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MICROSTRUCTURE EVOLUTION IN SAF 2507 SUPER DUPLEX STAINLESS STEEL

RAZVOJ MIKROSTRUKTURE V SUPERDUPLEKSNEM NERJAVNEM JEKLU SAF 2507

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The change of microstructure for a super duplex stainless steel SAF 2507 during hot rolling was investigated. Its evolution during hot deformation was very different in each phase. The dominant restoration mechanism for ferrite and austenite were dynamic recovery (DRV) and dynamic recrystallization (DRX), respectively. Also, the effect of temperature on the deleterious phase precipitation was investigated. The specimens were heat treated isothermally in the temperature range 800 °C to 1000 °C. Hardness tests, and optical and scanning electron microscopy were used to detect the sigma phase.

Key words: super duplex stainless steel, hot rolling, microstructural evolution, sigma phase, ageing, hardness

Med vročim valjanjem je bil raziskan mikrostrukturni razvoj v superdupleksnem nerjavnem jeklu SAF 2507, ki se med vročo deformacijo razlikuje v vsaki fazi. Prevladujoč mehanizem mehčanja v feritu in avstenitu je bila dinamična poprava in/ali dinamična rekristalizacija. V superdupleksnem nerjavnem jeklu je bil raziskan vpliv temperature na izločanje škodljivih faz. Vzorci so bili izotermno toplotno obdelani v temperaturnem območju od 800 °C do 1000 °C. Uporabljene so bile meritve trdote ter optična in elektronska mikroskopija za analizo sigma-faze.

Ključne besede: superdupleksno nerjavno jeklo, vroče valjanje, mikrostrukturni razvoj, sigma-faza, žarjenje, trdota

1 INTRODUCTION

Depending on the chemical composition and applied thermomechanical processing, the microstructure of super duplex stainless steels (SDSS) consists mostly of different shares of ferrite and austenite and eventually of deleterious intermetallic phases. As a result, the optimisation of the mechanical properties and corrosion resistance of SDSS depends on the precise control of the evolution of the microstructure during the hot deformation and the subsequent ageing process. On the other hand, a solidification mode and an appropriate treatment is necessary to avoid the formation of undesirable intermetallic phases, e.g., σ and χ.[1,2,3] It is supposed that among the intermetallic precipitates, the sigma phase is the most detrimental, as it causes a considerable drop in the toughness and the corrosion resistance.[4] Thus, the proper control of the thermomechanical processing and subsequent ageing treatment are obligatory, not only for avoiding harmful precipitates, but also for achieving the desired mechanical properties. The hot ductility of the SDSS turns out to be extremely poor, making the production of DSS sheet steel very challenging.[5,26] Some authors suggested that the strain partitioning between ferrite and austenite of internal stresses at the phase boundaries and the segregation of impurities may lead to crack formation.[5,6,7]

Duplex or ferritic-austenitic stainless steels have a history almost as long as stainless steels. Along with the increased knowledge of use of alloying elements the process techniques in steel mills were also improved. With AOD or VOD and similar refining processes it was possible to add nitrogen in an inexpensive way and so reduce the levels of harmful impurities. The increasing alloying content makes the microstructure more prone to the precipitation of intermetallic phases with a negative effect on the corrosion resistance and ductility. There has been ample discussion concerning the individual effects of molybdenum and tungsten and the conclusion was that the replacement of Mo with W or Cu has a negligible effect on the phase stability and corrosion resistance. Copper additions were made to improve the corrosion resistance in reducing acids and alloying with tungsten was used to further improve the pitting resistance.[8] On the other hand, copper has been found to segregate on the surface of ferritic steels. The intensity of its surface segregation depends on the annealing temperature and its bulk content.[9]

The purpose of our investigation was to determine the effect of ageing in the temperature range from 800 °C to 1000 °C and hot rolling in the range from 1250 to 900 °C on the microstructural evolution of SDSS grade SAF 2507.

2 EXPERIMENTAL WORK

The SDSS SAF 2507 with the composition in **Table 1** was received as 20-mm thick plate from an industrial hot-rolling line. The as-received microstructure of the SAF 2507 shown in **Figure 1** consisted of approximately 58 % austenite and 42 % ferrite. Flat-shaped specimens (dimension of (60 × 47 × 20) mm) were soaked for 30 min at 1250 °C, transferred to a furnace, held at the rolling temperature in the range from 1250 °C to 900 °C in steps of 50 °C. The specimens were hot rolled in three passes with 20 % of the pass deformation. Afterwards, the specimens were aged at a temperature of 800 °C to 1000 °C for different times of (30, 120, 240 and 420) min and water quenched. To characterize the microstructures, the specimens were treated with standard grinding and polishing techniques, etched and examined with optical and scanning electron microscopy using secondary-electron emission with a 15 kV to 20 kV electron beam.

The material was supplied with a PREN (pitting resistance equivalent number) of 43, calculated using equation 1, which estimates the influence of the alloying elements Cr, Mo and N on the corrosion resistance in Fe-Cr-Ni alloys. The chemical composition (w/%) of duplex stainless steel is balanced to give approximately equal amounts of ferrite and austenite in the solution-annealed condition. The higher the annealing temperature, the higher is the ferrite content.

$$PREN/\% = w(\mathrm{Cr}) + 3.3\,w(\mathrm{Mo}) + 16\,w(\mathrm{N}) \qquad (1)$$

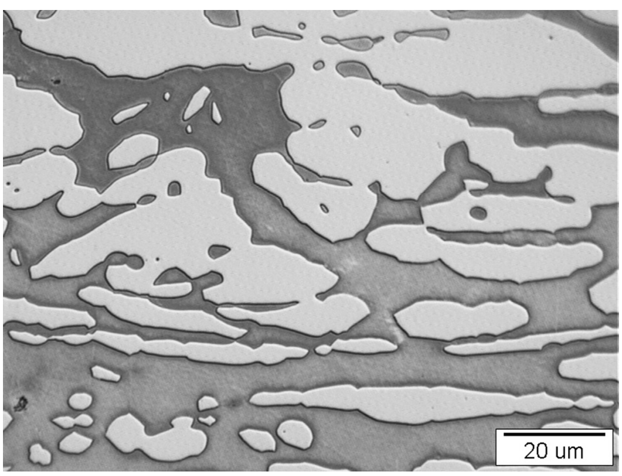

Figure 1: Microstructure of the as-received SAF 2507 super duplex stainless steel
Slika 1: Mikrostruktura superdupleksnega nerjavnega jekla SAF 2507

3 RESULTS AND DISCUSION

3.1 Evolution of the microstructure

The two-phase microstructure shown in **Figure 1** consists of austenite islands in a ferrite matrix. The microstructure after rolling with (3 × 20) % deformation is shown in **Figure 2**. The austenite islands are slightly elongated in the rolling direction. During test rollings the main change in microstructure is a more uniform distribution of ferrite and austenite. The presence of a bcc ferrite phase, which has numerous slip systems and a high stacking fault energy (SFE) in the vicinity of a fcc

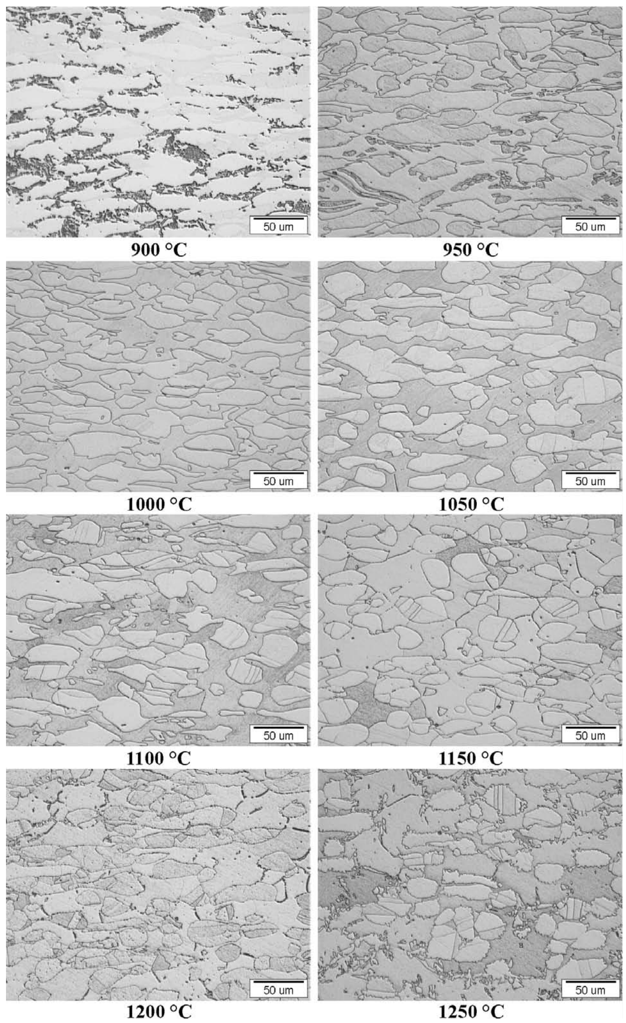

Figure 2: Microstructural evolution of SAF 2507 by (3 × 20)% per pass deformation
Slika 2: Razvoj mikrostrukture SAF 2507 po (3 × 20)-odstotni deformaciji

Table 1: Chemical composition of SDSS SAF 2507 in mass fractions, *w*/%
Tabela 1: Kemijska sestava SDSS SAF 2507 v masnih deležih, *w*/%

Elements	C	Si	Mn	P	S	Cr	Ni	Mo	Cu	N
w/%	0.023	0.3	0.73	0.023	0.0006	25.19	6.86	3.614	0.1	0.26

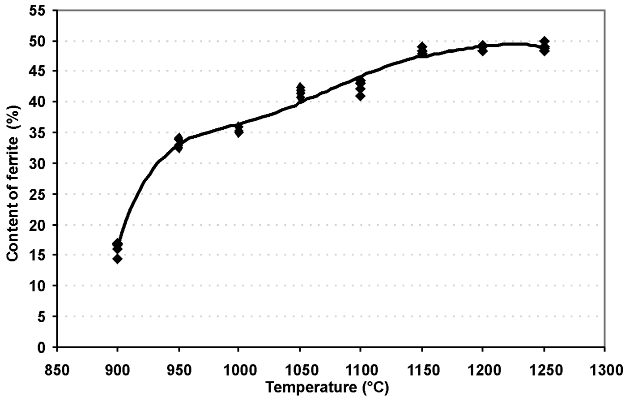

Figure 3: Evolution of the content of δ-ferrite with deformation temperature

Slika 3: Vsebnost δ-ferita v odvisnosti od temperature deformacije

austenite phase with less slip systems and low SFE strongly affects the recrystallisation behaviour. The kinetics of the austenite recrystallisation of austenite in the duplex structure is much slower than in a single-phase austenitic steel.[10] The dominant dynamic restoration mechanisms for ferrite and austenite are dynamic recovery (DRV) and dynamic recrystallization (DRX) respectively.[11] The coexistence of hard austenite and soft ferrite at high temperatures is found to result in a strain partitioning at the early stages of deformation, when the strain is mostly accommodated by the ferrite phase.[12] At higher strains, the load is transferred from the ferrite to the austenite leading to increment of dislocation density in the latter till triggering of DRX. An important difference between the DRX austenite phase of a duplex structure and a single-phase austenitic stainless steel is the role of grain-boundary serration and the bulging of new DRX grains with serrated boundaries (only above 1150 °C). Grain-boundary serration and bulging are the most important DRX mechanism in single-phase austenitic steels,[13] whereas this phenomenon is not often observed in the duplex structure, owing to the limited number of austenite/austenite grain boundaries. However, where these boundaries exist, they are the sites for new DRX grains on the serrated γ/γ boundaries (**Figure 2**, by 1200 °C and 1250 °C).

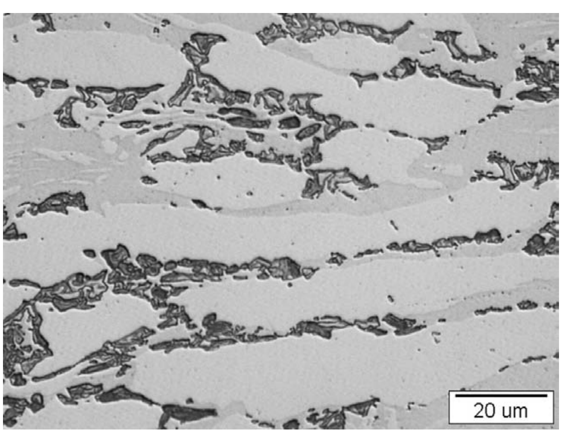

Figure 4: SEM secondary-electron micrograph after deformation at 900 °C

Slika 4: SEM-posnetek mikrostrukture po deformacji pri temperaturi 900 °C

The microstructure evolution during the hot deformation of the investigated duplex microstructure started with the formation of low-angle grain boundaries (LAGBs) in ferrite without any major influence on austenite[14]. These LABGs are the result of DRV as the dominant restoration mechanism in ferrite. These LABGs evolve and lead to a gradual build-up of higher misorientation between the neighbouring subgrains. The increase in ferrite subgrain size appears to be proportional to the increase in the average misorientation of the sub-boundaries in that phase.[14]

In contrast to ferrite, some discrete grain boundaries were observed in austenite. These actual grains were mostly formed on the serrated initial grain boundaries indicating DRX. The degree of recrystallization becomes larger with an increasing rolling temperature.

The volume fraction of each phase changed during hot deformation by hot rolling. **Figure 3** shows the evolution of the volume fraction of ferrite with the deformation temperature. The amount of ferrite increases between 1050 °C and 1250 °C with a maximum at 1250 °C. Above 1050 °C, the amount of γ phase decreases considerably with the deformation temperature, which is attributed to the $\gamma \rightarrow \delta$ phase transformation.

Figure 4 shows an SEM micrograph of a specimen deformed at 900 °C with a higher magnification. The content of δ-ferrite in the specimen was about 15 %. The δ-ferrite phase appears slightly darker than the bulk austenite, while the secondary sigma phases are brown. Secondary austenite (γ_2) appears in the form of islands in a matrix of ferrite, wrapped with a sigma phase having a lacy morphology.[15] It is known that the nucleation of the secondary austenite and sigma phase occurs through the eutectoid reaction $\delta \rightarrow \sigma + \gamma_2$.[16] As the precipitation continues, the ferrite stabilisers Cr and Mo diffuse from the ferrite to the sigma phase, which simultaneously force the ferrite to transform to the secondary austenite. While the Cr content only decreases slightly in ferrite, the decrease of Mo is pronounced and forces the Mo to diffuse from the inner parts of the ferrite matrix. This indicates that Mo is the main element controlling the

Table 2: Chemical composition of various phases obtained by EDS analysis (*w*/%)

Tabela 2: Kemijska sestava različnih faz z EDS-analizo, v masnih deležih, *w*/%

Elements	$w(\delta)$	$w(\gamma)$	$w(\sigma)$
Si	0.36 ± 0.04	0.34 ± 0.03	0.5 ± 0.08
Mn	0.69 ± 0.11	0.95 ± 0.18	0.77 ± 0.19
Cr	26.61 ± 0.59	24.41 ± 0.36	28.23 ± 0.56
Mo	5.11± 0.34	3.63 ± 0.22	8.16 ± 0.21
Ni	5.59 ± 0.45	8.03 ± 0.33	4.74 ± 0.24

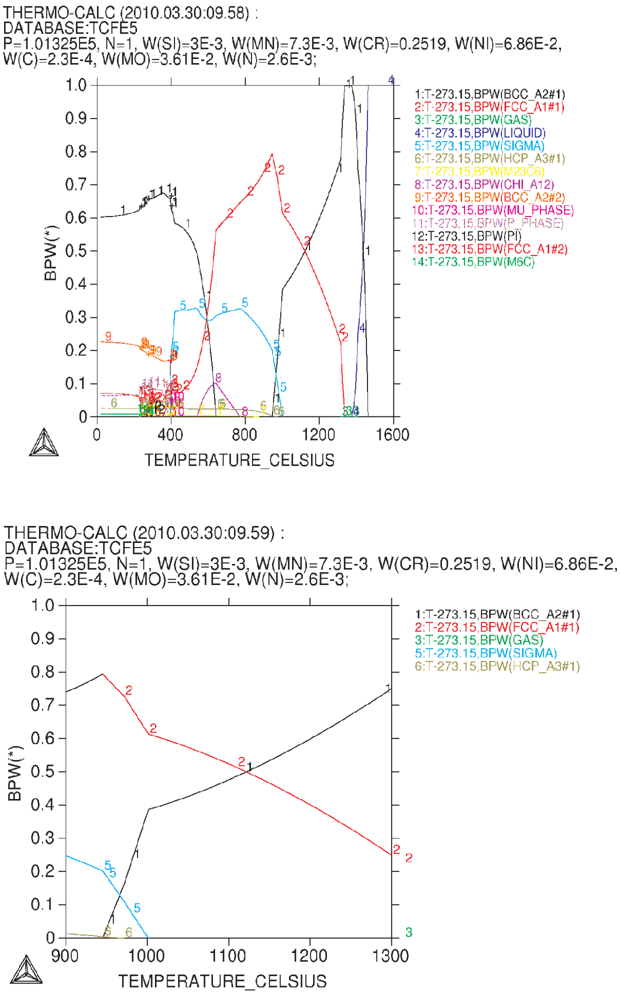

Figure 5: Calculated phase fractions in the investigated super duplex stainless steel SAF 2507

Slika 5: Izračunani deleži faz superdupleksnega nerjavnega SAF 2507

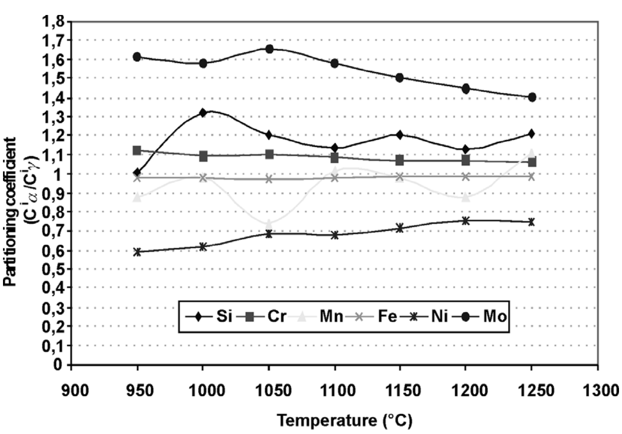

Figure 6: The partitioning coefficient of the alloying elements as a function of rolling temperature

Slika 6: Porazdelitveni koeficient legirnih elementov v odvisnosti od temperature valjanja

sigma phase precipitation.[16] The nucleation of the sigma phase predominantly occurs in ferrite/ferrite and ferrite/austenite grain boundaries. The nucleus then grows into the adjacent ferrite grains. The average compositions of the constituent phases, i.e., δ-ferrite, γ and sigma phases determined with EDS microanalysis are presented in **Table 2**. The results indicate that while δ-ferrite is rich in Cr and depleted with Ni, γ is rich in Ni and depleted in Cr. The EDS results further reveal that the sigma phase is rich in both Cr and Mo. These values are in good agreement with earlier reported results.[17,18]

As shown in **Figure 5** for the SAF 2507 (calculated with Thermo-Calc), intermetallic phase formation does not occur at temperatures above 1010 °C. With a decrease of the rolling temperature, the austenite volume fraction increases significantly from 33 % at 1250 °C up to 62 % at 1000 °C. This change of austenite volume fraction influences the mechanical behaviour of the duplex stainless steel because of the large difference in strength between ferrite and austenite.

3.2 Partitioning of elements

In the two-phase structure a clear compositional difference exists between the constituting phases. The elements Cr, Mo and Si are enriched in ferrite, while N, C, Ni and Mn are enriched in austenite and the change in the partitioning of elements as function of temperature occurs (**Figure 6**). The chemical composition of the phase influences its strength and SFE, hence its softening behavior.[19] Consequently, the changing partitioning of alloying elements with varying temperature contributes to the difference in the hot deformation behaviour of duplex stainless steel between the start and the end of hot rolling. Super duplex stainless steels show excellent hot deformability with a relatively low strain hardening up to at least 1230 °C. If hot rolling takes place at too low a temperature, deformation accumulates in the weaker but less ductile ferrite, which can result in cracking of the ferrite in the deformed region. Additionally, a large amount of sigma phase can be precipitated when the hot rolling temperature drops too low.

3.3 Precipitation of σ phase

The sigma phase is non-magnetic and intermetallic with the origin composition based in the iron-chromium system. According to the ternary iron-chromium-nickel system, the sigma phase is a thermodynamically stable phase that forms on the chromium-rich side of the ternary phase diagram Fe-Cr-Ni.[20] The mechanism of precipitation is a eutectoid transformation of ferrite into austenite and the sigma phase. The morphology of the sigma-phase precipitation changes depending on the temperature (**Figure 7**). At the lower temperature of 800 °C, a coral-like structure of sigma phase can be found. The number of single sigma nuclei at the beginning of the formation is rather high and it depends on diffusion distances that are smaller at a lower temperature. The different precipitation behaviour can be observed at higher temperatures of 1000 °C. The sigma phase is

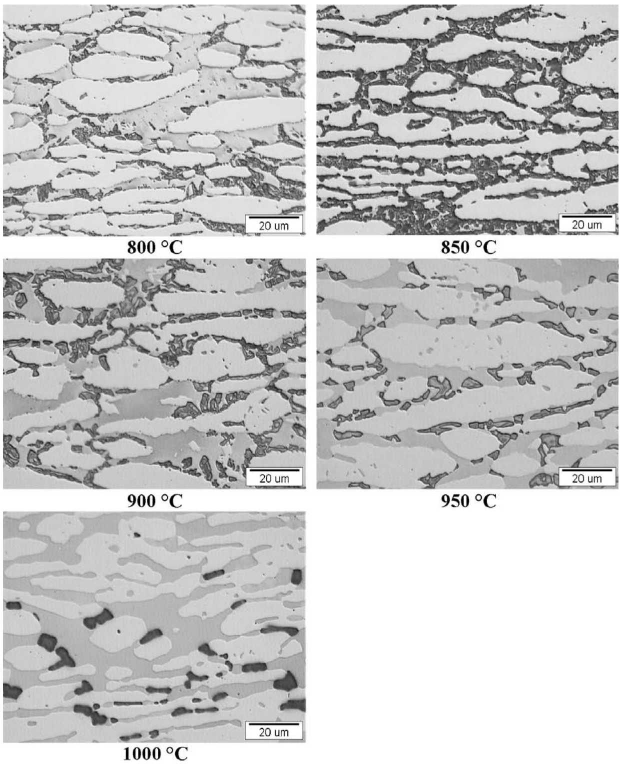

Figure 7: Morphology of the sigma phase at different isothermal annealing temperature, annealing time – 30 min

Slika 7: Morfologija sigma-faze pri različnih temperaturah izotermnega žarjenja; čas žarjenja 30 min

coarser and more compact and the difference is explained by the lower nucleation rate and higher diffusion rate at elevated temperatures.[21] For the SAF 2507 super duplex stainless steel, the precipitation level is pronounced, especially at 850 °C, where the intermetallic sigma phase formed after only 1 minute. In the super duplex stainless steel SAF 2507, ferrite did transform almost completely after only 1 h of ageing at 850 °C.[22]

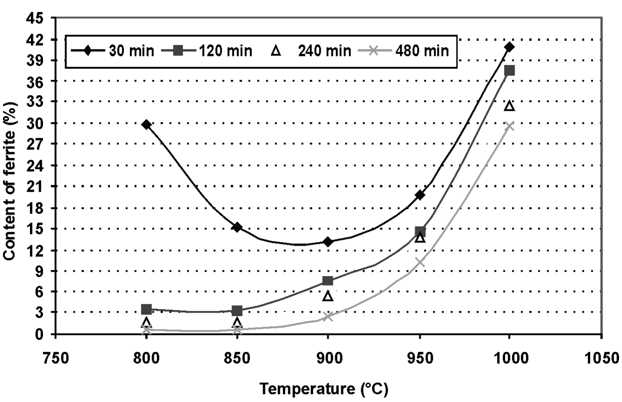

Figure 8: δ-ferrite content depending on temperature and time of isothermal annealing

Slika 8: Vsebnost δ-ferita v odvisnosti od temperature in časa izotermnega žarjenja

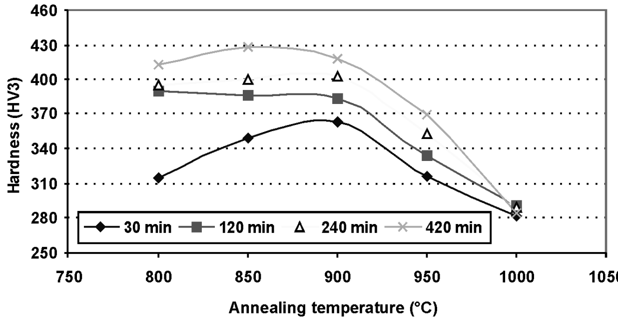

Figure 9: Effect of ageing temperature on the hardness of the steel at different ageing times

Slika 9: Vpliv temperature in časa žarjenja na trdoto jekla

Depending on the temperature and time of isothermal annealing, the microstructure of SAF 2507 super duplex stainless steel may consist of ferrite, austenite and sigma phase delimiting ferritic grain boundaries. The micrographs in **Figure 7** show that SAF 2507 is susceptible to sigma-phase formation in the temperature range 800 °C to 900 °C. Mostly, sigma phase is formed preferentially at the ferrite grain boundaries. The high susceptibility of the duplex stainless steels to sigma-phase formation is often attributed to the ferrite chemical composition, since ferrite is rich in sigma-forming elements such as Cr, Mo and Si, and poor in C, N and Ni, which are less soluble in the sigma phase than in austenite.[23] The chemical composition of austenite differs significantly from that of the ferrite due to the presence of ferrite-promoting elements (Cr, Mo and Si), that are enriched in ferrite during the solidification, while austenite-promoting elements (C, Ni and N) are enriched in austenite. With increasing annealing the quantity of sigma phase is increased with gradual growth through ferrite until the eventual consumption of entire ferrite grains.

The content of ferrite in the microstructure as a function of the annealing treatment is shown in **Figure 8**. It depends on the temperature and time of isothermal annealing.

The formation of σ phase is considered to be the main reason for the increase of hardness with annealing time and temperature. **Figure 9** shows the dependence between the hardness and the annealing time for different temperatures. The curves are similar in shape in the temperature range of 800 °C to 1000 °C for annealing times of (120, 240 and 480) min. For 30 min annealing the hardness is increased in the temperature range 800 °C to 900 °C from an initial non-aged value of 256 HV3, for the microstructure in **Figure 1**, to a maximum hardness value of 363 HV3 at 900 °C. The increased hardness is caused by the presence of a greater amount of secondary austenite and σ phase. After the ageing at 1000 °C, the hardness was slightly higher (282 HV3) than that measured at the solution annealed material (256 HV3). A pronounced increase in hardness was found in the temperature range 800 °C to 900 °C with an increase in the ageing time from 30 min to 120 min. The hardness values are in general agreement with the microstructure evolution and it seems that the longer-time isothermal ageing is much more effective in hardening the super duplex stainless steel.[24]

After solution annealing at 1075 °C, 1100 °C and 1125 °C and quenching in water the sigma phase is decomposed and a duplex microstructure of ferrite and austenite is obtained. No intermetallic phase was found at the grain boundaries and inside the ferrite grains. **Table 3** shows the properties obtained after solution annealing. Similar results have been reported for the UNS S32750 super duplex stainless steel after the same testing conditions.[25]

Table 3: The tensile test results obtained after solution treatment
Tabela 3: Mehanske lastnosti jekla po raztopnem žarjenju

Tempera-ture T/°C	σ_{YS}/MPa	σ_{UTS}/MPa	Elongation (%)	Reduction of area (%)
1125	616	869	31	64
1100	613	864	31,1	64
1075	612	859	31,9	64

4 CONCLUSIONS

The microstructure of duplex stainless steel SAF 2507 consists of different amounts of ferrite and austenite as well as unwanted intermetallic phases. The optimisation of the mechanical properties and corrosion resistance of this steel depends on the development of the microstructure of the alloy between hot deformation and latest process of annealing for preventing the formation of intermetallic phases. From the results of the investigation of the microstructure after rolling and isothermal annealing in the range of temperature between 800 °C and 1250 °C it is concluded that:

During hot deformation, dynamic recovery and polygonization in the ferrite occurs. In austenite there are nuclei of recrystallized grains on serrated boundaries at the temperature of rolling equal to 1200 °C and above. Practically at all temperatures of super duplex deformation over 1000 °C the deformation twins in grains of austenite appear. The dominant dynamic restoration mechanisms for ferrite and austenite are dynamic recovery (DRV) and dynamic recrystallization (DRX), respectively. However, owing to the limitation in the number of austenite/austenite boundaries, the evolution of DRX in austenite was limited. In stainless steel SAF 2507 the intermetallic phase σ at temperature of deformation 950 °C and lower is also formed.

In the area of hot deformation the proportion of phases ferrite and austenite is changed, also. The content of ferrite after triple deformation at initial temperature of deformation 1250 °C is of 47 % and it is reduced to 34 % at a temperature of deformation of 950 °C. At a deformation temperature of 900 °C, the share of ferrite is drastically reduced because of the eutectoid transformation in the phase σ and in the secondary austenite.

In a two-phase microstructure the differences in the contents of alloying elements between the phase constituents exist. The elements chromium, molybdenum and silicon are enriched in ferrite, while nitrogen, carbon, manganese and nickel are enriched in austenite. At a higher temperature of deformation the differences in the composition of both phases are lower, because of the change of their ratio.

Within the optimal area of hot processing and air cooling the microstructure of the duplex stainless steel remains within the two-phase field of the phase diagram Fe-Cr-Ni. The microstructure consists of alternative lamellas of ferrite and austenite.

The volume share of the σ-phase is relatively great at a temperature of deformation of 900 °C and is he cause for an increase of the deformation resistance and the mechanical properties of steel. The temperature of isothermal annealing affects strongly the volume share and morphology of the phase σ. At a lower temperature of precipitation the phase σ has a coral morphology. The higher propensity to precipitation of the phase σ in the duplex stainless steel is connected with the ferrite composition, which is enriched by elements that form phase σ (Cr, Mo and Si) and depleted of elements that are less soluble, for example, C, N and Ni. The phase σ grows into ferrite grains because it is thermodynamically more stable and with its formation the system achieves the equilibrium state.

The equilibrium microstructure in the temperature range between 800 °C and 900 °C is a mixture of austenite and phase σ. The results show that the super duplex stainless steel SAF 2507 is very sensitive to the formation of phase σ in the temperature range between 800 °C and 900 °C.

The investigation verified that the formation of the phase σ is the main reason for an increase of the hardness independent of the annealing time and temperature. By annealing at 1075 °C, 1100 °C and 1125 °C the sigma phase is dissolved and ferrite and austenite are obtained, which is typical for the duplex structure.

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