2.8	0.64

Development of the steelmaking techniques advanced in 1970s and allowed to achieve well-controlled high contents of nitrogen in duplex stainless steels. Nitrogen resides mostly in the austenitic phase and has a significant strengthening effect. Besides significant strengthening effect in the austenitic phase, nitrogen affects partitioning of the alloying elements, like Cr and Mo, producing, thus, an indirect effect on the precipitation kinetics of secondary phases, mainly σ and χ [WEBER and UGGOWITZER 1995]. The concentration of chromium and molybdenum in ferrite can be estimated with the following formula:

$$c_{Cr,Mo}^{\delta} = \frac{c_{Cr,Mo}^{tot}}{V_v^{\gamma} \left(\frac{1}{P_{Cr,Mo}^{\gamma}} - 1 \right) + 1}, \quad (2)$$

where $c_{Cr,Mo}^{\delta}$ is the concentration of Cr or Mo in ferrite, $c_{Cr,Mo}^{tot}$ is the average concentration of Cr or Mo, V_v^{γ} is the volume fraction of austenite, $P_{Cr,Mo}^{\gamma}$ is partitioning coefficient of Cr or Mo. The effects of nitrogen and nickel on partitioning of chromium and molybdenum were studied by the same authors later, also applying thermodynamic calculations with the Thermo-Calc software [WEBER and UGGOWITZER 1998]. They confirmed the conclusions made earlier.

Expression 2 was used to explain two apparently opposite influences of nitrogen on the solution temperature of σ phase, observed by WEBER and UGGOWITZER 1995. The influence was related to the changes in the volume fraction of the austenitic phase in one case and caused a stabilization of σ phase to higher temperatures. In the other case, nitrogen affects the partitioning of alloying elements at a nearly constant volume fraction of austenite decreasing significantly chromium content in ferrite and, thus, retarding precipitation of σ phase.

Nitrogen is an important alloying element affecting not only the tensile properties and the precipitation kinetics of intermetallic phase. Nitrogen has strong effects on the fatigue behavior, corrosion and stress corrosion resistance, ferrite decomposition in the temperature range of 300-500 °C, etc. An excellent review on the nitrogen effects and their mechanisms in duplex stainless steels was published by HÄNNINEN, ROMU, ILOLA et al. (2001).

3.3. Powder metallurgy production technique and hot isostatic pressing

Duplex stainless steels are manufactured as various wrought products, such as hot-rolled plates, cold-rolled sheets, tubes, pipes, bars, wires, different forgings and castings. Production of complex shapes from DSS with significant amount of welding involved in the design can meet severe problems or become very costly considering difficulties with workability and weldability of DSS. The manifolds on oil platforms or valve bodies or similar equipment where castings are not possible because of the integrity issues can be examples of such components. In such cases the methods of powder metallurgy (P/M) can become efficient.

Powder metallurgy is a manufacturing process of compacting metallic or ceramic powder by applying high temperature and/or high pressure. The compaction is usually carried out by one of the following methods:

- sintering;
- powder forging;
- cold isostatic pressing (CIP);
- hot isostatic pressing (HIP).

The best mechanical properties and corrosion resistance can be achieved using HIP, which gives 100 % dense materials.

One of the ways of producing the raw material for the pressing – powders – is atomizing. Atomizing is widely used for the duplex stainless steel production. Powders are manufactured by spraying a molten alloy stream into small droplets inside a special chamber – atomizer – using gas jet, usually nitrogen or argon. The droplets solidify with the cooling rate of 10^2 to 10^5 °C/s producing ultrafine grain structure.

Powder is packed into a special container manufactured from low-alloy steel, usually by welding. The design and fabrication of container itself is one of the most important aspects of the HIP process affecting the quality of the end product. The containers are carefully inspected and the oxidized surface layers near the welds must be removed to ensure contamination-free end product. Filling of the container is usually accompanied with vibration to provide the packing density as close to the maximal theoretical value (for spherical particles – 65-70 %) as possible. The container is evacuated to 10^{-2} - 10^{-4} torr, often at temperatures of 300-500 °C to facilitate the removal of internal gases. Finally, the container is sealed by welding.

Container is placed in a special vessel with inert gas at high pressure and high temperature. The pressure is typically 100-150 MPa and the temperature is 1100-1200 °C in the case of DSS production. Under these conditions the powder particles yield, the grain boundaries creep and the diffusion occurs giving rise to coalescence of powder particles to produce densified material with no porosity. The container and, thus, the end component do not change their geometry, only some shrinkage occurs, 10-15 % of linear dimensions. HIPping can be interpreted as three-dimensional forging. After the HIPping process is finished, the container metal is removed by machining or by acid pickling.

The most common reason for the deteriorated properties of a HIPped material in the manufacturing of stainless steel components is the oxidation of the powder particles. The oxidation can happen during the atomization because of improper methods or during the handling and the storage of the powders, e.g., because of increased moisture content. Surface layers of the particles oxidized during the atomization consist of binary or ternary oxides – the inner layer of $\text{Cr}_2\text{O}_3/\text{Fe}_2\text{O}_3$ and the outer layer of MnO. The thickness of the oxide layers is typically few nanometers independent of the size of the particles. Apparently, the finer the particles the higher oxygen content due to the increased surface area to volume ratio. Oxide layers prevent the metal particles from proper compacting and lead, thus, to poor material properties of the end product [BRACCONI and GASC 1994, NYBORG and OLEFIJORD 1988, TUNBERG and NYBORG 1994].

The following advantages of the HIP manufacturing route can be mentioned [LINDENMO 1992, BYRNE et al. 1994, HÄMÄLÄINEN et al. 1994, RHODES, BECKMAN and ECKENROD 1994]:

- Low tooling cost;
- Short delivery times;

- A 100 % dense material with homogeneous and isotropic mechanical and corrosion properties;
- Fine grain size microstructure, which develops due to high cooling rate during the solidification of the powder and is maintained in the final products. Some coarsening may, however, take place during the densification process;
- Non-destructive ultrasonic inspection may be used due to the fine microstructure. Coarse grains cause the attenuation of the ultrasonic waves and makes the NDT difficult in conventional cast and forged DSS;
- Near net shape (NNS) production, which decreases the need for forging, machining and welding;
- Material is free of hot cracking.

Deformation-free manufacturing method allows to avoid cold-work enhanced precipitation of σ/χ phase [JACKSON and MATTHEWS 1991] and α' phase [CHARLES 1991, NYSTRÖM, KARLSSON and WASÉN 1991].

3.4. Phase transformations

The ferritic phase in duplex stainless steels is essentially unstable because of the high content of alloying elements. As a consequence, a large variety of secondary phases may precipitate in DSS in the temperature range of 300-1000 °C during isothermal aging or other heat treatment. Precipitation of secondary phases in DSS is usually considered in two separate temperature regions – below 600 °C and from 600 to 1000 °C (Figure 1).

The following phases have been observed: σ phase, Cr_2N , CrN , secondary austenite γ_2 , χ phase, R phase, π phase, M_7C_3 , M_{23}C_6 , and τ phase. If the grade contains copper it can also precipitate as copper-rich ε -phase. Additionally, spinodal decomposition of ferrite can occur in the temperature range of 300-500 °C. Long exposure times are usually required for this. Some parameters of the phases are listed in Table 4. A schematic TTT diagram of precipitation occurring in SAF 2507 super DSS is given Figure 1.

σ phase is undoubtedly the most important of the listed secondary phases because of its significant volume fraction and its strong influence on toughness and corrosion behavior. Already 4 vol. % of σ phase can result in decrease of impact toughness down to the value of less than 27 J from 230-300 J.

Table 4. Phases observed in duplex stainless steels [NILSSON 1992, HEINO 1998].

Type of precipitate	Nominal composition	Lattice type	Space group	Temperature range in DSS, °C	Lattice parameter, nm
σ	Fe 35-55, Cr 25-40, Mo 11-25	BCT	P4 ₂ mm	600-1000	$a=0.880, c=0.454$
Chromium nitride	Cr ₂ N	Hexagonal	P31m	700-900	$a=0.480, c=0.447$
Chromium nitride	CrN	Cubic	Fm3m	N/A	$a=0.413-0.447$
χ	Fe ₃₆ Cr ₁₂ Mo ₁₀ , Fe 35-50, Cr 20-35, Mo 20-22	BCC	I43m	700-900	$a=0.892$
R	Fe 30-40, Cr 17-20, Mo 25-45	Hexagonal	R3	550-650	$a=1.0903, c=1.9342$
		Rhombohedral			$a=0.9011, \alpha=74^{\circ}27'30''$
π	Fe ₇ Mo ₁₃ N ₄	Cubic	P4 ₁ 32	550-600	$a=0.636-647$
τ	Not determined		Fmmm	550-650	$a=0.405, b=0.484, c=0.286$
Carbide	M ₇ C ₃		Pnma	950-1050	$a=0.452, b=0.699, c=1.211$
Carbide	M ₂₃ C ₆	FCC	Fm3m	600-950	$a=1.0560-1.065$

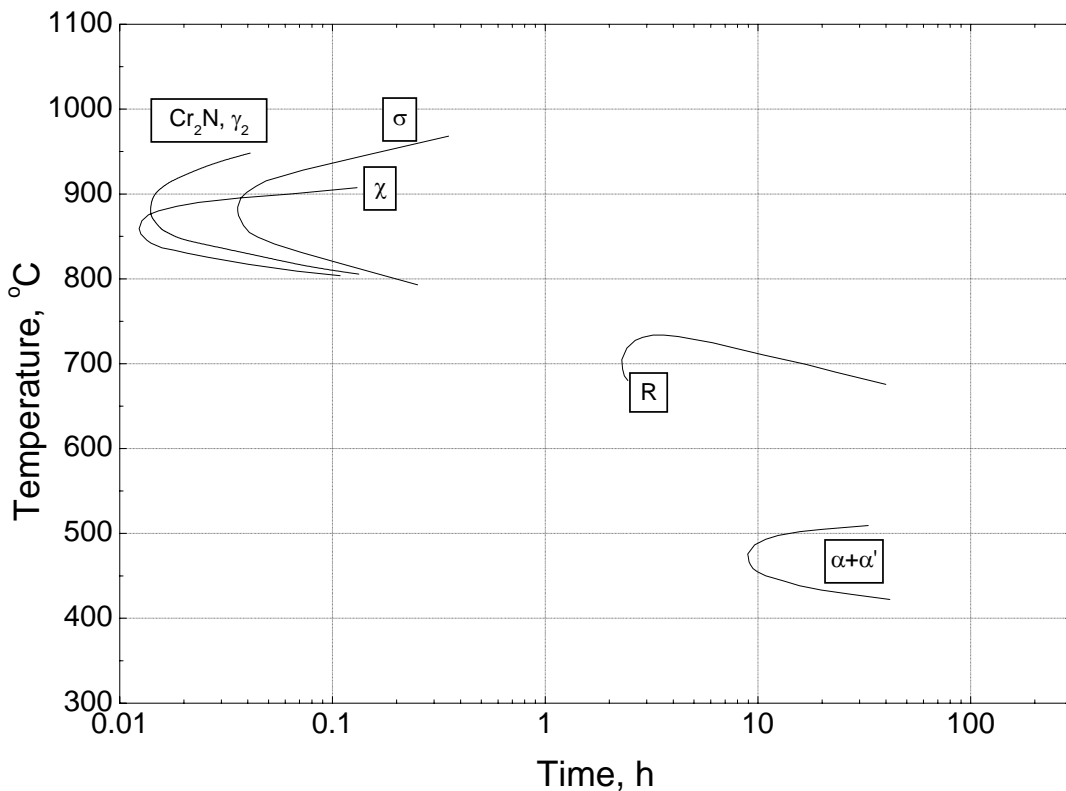


Figure 1. TTT diagram for various precipitates appearing in SAF 2507. Curves indicate 1 % volume fraction of precipitates [NILSSON 1992].

3.4.1. Sigma σ phase

σ phase is formed in a large variety of DSS, as well as in some austenitic stainless steels. It usually precipitates in large volume fraction and has strong influence on toughness and corrosion behavior. σ phase is a hard brittle intermetallic compound enriched with Cr, Mo and Si [MAEHARA et al. 1983, SOLOMON and DEVINE 1979]. Precipitation of σ phase most often starts at triple junctions or at ferrite/austenite boundaries [NILSSON 1992], and continues at incoherent twin boundaries and finally intragranularly [WEISS and STICKLER 1972].

The increased amounts of Cr and Mo in super DSS as compared to conventional DSS enhance σ phase precipitation for shorter times and expand the region of its stability towards higher temperatures. Tungsten and copper effects were studied, as well [CHARLES 1991]. Tungsten, like molybdenum, was reported to increase the precipitation rate of σ phase and displace the corresponding kinetic C-curve to higher temperatures, while no effect of copper was observed. Nickel was found to accelerate the precipitation kinetics of σ phase, although the equilibrium volume fraction was reduced [MAEHARA et al. 1983]. Hot working was shown to enhance σ phase formation. MAEHARA, FUJINO and KUNITAKE [1983] have shown that plastic deformation at 800-900 °C can increase the precipitation rate of σ phase by an order of magnitude.

3.4.2. Chi χ phase

Intermetallic χ phase (see Table 4) is commonly found in DSS after aging at temperatures 700-900 °C (Figure 1). It appears often with σ phase, although the “nose” of its C-curve appears at somewhat lower temperatures and shorter exposure times [NILSSON et al. 1992]. The effects of χ phase on toughness and corrosion properties are detrimental, however, it is often difficult to separate them from those of σ phase. Although the volume fraction of χ phase is not usually very high, it consumes significant amounts of chromium and molybdenum from the parent matrix, and simultaneously forming secondary austenite becomes depleted of these elements. This can lead to a decrease of the pitting corrosion temperature [NILSSON et al. 1992]. Interesting to note, that higher content of molybdenum in χ phase together with its large atomic scattering factor allows to distinguish χ phase on scanning electron microscope (SEM) images recorded with backscattered electrons, where it appears with brighter contrast than that of σ phase [NILSSON 1992].

3.4.3. Chromium nitrides

Precipitation of Cr_2N chromium nitride has become an important issue with the increased use of high nitrogen content in modern DSS. Formation of Cr_2N takes place at temperatures 700-900 °C during fast cooling from high solution annealing temperatures, presumably because of the supersaturation of the ferritic phase with nitrogen, or during isothermal heat treatment. In the former case, Cr_2N particles precipitate mostly intragranularly with the crystallographic relationship $\langle 0001 \rangle_{\text{Cr}_2\text{N}} \parallel \langle 011 \rangle_{\delta}$. In the latter case, nitride particles precipitate intergranularly at δ/δ grain boundaries or γ/δ phase boundaries. Again, like in the case of χ phase, simultaneously forming secondary austenite

becomes depleted in chromium. In corrosive environments, this leads to the formation of numerous pits close to prior austenite/ferrite phase boundaries, contributing, thus, to the degradation of corrosion resistance of DSS.

Cubic CrN nitride was observed by HERTZMAN, ROBERTS and LINDENMO [1986] in the heat-affected zone of welds of SAF 2205 DSS. Very little or no effect on toughness or corrosion properties was detected. This seems to be the only reported observation of CrN nitride in DSS by now.

3.4.4. *Secondary austenite*

The duplex structure is the result of quenching from high temperatures, at which the equilibrium share of ferrite is higher. Thus, decomposition of ferrite can take place at lower temperatures. Several mechanisms of the decomposition are usually mentioned [NILSSON 1992]:

- *Eutectoid reaction* $\delta \rightarrow \sigma + \gamma$ is facilitated by rapid diffusion along γ/δ boundaries and produces a typical eutectoid structure of σ phase and austenite in former ferrite grains. Transformation occurs at temperatures 700-900 °C and is provoked by the σ phase precipitation and depletion in chromium and molybdenum of the host ferrite matrix.
- *Widmannstätten precipitates* with various morphologies form at temperatures above 650 °C, involving fast diffusion rates [SOUTHWICK and HONEYCOMBE 1982]. Austenite obeys the Kurdjumov-Sachs orientation relationship and contains higher amounts of nickel as compared to the host ferrite matrix, which is a sign of the diffusion mechanism of the transformation.
- A *martensitic process* is involved at temperatures below 650 °C [SOUTHWICK and HONEYCOMBE 1982]. Austenite precipitates isothermally and obeys the Nishiyama-Wasserman orientation relationship. No differences were detected in the composition as compared to the host ferrite matrix indicating, thus, a diffusionless character of the transformation with respect to the substitutional elements.

3.4.5. *R phase*

R phase is an intermetallic compound enriched in molybdenum. It has complicated trigonal crystal structure with the unit cell consisting of 159 atoms. Precipitation occurs in the range of 550-700 °C. *R* phase was found to contain approximately 30 % Fe, 25 % Cr, 6 % Ni, 35 % Mo and 4 % Si [NILSSON and LIU 1991]. Reduction of toughness and critical pitting temperature was detected because of the *R* phase formation. Both intergranular and intragranular precipitates were observed. It was noticed that intergranular precipitates could be more deleterious from the pitting corrosion point of view since they may contain as much as 40 % Mo causing thus Mo-depletion in the surrounding matrix [NILSSON and LIU 1991]. *R* phase becomes unstable after long aging times (Figure 1) [NILSSON 1992].

3.4.6. *Pi π phase*

The nitride π phase was discovered by NILSSON and LIU 1991 in the duplex weld metal 22Cr-3Mo-8Ni DSS. π phase has a cubic crystal structure and it precipitates intragranularly in isothermally at 600 °C aged material and, like R phase, it contributes to the toughness and corrosion resistance reduction. π phase was found to contain approximately 28 % Fe, 35 % Cr, 3 % Ni and 34 % Mo as compared to the nominal composition of $\text{Fe}_7\text{Mo}_{13}\text{N}_4$.

3.4.7. *Carbides*

Both types of carbides, M_7C_3 and M_{23}C_6 , were found to precipitate at temperatures 950-1050 °C and below 950 °C, respectively, in DSS, relatively rich in carbon. Precipitation of both types of carbides occurs preferentially at δ/γ phase boundaries [SOUTHWICK and HONEYCOMBE 1982], but precipitates were also observed at δ/δ and γ/γ boundaries [THORVALDSSON et al. 1985]. However, precipitation of carbides becomes less important in modern DSS, where the carbon content is very low. SAF 2507, for example, has not revealed carbide precipitates of any type [NILSSON 1992]. Thus, intergranular corrosion caused by carbide precipitation and, as a result, by chromium depletion near grain boundaries seems to be improbable in modern DSS.

3.4.8. *Copper-rich precipitates*

Copper has always been of interest as an alloying element in duplex stainless steels. The majority of the previous studies on the state of copper in steels have been performed on cast or low-alloy steels. It has been found that because the solubility of Cu decreases with decreasing temperature, copper-rich particles precipitate in the supersaturated ferritic phase. The process can be divided into three stages:

- the formation and growth of coherent BCC Cu-rich clusters;
- the transformation of these clusters to FCC-phase particles; the phase contains in addition to copper small amounts of iron and other elements and is sometimes referred to as ε -phase;
- the subsequent growth of these particles to rod-like precipitates after prolonged aging.

KRISHNADEV and LE MAY (1970) found that the precipitation of copper-rich phase takes place both along dislocations and uniformly throughout the matrix in Cu-containing HSLA steels. Other researchers have reported predominant precipitation either along dislocations [COX 1967], or uniformly [HORNBOGEN and GLENN 1960] in Fe-Cu systems. The change of the shape of the copper precipitates from spherical to rod-like has been attributed to the minimization of the strain energy [NABARRO 1940] and to the anisotropy of the surface energy [SPEICH 1965]. The length-to-radius ratio of the rod-like precipitates was reported to be nearly constant, about 10 in a Fe-Cu alloy [SPEICH 1965], as well as to vary in the range of 20 to 50 [LE MAY and KRISHNADEV 1982].

The state of copper in highly alloyed modern super duplex stainless steels, its behavior during industrial heat treatments, its effects on precipitation of intermetallic secondary phases, primarily σ -phase and secondary austenite, as well as on mechanical and corrosion properties is not well documented.

Copper additions to stainless steels have been used to improve the corrosion resistance properties and to induce precipitation hardening [SOYLU and HONEYCOMBE 1991, CHARLES 1991]. Significant extension of the low temperature hardening range of duplex stainless steels was attributed to the precipitation of fine particles enriched in copper [CHARLES 1991]. On the other hand, it was noted that additions of copper emphasize the drop in impact toughness due to heat treatment in the range of 260-320 °C [CHARLES 1991]. These observations are referred to the copper particles after the first and second stages of precipitation.

The presence of copper in duplex stainless steels increases the pitting potential in NaCl and HCl solutions with less evident effect on the critical pitting temperature [TUCK, GARFIAS-MESIAS and SYKES 1997]. In [BANAS and MAZURKIEWICZ 2000], agreeing that in solid solution copper facilitates passivation in austenite, it was, however, concluded that the precipitation of copper-rich phase decreased the resistance of ferrite to pitting corrosion in 1M H₂SO₄ + 1M NaCl solution by decreasing the stability of the passive film because of poor passive behavior of copper-rich phases in chloride environments.

In copper rich DSS, precipitation of copper particles was detected by SOUTHWICK and HONEYCOMBE (1982). They pointed out that fine copper precipitates in the ferritic structure provide homogeneously distributed nucleating sites for the subsequent formation of austenite, which led to a refinement of the austenite grain size by an order of magnitude [SOYLU and HONEYCOMBE 1991]. Copper particles were found to pin the growing δ/γ phase boundaries. Refinement of the microstructure of DSS after aging at 850 °C associated with the copper precipitates was observed [SOUTHWICK and HONEYCOMBE 1982].

BANAS and MAZURKIEWICZ 2000 concluded that high concentration of copper in the ferritic phase leads to the precipitation of copper-rich phase in ferritic steels and ferrite constituent of duplex steels. Precipitated particles increase the hardness of the material and diminish corrosion resistance of ferrite.

3.4.9. 475 °C embrittlement

The phenomenon of “475 °C embrittlement” has been observed in ferritic steels below approximately 500 °C [LAGNEBORG 1967, COURTNALL and PICKERING 1976] and later in DSS [MILLER and BENTLEY 1990, BROWN et al. 1990, AUGER et al. 1990]. The reason for this is believed to be the miscibility gap in the Fe-Cr binary system, proposed by WILLIAMS 1958. The observed embrittlement is associated with decomposition of ferrite into chromium-rich α' phase and iron-rich α . Two different mechanisms of the decomposition were proposed. The first one is related to the spinodal decomposition of the solution within the spinodal, while the second mechanism is based on the classical nucleation and growth of α' phase outside the spinodal but still within the miscibility gap [HILLERT 1961, CAHN 1968]. The reaction of the decomposition results in embrittlement and increased

hardness independent of the mechanism. The effects were observed for lower temperatures, as well, e.g., at 280 °C, although longer times are needed, 1000 h and more [HERTZMAN 1998].

Chromium, molybdenum [GUTTMANN 1991] and copper [CHARLES 1991] were found to enhance 475 °C embrittlement. Copper effects, however, seem to be related to some other mechanism, involving nucleation of copper-rich precipitates. Nickel has an indirect influence promoting chromium and molybdenum partitioning to ferrite. Spinodal decomposition of ferrite is affected by nitrogen [HENDRY, MAZUR and JACK 1979]. The decomposition can be observed directly by TEM as a modulated contrast [NILSSON 1992].

3.4.10. G phase

In addition to the mechanism of spinodal decomposition of ferrite in the temperature range of 300-500 °C, precipitation of *G* phase was mentioned as a possible mechanism of 475 °C embrittlement [MILLER and BENTLEY 1990, AUGER, DANOIX, MENAND et al. 1990]. *G* phase is a silicide with nominal composition $Ti_6Ni_{16}Si_7$ with molybdenum substituting titanium in duplex stainless steels. Precipitation of *G* phase was observed in the ferrite phase of duplex stainless steels after long exposures (7 500 to 70 000 h) at 300-500 °C. Typical size of *G* phase precipitates is 2-6 nm in the matrix, can be up to 10 nm on dislocations [AUGER, DANOIX, MENAND et al. 1990]. The nucleation of *G* particles is enhanced by the spinodal decomposition of the ferrite matrix and takes place at the interface between Cr-rich and Cr-depleted domains. However, the effects of *G* phase are usually not considered alone, but rather as the net effect together with the spinodal decomposition.

3.4.11. The role of residual stresses in duplex stainless steels

The exploitation properties of duplex and super duplex stainless steels depend crucially on the achieved microstructure. Complicated chemical composition of DSS demands for a very precise route of thermomechanical treatment. However, the requirements are often contradictory: to avoid precipitation of σ phase a rapid cooling from high temperatures is needed. On the other hand, this can result in high residual stresses.

The role of residual stresses is significantly more essential in DSS, as compared to single phase austenitic or ferritic steels. DSS consist of two phases possessing different physical properties, like yield strength [SIEGMUND, WERNER and FISCHER 1993, POHL 1994], thermal expansion coefficient [FISCHER, RAMMERSTORFER and BAUER 1990] and thermal conductivity, solubility of alloying elements, etc.. These differences result in internal stresses after cooling or deformation, i.e., caused by different internal stress states of different phases.

In many other materials, e.g., in low-alloy steels, internal stresses may be decreased by applying a stress-relieving annealing treatment. In DSS, however, the stress-relieving annealing is more complicated because of precipitation of secondary phases. In some duplex grades, internal residual stresses may be lowered by approximately 50 % without any extra precipitation, provided the treatment is performed in the temperature-time region between the σ - and α' -phase regions [NEUBERT 1994, BOPPER and SCHRAM 1994]. Stress-

relieving annealing treatments were performed at 600 °C [POHL 1994], as well as above [MADERUD, ANDERSSON and LILJAS 1992] and below [HOCHÖFTLER and HABERFELLNER 1993]. INAL et al. (1994) have studied the effect of increasing tensile prestrain on internal stresses of the phases. The internal stresses were found to be tensile in the austenite phase and compressive in the ferrite one.

3.5. Mechanical properties

3.5.1. *Tensile strength*

A linear law of mixture may be expected to be valid for determining mechanical properties of DSS, considering the corresponding properties of ferrite and austenite. This was indeed observed for the elongation to rupture [NILSSON 1992]. The situation with the tensile strength is, however, more complex. Ferrite is usually stronger than austenite for the same interstitial content. The solubility of carbon or nitrogen in austenite is much higher than that in ferrite. Thus, in duplex structure nitrogen is partitioned in a way that austenite can become stronger than ferrite [JOHANSSON and ODÉN 1999, JOHANSSON and ODÉN 2000]. For example, CHARLES 1991 reported that the amount of nitrogen dissolved in austenite in a super DSS was as high as 0.45 wt. % at average content of 0.27 wt. %. It was also found that despite greater strength more plastic deformation occurs in austenite than in ferrite. The reason for that is compressive residual stress built up in the ferrite phase during cooling [JOHANSSON and ODÉN 1999, JOHANSSON and ODÉN 2000].

On the other hand, tensile strength is grain-size dependent. The grain size in DSS is usually smaller than in both ferrite and austenite of the corresponding chemical composition [NILSSON 1992]. This is explained by the mutual hindering of the growth of the ferrite and austenite grains. Thus, in practice a duplex alloy achieves higher strength values than its constituents. If the effects of grain size and partitioning of interstitials is compensated, the strength of a DSS is controlled by the stronger ferrite component [FLOREEN and HAYDEN 1968].

Table 5. Typical values of mechanical properties of some solution annealed DSS. Values for austenitic and ferritic steels are given for comparison [NILSSON 1992].

Grade	Standard	Yield strength 0.2%, MPa	Ultimate tensile strength, MPa	Elongation, %	Impact toughness at RT, J	Fluctuating tension fatigue strength, MPa
AISI 304	UNS S30400	210	515-690	45	> 300	120± 120
AISI 430	UNS S43000	205	450	20	-	-
23Cr-4Ni (SAF 2304)	UNS S32304	400	600-820	25	300	245±245
22Cr-5Ni-3Mo (SAF 2205)	UNS S31803	450	680-880	25	250	285±285
25Cr-7Ni-4Mo (SAF 2507)	UNS S32750	550	800-1000	25	230	300±300

3.5.2. Toughness

DSS have good toughness properties, which is explained by the presence of the austenite phase [FLOREEN and HAYDEN 1968]. Austenite retards the cleavage fracture of ferrite. High alloying results in some decrease of the impact toughness (Table 5) to about 230 J, although this value is also very high. CHARLES 1991 reported that ductile-to-brittle transition in the fracture mode of DSS occurs at $-60\text{ }^{\circ}\text{C}$, which is satisfactory for the great majority of applications.

Toughness is very sensitive to the precipitation of secondary phases. In the temperature range of $600\text{-}900\text{ }^{\circ}\text{C}$ σ , χ , R and π phases can precipitate, while at the temperatures below $500\text{ }^{\circ}\text{C}$ spinodal decomposition of ferrite takes place. Appearance of these phases in the microstructure of DSS reduces toughness significantly. This means that sufficiently high cooling rates must be provided to avoid the precipitation. NILSSON 1992 reported that cooling SAF 2507 DSS from the temperature of solution treatment $1060\text{ }^{\circ}\text{C}$ with the rate of 0.4 K/s results in the formation of 1% of σ phase. SAF 2507 can tolerate as much as 4% of σ phase before it reaches the critical value of 27 J of the impact energy, although this amount of σ phase is not allowed because of low corrosion resistance [NILSSON 1992].

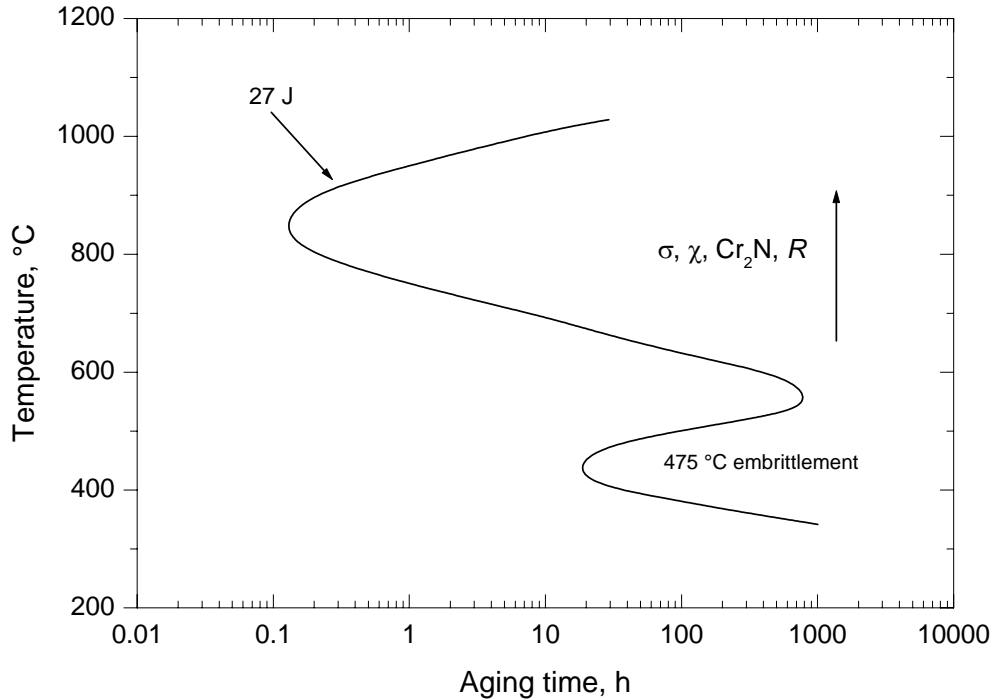


Figure 2. Time-temperature-transformation (TTT) diagram for SAF 2507 super DSS. The curve corresponds to 27 J impact toughness indicating the rate of embrittlement at different temperature regions [NILSSON 1992].

The exact mechanism of the embrittlement and toughness reduction at temperatures below 500 °C remains still unclear. However, it is believed that it is related either to the true spinodal decomposition of the ferrite phase, or to the classical nucleation and growth of α' phase. Low-temperature embrittlement can occur even at temperatures below 300 °C. Very long aging times are required, however. Different aging times can be expected for the welds as compared to the base materials. As a consequence, there are limits for the temperature range allowed for the DSS applications. The maximum recommended temperature is very much dependent on the chemical composition of an alloy.

3.5.3. Fatigue and corrosion fatigue

Fatigue and corrosion fatigue properties of DSS, especially P/M-HIPped grades were extensively studied at the Laboratory of Engineering Materials, Helsinki University of Technology [LAITINEN 1995, LAITINEN 1997]. It was concluded that duplex stainless steels reveal generally very good fatigue properties, better than those of austenitic stainless steels due to the higher strength of DSS. It was shown that P/M-HIP DSS posses better fatigue and corrosion fatigue resistance than the corresponding conventional forged DSS. The reasons for this were as follows [LAITINEN 1997]:

- P/M-HIP DSS are isotropic and insensitive to the test direction.
- Non-modified spherical inclusions are more corrosion resistant.

- Smaller phase size and homogeneous microstructure better resist crack initiation and growth.

It was also recognized that fatigue cracks grow preferentially in the ferritic phase and the austenite phase retards the crack growth.

Fatigue properties can apparently be improved by stress-relieving heat treatments resulting in formation of small amounts of σ phase. Finding the balance between the improved fatigue resistance and reduction in impact toughness and corrosion resistance because of precipitated secondary phases is not an easy task, and the dilemma is often solved in favor of as low amount of intermetallic secondary phases as possible.

3.6. Corrosion and stress corrosion cracking

The corrosion resistance of the duplex stainless steels, like any other stainless steel, can be described as the ability to passivate and to remain in the passive state in a given environment. Duplex stainless steels have essentially different alloying design as compared to austenitic stainless steels that is why DSS have shown significantly different rates of general corrosion. The corrosion properties of a duplex stainless steel constructions are defined, of course, not only by the average chemical composition of the grade, but by a number of different other factors, such as grain size, precipitation of intermetallic secondary phases, surface quality etc. However, the corrosion properties of the welded joints are undoubtedly one of the most important areas of research of duplex stainless steels today.

Chromium, molybdenum and nitrogen are the most important alloying elements in duplex stainless steels with respect to corrosion properties. Nickel serves mostly as the stabilizer of the austenite phase. Austenite phase is in general the weakest phase. Chromium and molybdenum prefer to reside in the ferrite phase, while nickel and nitrogen - in the austenite one. The strong partitioning of nitrogen (see 3.2) assists in obtaining proper balance between the phases and improves not only mechanical strength, but also, for example, the stress corrosion cracking (SCC) resistance.

3.6.1. General and local corrosion

PREN coefficient used for alloy ranking is, of course, unable to take into consideration effects of heat treatments, microstructural inhomogeneities and some important alloying elements, such as copper. NICHOLLS (1994) showed that copper has beneficial effect on the corrosion resistance of duplex stainless steel in pure sulfuric acid and sulfuric acid with chlorides environments. The alloying elements introduced to improve the corrosion resistance of a steel can, however, often form precipitates, leading at the same time to a local depletion of the matrix. The depletion, in turn, may result in a passivity breakdown.

Local corrosion attack most frequently occurs in DSS at the austenite/ferrite phase boundaries [NILSSON et al. 1992]. In modern DSS grades segregation of impurities does not seem to be a probable reason for that, since the steels are extremely pure (e.g., sulfur content can be achieved as low as 0.0015 wt. % or even less). Phase transformations

occurring at the grain and phase boundaries may indeed lead to a passivity breakdown. In SAF 2507 precipitation of Cr_2N , χ phase and secondary austenite during isothermal aging at 800 °C was found to initiate numerous pits in the secondary austenite close to the prior austenite/ferrite boundaries. Taking into account that secondary austenite is poor with chromium as compared to the primary one (21 wt. % vs. 24 wt. %, respectively), the idea of depletion in the elements capable of prevention pitting seems to be promising. However, precipitation of σ phase is much more harmful with respect of the corrosion properties because of its large volume fraction and associated depletion of surrounding matrix of chromium and molybdenum [NILSSON et al. 1992, JOSEFSSON, NILSSON and WILSON 1991].

Interesting to note that all modern duplex stainless steels are resistant in organic acids, such as acetic acid, whereas austenitic AISI 304L grade corrodes at high temperatures, and may also crack at high concentrations. In the formic acid, the most aggressive organic acid, most austenitic stainless steels and titanium corrode heavily at intermediate concentrations and high temperatures, while SAF 2507 is resistant almost to the boiling point [NICHOLLS 1994].

3.6.2. Pitting corrosion

The alloying elements determining the pitting corrosion properties of the stainless steels are again chromium, molybdenum and nitrogen. To determine quantitatively the effects of these elements on the corrosion resistance of stainless steels, pitting resistance equivalent, PREN, coefficient was introduced. Expression 1 gives the most commonly used formula. Sometimes different multiplying factor for the nitrogen content, varying from 10 to 30, is used for different types of stainless steels. For duplex steels, for example, the following formula is given in the literature [NILSSON 1992]:

$$\text{PREN} = [\text{wt.}\% \text{Cr}] + 3.3 \cdot [\text{wt.}\% \text{Mo}] + 10 \div 30 \cdot [\text{wt.}\% \text{N}]. \quad (3)$$

Other alloying elements, e.g. tungsten, also are sometimes taken into account [OKAMOTO 1992]:

$$\text{PREN} = [\text{wt.}\% \text{Cr}] + 3.3 \cdot [\text{wt.}\% \text{Mo} + \frac{1}{2} \text{wt.}\% \text{W}] + 16 \div 30 \cdot [\text{wt.}\% \text{N}] \quad (4)$$

In duplex stainless steels it is necessary to consider the pitting resistance for the two phases separately.

Initiation of pitting is very much affected by the condition of the surface – grinding, pickling, cold work, dirt, as well as the grain size, the presence of possible inclusions, and, of course, intermetallic phases.

3.6.3. Crevice corrosion

Crevice corrosion resistance of stainless steels is usually related to the pitting corrosion resistance. The critical crevice corrosion temperature (CCT) is roughly proportional to the critical pitting temperature (CPT). In crevice corrosion testing the tendency for corrosion is strongly dependent on the exact experimental parameters, such as the quality of the surface and the method of grinding, the material of crevice formers (metal, glass, ceramic, plastic) and crevice width (applied pressure). Thus, the experimental conditions are very difficult to control and reproduce, even if the standard procedures such as ASTM G48 and MTI-2 are observed [NICHOLLS 1994].

3.6.4. Stress corrosion cracking (SCC)

One of the first advantages of duplex stainless steels is their superior resistance to the stress corrosion cracking in chloride environments. The temperature limit increases with increasing alloying. AISI 316L austenitic stainless steel suffers from SCC even at a low chloride concentration of 0.1 % at approximately 60 °C, while no SCC was observed on super duplex alloys in 3 % sodium chloride solution even at 250 °C [FRANCIS 1994].

Susceptibility of duplex stainless steels to sulphide SCC depends on numerous factors, the major ones are temperature, sulphide concentration, pH and chloride content. 22Cr type steel in the annealed condition or lightly cold worked and super duplex stainless grades reveal maximum susceptibility to sulphide SCC in the temperature range of 70 to 100 °C. At higher levels of cold work, the susceptibility increases with increasing temperature with no indication of a maximum [FRANCIS 1994].

3.6.5. Hydrogen embrittlement

In the ever growing off-shore and subsea applications duplex stainless steels are cathodically protected. The cathodic protection is usually by aluminum alloy anodes with a potential of about -1 V standard calomel electrode. At this potential hydrogen is generated as a part of the cathodic reaction, it penetrates into the metal and can cause hydrogen embrittlement. It was, however, concluded [FRANCIS 1994] that very high loads, close to UTS, are required, so that the austenitic phase deforms plastically and the crack can propagate through it or along the phase boundary. Fine grain size increases the resistance of duplex stainless steels to the hydrogen embrittlement.

3.7. Welding of duplex stainless steels

During the welding virtually all duplex stainless steels solidify as ferrite. Partial transformation to austenite occurs at lower temperatures [LILJAS 1994]. The ratio of the ferrite content to that of austenite can be changed, which results in degradation of mechanical and corrosion properties of the weld joints and heat affected zones (HAZ). This behavior determines to a large extent the peculiarities of the welding of duplex steels. Additionally, during cooling secondary phases can precipitate.

It is clear that the main but not the only factor affecting strongly the quality of the weldments of duplex stainless steels is the chemical composition. The chemical composition determines the ferrite solvus and the precipitating phases. Other parameters determining, for example, the cooling rate are the heat transfer rate, the deposition rate, the physical dimensions of the components. The welding consumables such as shielding gas and the filler metal can adjust the phase balance. Filler metals with increased content of austenite-stabilizing elements (Ni) are often used. Nitrogen is used in shielding gas for the same purposes. Additionally, nitrogen contributes to the strengthening of the welds. A general approach for obtaining a favorable balance of the ferrite and austenite phases is to increase the heat input, preheat and increase the interpass temperature in the multipass technique to reduce the cooling rate and promote a complete ferrite transformation.

In this case, however, other factors leading to the deterioration of mechanical and corrosion properties, come into play, such as grain growth and secondary phase precipitation. Additionally, the efficiency of welding techniques giving good results is not very high, which makes them rather expensive. One possible alternative is narrow gap welding, which can provide some advantages as compared to the conventional GTA (gas tungsten arc) welding, namely lower heat input, reduced weld volume, smaller consumption of the filler metal and shielding gas, lower residual stresses [KORHONEN et al. 2000]. This technique requires more advanced equipment, accurate joint preparation and more expensive shielding gas. The method was successfully applied to welding of thick-wall Duplok 27 P/M HIP super duplex stainless steel components with improved welding quality [KORHONEN et al. 2000].

Despite the significant progress achieved in the welding of duplex stainless steels the subject will be one of the most important research topics in the future.

3.8. Internal friction

Internal friction is a manifestation of an anelasticity of solid. The study of internal friction started some 60 years ago with the discovery of the elastic aftereffect in carbonyl iron. SNOEK 1941 gave the explanation and developed the theory of the anelastic relaxation. According to the theory, the effect was caused by carbon atoms. Interstitial atoms produce local distortion of the BCC lattice. The symmetry of the distortion is tetragonal, i.e., lower than that of the parent matrix. In the applied external stress field, interstitial positions attain some difference with respect to the energy of elastic interaction with the field. The interstitial positions become distinguishable and carbon atoms migrate in the lattice finding the positions with the most favorable orientation in the applied stress field. The process of the carbon redistribution is the anelastic relaxation in the case of the Snoek effect. Activation enthalpy of the Snoek relaxation is apparently the activation enthalpy of the carbon diffusion.

The Snoek relaxation is, perhaps, the most well known type of anelastic relaxation. It has been mainly used for studying light interstitial (C, N, O) behavior in BCC metals. Recently, the development of the internal friction technique gained a new spin. Study of the Snoek relaxation was extended to FCC alloys. A new theory of the Snoek-like relaxation in multicomponent industrial alloys was developed [AALTONEN et al. 1998 (A), JAGODZINSKI, HÄNNINEN et al. 1999, and SMUK 1999]. The method was applied to studying the hydrogen behavior in industrial multicomponent FCC [JAGODZINSKI et al. 1998, AALTONEN et al.

1998 (A), SMUK et al. 1999 (A), and SMUK et al. 1999 (B)] and BCC [JAGODZINSKI, TARASENKO et al. 1999] alloys.

Besides the Snoek relaxation, many other relaxations exist and can be used for studying materials behavior. Snoek-Köster relaxation is related to the dragging of interstitials by mobile dislocations [KÖSTER, BANGERT and HAHN 1955, SCHOECK and MONDINO 1963, GAVRILJUK and YAGODZINSKIY 1986]. Zener relaxation was discovered in 70:30 α -brass near 400 °C for a frequency of 620 Hz [ZENER 1947 (A)]. It was assumed that the relaxation is due to a stress-induced reorientation of substitutional solute atoms in a nearest-neighbor positions [ZENER 1947 (B)]. The theory is restricted to only dilute solutions, where the number of solute pairs is relatively small. Hasiguti peaks related to dislocation-vacancy interaction were observed in copper [NOWICK and BERRY 1972, AALTONEN et al. 1998 (B)]. Using internal friction method, the excessive vacancy production resulted from the interaction of an alloy with environment was studied, as well [JAGODZINSKI, AALTONEN et al. 1999].

Internal friction has been, thus, proven to be a powerful method of scientific studies in materials science and can be applied to studying duplex steels, as well.

3.9. Hydrogen effects in duplex stainless steels

Hydrogen embrittlement (HE) is one of the potentially dangerous types of environmentally assisted cracking (EAC) of duplex stainless steels (see 3.6.5). Several sources of hydrogen accumulation in DSSs can be listed [GUNN 1997]:

- Local corrosion in hydrogen sulfide containing environments [OUDAR and MARCUS 1979]. Presence of sulfur in the solution and at the metal-environment interface inhibits the reaction of recombination of adsorbed atomic hydrogen to molecular hydrogen, and promotes hydrogen ingress into the metal [ZAKROCZYMSKI 1985].
- Cathodic reactions accompanying the cathodic protection used for the off-shore applications of DSS. In this case hydrogen is generated on the surface of the steel by cathodic reactions, and it diffuses into the bulk of the metal.
- Finally, hydrogen may enter the DSS during welding processes due to thermal decomposition of moisture or from shielding gas.

Diffusive transfer of hydrogen into the bulk of the metal is one of the limiting stages of the development of hydrogen embrittlement of DSSs. Therefore, a study of hydrogen diffusion parameters in DSSs of different compositions and microstructures is a necessary element of understanding the mechanisms of the development of hydrogen embrittlement and elaborating the ways of decreasing the sensitivity of duplex stainless steels to this type of EAC.

Turnbull *et al.* [HUTCHINGS, TURNBULL and MAY 1991, TURNBULL, LEMBACH-BEYLEGAARD and HUTCHINGS 1994, TURNBULL and HUTCHINGS 1994] studied diffusive transfer of hydrogen in a number of DSSs using the electrochemical permeation technique.

These studies revealed an exceptionally important role of ferrite-austenite interfaces as the reversible traps of hydrogen in DSSs.

A diffusive transfer of hydrogen in multiphase alloys of DSS type is of great interest, because a problem of mass transfer in heterogeneous systems remains still unsolved in a general form. Hydrogen has several orders higher diffusion rate in ferrite, while the solubility is higher in austenite, also several orders of magnitude, as compared to that of ferrite. Depending on the phase balance and the grain shape (e.g. P/M vs. wrought manufacturing technologies), different duplex stainless steels can behave essentially differently under the same environmental conditions.

Very little studies have been performed on the effects of hydrogen on mechanical properties, and fatigue properties in particular, so far. In the presence of hydrogen in an investigation of Zeron 100 DSS, enhanced crack growth involving cleavage fracture of ferrite was observed [MARROW, HIPPSLEY and KING 1991].

3.10. Thermodynamic calculations

Computational thermodynamics has been extensively used, especially through the CALPHAD approach, for more than 20 years [SAUNDERS and MIODOWNIK 1998]. Thermodynamic models of solid phases are based on the structure of the phase. The compound energy formalism is considered to be one of the most powerful methods to describe both liquid and solid phases [HILLERT 2001]. The CALPHAD technique can be summarized as follows:

- All available thermochemical and phase diagram information on the system is collected.
- Gibbs energy is defined for each phase of the system depending on the external conditions – temperature and pressure, and the composition. The model is based on the structural information, which takes into account other physical properties, as well, such as, for example, magnetism.
- The model parameters are adjusted to produce the best possible fit to the data.
- The model parameters can be used for extrapolation to more complex systems and experimental conditions, where there are no experimental data available.
- The obtained data are stored in database and can be used for modeling of other systems. Extended database is a necessary prerequisite for reliable modeling.

First-principles, *ab initio*, calculations can be applied in cases when no experimental input is available. Recent progress in refining the techniques for thermodynamic modeling and availability of ever-faster computers make *ab initio* calculations a valuable complement to the calculations based on the collected database. However, experiments are needed to verify both extrapolations and purely theoretical calculations.

The steel database TCFE3 has been used for calculations with the Thermo-Calc software for multicomponent iron-base alloys, also duplex stainless steels, and has been proven to be able to produce reliable results [ANDERSSON, HELANDER, HÖGLUND et al 2002, THERMO-CALC SOFTWARE 2002].

Thermodynamic calculations with the Thermo-Calc software were intensively used by Nilsson with co-authors to study the properties of duplex and super duplex stainless steels and their weld metal. Equilibrium phase diagram was calculated for the weld metal of 22Cr-3Mo-8Ni duplex stainless steel forcing R phase as an equilibrium one to obtain the chromium content in ferrite and the temperature range of miscibility gap, within which two different compositions of ferrite are simultaneously thermodynamically stable [NILSSON and LIU 1991]. The austenite-ferrite balance at high temperatures was modeled in [NILSSON, KARLSSON and ANDERSSON 1995], as well as the formation of secondary austenite. Two different approaches were used for the calculations of the formation of secondary austenite. One did not allow any diffusion transfer from the primary austenite, while the other one took the diffusion of carbon and nitrogen from the primary austenite to ferrite into account. Formation of secondary austenite at welding of super duplex stainless steels was studied using Thermo-Calc modeling also in [NILSSON, HUHTALA, JONSSON et al 1996, HUHTALA, NILSSON and WILSON 1994, NILSSON, JONSSON and WILSON 1994]. In these studies, the secondary austenite was allowed to achieve equilibrium simultaneously with ferrite and austenite. The restriction, however, was that both primary and secondary austenite had the same chemical composition, and the difference between the two types of austenite was solely the origin of formation. Alternatively, secondary austenite was set in the equilibrium with ferrite only, and primary austenite did not participate in the process at all. Temperature ranges of precipitation of secondary phases – Cr_2N , M_{23}C_6 and σ - in 29Cr-6Ni-2Mo-0.38N super duplex stainless steel, as well as the influence of nitrogen on the high-temperature limits of precipitation was studied by thermodynamic calculations in [NILSSON, KANGAS, KARLSSON et al 2000]. Thermo-Calc was used for calculations of element partitioning between ferrite and austenite [WEBER and UGGOWITZER 1998], estimation of PRE and evaluation of corrosion properties of duplex stainless steels [VANNEVIK, NILSSON, FRODIGH et al 1996]. In all the cases, the qualitative agreement between the calculations and the experimental data was good. The quantitative description provided by Thermo-Calc in some cases was poor, while in others it was sufficiently close to the experimental data.

TCFE3 database has been tested for the copper content of up to 1 wt. %. The steels studied with the Thermo-Calc software in the present work contain 1.6 and 2.3 wt. % Cu. Testing of the applicability of the database to such systems was one of the goals of the study.

Pooh looked at his two paws. He knew that one of them was the right, and he knew that when you had decided which one of them was the right, then the other one was the left, but he never could remember how to begin.

A. A. Milne, Winnie-the-Pooh

4. SUMMARY OF THE MAIN RESULTS

4.1. Precipitation kinetics in P/M-HIP duplex stainless steels

For establishing the main features and differences in the precipitation behavior of P/M duplex stainless steels industrial grades DUP 27 and Duplok 27 supplied by Rauma Materials Technology Oy (at present Metso Oyj) (Finland), and SAF 2507 supplied by Sandvik AB (Sweden) were selected. Additionally, a P/M equivalent of SAF 2507 super DSS, supplied by Bodycote Powdermet AB (Sweden), was used for comparison with widely used and well-documented SAF 2507 super duplex stainless steel. Table 6 gives the chemical compositions of the duplex and super duplex stainless steels studied at the first stage of the work after isothermal heat treatments. The composition of Duplok 27 is given in Table 7.

Table 6. Chemical compositions of the studied duplex and super duplex stainless steels.

Grade	C	Mn	Cu	Cr	Mo	Ni	N	Si
DUP 27	0.020	0.80	2.31	24.3	2.90	7.40	0.204	0.80
SAF 2507 P/M	0.024	0.72	0.13	24.7	3.95	6.98	0.260	0.51
SAF 2507	0.019	0.87	0.20	24.8	3.82	6.77	0.281	0.37

4.1.1. Microstructure of P/M-HIP super duplex stainless steels

Analytical transmission electron microscopy (ATEM) was applied for studying the precipitation kinetics of secondary phases. The isothermal heat treatments of 600 °C / 10 h, 700 °C / 2 h and 800 °C / 30 min were chosen. According to the TTT diagram of SAF 2507 steel, two latter treatments correspond to the precipitation of approximately 1 % volume fraction of different secondary phases, which gives a chance to detect the differences in the precipitation kinetics of the two grades. The first heat treatment is essentially inside the area of the precipitation of *R* phase.

The results of the ATEM study can be summarized as following:

- Aging treatment at 600 °C for 10 h results in precipitation of significant amounts of *R* phase in SAF 2507 DSS, while in DUP 27 alloy no intermetallic phases were detected.
- Very fine, 15-20 nm, coherent Cu-rich particles were observed in the ferrite phase of DUP 27 after the aging treatment at 600 °C for 10 h.

- Aging treatment at 700 °C for 2 h results in precipitation of large amounts of R phase in SAF 2507. Additionally, in SAF 2507, grain and, especially, phase boundaries are covered with an intermetallic film with the composition close to that of R phase. Respectively, in DUP 27 DSS, the amount of R phase is smaller and it precipitates as separate particles primarily on the austenite-ferrite phase boundaries. The continuous film of intermetallic phase at the phase boundaries similar to that observed in SAF 2507 was not detected in DUP 27.
- The amount of secondary austenite in DUP 27 is higher than in SAF 2507 and it is formed in the bulk of ferrite, apparently, by the Widmannstätten mechanism. In SAF 2507, secondary austenite is mainly formed at austenite-ferrite and ferrite-ferrite boundaries.
- In DUP 27, copper particles grow up to 80-100 nm long having the width of 30 nm and lose their coherency with the ferrite matrix after aging at 700 °C / 2 h, as compared to the 600 °C / 10 h aged condition.
- Aging treatment at 800 °C for 30 min results in drastically increased amounts of precipitated secondary phases. Sigma σ phase becomes the most important precipitation, along with secondary austenite. In DUP 27 the amount of precipitated σ phase and secondary austenite is close to 100 volume % in some grains. After the specified aging treatment, the mechanism of the secondary phase formation is clearly the eutectoid decomposition of ferrite into σ phase and secondary austenite in both grades.

4.1.2. Internal friction

Internal friction method was applied to studying duplex stainless steels for the first time. In the present study the anelastic response of two different origins was investigated in SAF 2507 duplex stainless steel after different aging treatments. One type of anelastic relaxation is caused by reorientation of pairs of chromium atoms in the ferrite lattice in the applied external elastic stress field. The other type of relaxation is caused by interstitial atoms – carbon (if present), nitrogen and hydrogen – in both the ferrite and austenite lattices.

As the result of the study, TTT-diagram of SAF 2507 type DSS was supplemented with the region where secondary austenite forms. At the annealing temperatures of 900 and 800 °C γ_2 phase starts to form after 30 min from the beginning of annealing, and at 700 °C after 2 h. The formation of the intermetallic phases and growth of the γ_2 phase content are accompanied by redistribution of nitrogen and substitutional alloying elements between phases of SAF 2507 type DSS.

Internal friction method is particularly useful in studies of hydrogen effects. Hydrogen produces a clear peak on the temperature dependence of internal friction. The area under the peak corresponds to the amount of hydrogen atoms participating in the Snoek-like relaxation. Hydrogen effects were studied by the internal friction method in conventional SAF 2507 and its P/M equivalent. Diffusion coefficients for hydrogen at room temperature (the temperature of hydrogen charging) were determined for both the ferrite and austenite phases in conventional and P/M super duplex stainless steels.

4.2. Development of heat treatment route for large industrial components manufactured from P/M-HIP super duplex stainless steel Duplok 27

At the second stage of this study the attention was focused on an industrial P/M-HIP super duplex stainless steel Duplok 27, an improved version of DUP 27, studied during the first stage. Table 7 shows the chemical composition of Duplok 27. A comprehensive investigation of the microstructure of Duplok 27 after a large variety of heat treatments was the main goal of this stage [SMUK et al. 2002]. The task was to determine a complex heat treatment route providing to large industrial components the best possible microstructure from the point of view of the secondary phase precipitation. Such a treatment is a trade off between the amount of precipitating secondary phases, possible build-up of residual stresses, high-temperature creep of large components and the limitations on the heating and cooling rates imposed by the equipment.

Table 7. Chemical composition of P/M-HIP super duplex stainless steel Duplok 27 studied at Stage 2.

Material	C	Si	Mn	S	P	Cr	Ni	Mo	Cu	Al	W	V	Ti	Co	O	N
Duplok 27	0.015	0.44	0.49	0.005	0.010	25.45	6.32	2.76	1.61	<0.01	<0.01	0.03	<0.01	0.03	0.0235	0.26

The main screening was performed using optical microscopy. ATEM was carried out for different cooling rates from the soaking temperature of 1020 °C. Mechanical and corrosion tests were carried out for these treatments. Microstructure and corrosion properties of welded joints and their HAZ subjected to selected heat treatments were studied, as well.

4.2.1. Microstructure of Duplok 27

The TTT diagram of SAF 2507 was used as the reference in studying the precipitation of intermetallic secondary phases in Duplok 27. It was found that Duplok 27 follows this diagram rather well, except for the boundary of precipitation of secondary phases in the temperature range of 1000-1100 °C and for the exposure time range of 0 to 3 h. In Duplok 27 this boundary rises faster and locates at higher temperatures than that for SAF 2507. Thermodynamic calculations performed later confirmed that the stability region of chromium nitride extends to higher temperatures in copper-containing Duplok 27 as compared with copper-low SAF 2507.

It was found that cooling rate of 20 °C/min results in rather clean duplex microstructure with virtually no intermetallic phases. The biggest difference as compared to the water quenched condition is the precipitation of fine copper-rich particles. Copper precipitates as copper-rich particles of two types – elongated rod-like particles with the width of 30-35 nm and the length of up to 700 nm, and nearly spherical particles of typical size from 50 to 100 nm. The mean distance between the particles is approximately 300 nm. The particles precipitate not only at isothermal treatment, but also at cooling with the rates up to at least 20 °C/min.

4.2.2. *Mechanical properties*

Tensile testing and impact toughness testing were performed for selected heat treatments of Duplok 27. It was shown that heat treatments resulted in precipitation of copper-rich particles of FCC phase alone without significant amounts of intermetallic secondary phases, such as cooling rate 20 °C/min, led to an increase of yield and ultimate tensile strength values by 10 and 20 MPa, respectively, as well as to a marginal (1 %) increase in the elongation and a slight (5 %) decrease in the reduction of area. This is an evidence of the positive effect of copper on hardening and more uniform plastic deformation during the tensile tests.

The nearly spherical copper particles are pinning points for dislocations, but the effect of the pinning on the yield strength is not very significant. Even after relatively fast (for the heat treatment of a large component) cooling with the cooling rate of 20 °C/min, the copper-rich particles have rather large size – the diameter 30 nm and the length approximately 400 nm, and large mean distance of 300 nm between them. The estimation of the hardening using the formula for Orowan mechanism [FRIEDEL 1964] results in fairly small value of approximately 50 MPa. The hardening observed experimentally is somewhat smaller of the same order of magnitude.

Impact toughness drops drastically for all studied cooling rates, even 20 °C/min, down to 4-22 J/cm², as compared to a rather high value of impact toughness 186 J/cm² after water quenching. This behavior was attributed to precipitates and precursors of secondary phases formed during soaking. It was suggested that soaking time shorter than 1 h would be beneficial for the mechanical properties of Duplok 27.

4.2.3. *Corrosion properties*

Critical pitting corrosion temperature (CPT) decreases also with decreasing cooling rate. The highest value of 77.5 °C was observed for the material water-quenched from 1020 °C. It was found to be higher than that for the material soaked for 1 h at the same temperature of 1020 °C and water-quenched. Copper-rich particles did not form in either case, neither precipitates of other secondary phase were found by TEM, SEM and optical microscopy. It was thus suggested that precursors of some secondary phase were responsible for the decrease of CPT after soaking. As thermodynamic calculations showed later, chromium nitride is a stable phase in Duplok 27 at the temperature of 1020 °C. Apparently, it were precursors of chromium nitride, which caused the observed decrease in CPT.

Consistently lower CPT values of the NG-GTAW welded joint than those of the base material are explained by the lower alloying level of the filler material used for welding of the samples and the lower local PRE value.

4.2.4. *Copper, its effects on properties of super duplex stainless steels*

The main features of copper precipitation in Duplok 27 are similar to those established previously for low-alloy steels. After the simulated industrial heat treatments with cooling rates of 20 and 10 °C/min, copper precipitates in the ferrite constituent of the duplex stainless steel as FCC phase containing, according to the Thermo-Calc, in addition to

copper small amounts of molybdenum and iron. Water quenching from the soaking temperature of 1020 °C does not result in copper precipitation.

Morphologically, the copper precipitates consist of nearly spherical particles with typical dimensions from 50 to 100 nm and rod-like particles with typical width of 30-35 nm and length of 250 to 700 nm depending on the cooling rate. The length-to-radius ratio of the rod-like particles varies from 8 to 25.

The precipitation of copper starts on dislocations and different interfaces at higher temperatures. This makes the fast growth of these particles possible, and they become those of the rod-like type. During further cooling, precipitation of copper-rich phase continues through the ferrite matrix producing particles of the nearly spherical morphology.

Secondary austenite formed during the eutectoid decomposition is often observed around copper-rich particles. It can thus be suggested that the copper-rich precipitates serve as the nucleation sites for the formation of secondary austenite during the eutectoid decomposition of ferrite. TEM investigation also showed that copper particles pin $\sigma - \gamma_2$ secondary austenite interfaces hindering the expansion of sigma phase.

4.3. Thermodynamic calculations with the Thermo-Calc software

In the present work thermodynamic calculations were performed for Duplok 27, DUP 27 and SAF 2507 industrial duplex and super duplex stainless steels, previously studied experimentally. The studied steels contain 1.6 (Duplok 27) and 2.3 (DUP 27) wt.% of copper. TCFE3 database used for modeling of iron-base alloys and steels was proven to work reliably for the copper content of up to 1 wt. %. The goal of the calculations was to investigate whether the experimental results obtained for high-copper duplex stainless steels can be reproduced using available thermodynamic descriptions and to analyze the behavior of the materials under conditions not studied experimentally.

Thermodynamic modeling with the Thermo-Calc software and available databases is a powerful modern tool for designing new materials. In addition to the information about the equilibrium phases present at the given conditions in the system, equally important role of such calculations is that they improve remarkably the understanding of the processes taking place in duplex stainless steel during heat treatment.

The Thermo-Calc Steel database, TCFE3, was proved to be capable of predicting qualitatively correctly precipitation of copper-rich phase in duplex stainless steels with the copper content as high as 2.3 wt. %. The main features of the precipitation of secondary phases, such as sigma, chi, and chromium nitride, were also described appropriately. According to the calculations copper affects strongly the ferrite-austenite balance at high temperatures, shifts significantly the high-temperature limit of the precipitation range of chromium nitride towards higher temperatures, and also affects the amounts and the precipitation range of intermetallic phases in duplex stainless steel .

Pooh knew what he meant, but being a Bear of Very Little Brain, couldn't think of the words.

A. A. Milne, Winnie-the-Pooh

5. MAIN CONTRIBUTIONS OF THIS STUDY

1. The morphology and kinetics of copper precipitation in duplex stainless steels was studied in detail. It was shown that copper precipitates as copper-rich FCC phase during cooling with cooling rate of 20 °C/min and slower and isothermal heat treatments above 600 °C. Precipitation of copper-rich particles starts at dislocations and different interfaces.
2. It was shown that particles of copper-rich phase serve as pinning points for dislocations, which leads to an improvement of tensile properties in the absence of intermetallic phases, though the improvement is rather small for the studied industrial heat treatment because of relatively large size and low volume fraction of the particles.
3. It was demonstrated that copper-rich particles act as nucleating sites for the formation of secondary austenite during the eutectoid decomposition of ferrite. Copper-rich particles pin the interface between secondary austenite and σ phase, hindering thus the expansion of σ phase.
4. Internal friction method was applied for the first time to studying the kinetics of phase transformations and hydrogen behavior in duplex stainless steels. TTT diagram of SAF 2507 was supplemented with the region where secondary austenite forms.
5. Diffusion coefficients of hydrogen in super duplex stainless steel were determined separately for the ferrite and austenite phases of both conventional SAF 2507 and its P/M equivalent using internal friction method.
6. A complex heat treatment route optimizing the microstructure was developed for commercial P/M-HIP duplex stainless steel Duplok 27 designed for the pulp and paper industry. The route takes into account dissolving of intermetallic secondary phases, avoiding the problems of high-temperature creep and build-up of high residual stresses, as well as limitations imposed by modern heat treatment equipment on the heating and cooling rates.
7. Comparative study of the precipitation kinetics of intermetallic secondary phases was carried out for a copper-rich duplex stainless steel DUP 27 and widely-used super duplex stainless steel SAF 2507 with low copper content. It was shown that at temperatures 600-700 °C copper-rich duplex stainless steel is less liable to the precipitation of intermetallic phases. As thermodynamic calculation showed later this difference in the precipitation behavior cannot be attributed solely to the decreased molybdenum content in copper-rich steel.

8. The thermodynamic calculations performed for duplex stainless steels of different compositions showed that copper decreases the high-temperature limit of precipitation of the harmful intermetallic sigma and chi phases and reduces the amount of precipitated chi phase.
9. The thermodynamic calculations showed that copper increases the high-temperature limit of precipitation of chromium nitride in duplex stainless steels. Early stages of precipitation of chromium nitride can be experimentally detected as degradation of corrosion resistance properties, even if precipitated particles cannot be observed by TEM.
10. It was suggested that copper addition to the steel affects the ferrite-austenite balance at temperatures above 900 °C in two ambivalent ways. Copper facilitates precipitation of chromium nitride phase destabilizing thus austenite but, being austenite-stabilizer, copper contributes of course to the direct stabilization of austenite in the system.

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