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TEM STUDY OF DISLOCATIONS IN DUPLEX STAINLESS STEEL

ŠTUDIJA DISLOKACIJ V DUPLEKSNEM NERJAVNEM JEKLU S PRESEVNO ELEKTRONSKO MIKROSKOPIJO

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Specimens of duplex stainless steel (DSS, the 258-alloy type) were isothermally annealed (aged) at 300 °C and 350 °C for 10000 h and 30000 h. Spinodal decomposition of the solid solution in ferrite occurs during the thermal ageing of this material with a redistribution of mainly Cr and Ni and a formation of nanocellular domains. This causes significant changes in the mechanical properties (the hardness and the tensile strength increase, while the ductility and the notch toughness decrease). The change in the mechanical properties may be related to the changes in the material's internal structure (stacking faults, the morphology and density of dislocations) or/and internal stresses. Therefore, non-aged and aged specimens were studied using transmission electron microscopy (TEM).

Keywords: duplex stainless steel, ferrite, austenite, spinodal decomposition, transmission electron microscopy, dislocations

Vzorci dupleksnega nerjavnega jekla (DSS, tip zlitine 258) so bili izotermno žarjeni (starani) pri temperaturah 300 °C in 350 °C v trajanju 10000 h in 30000 h. Med toplotnim staranjem naj bi se v materialu pojavil spinodalen razpad trdne raztopine v feritu, predvsem s prerazporeditvijo Cr in Ni ter oblikovanjem nanoceličnih domen. To povzroča znatne spremembe mehanskih lastnosti (povečanje trdote in natezne trdnosti ter zmanjšanje razteznosti in zarezne žilavosti). Sprememba mehanskih lastnosti je lahko povezana s spremembo notranje strukture materiala (napak zloga, morfologije in gostote dislokacij) in/ali notranjih napetosti. Zato je bila izvedena študija s presevno elektronsko mikroskopijo (TEM) nestaranih in staranih vzorcev.

Ključne besede: dupleksno nerjavno jeklo, ferit, avstenit, spinodalni razpad, presevna elektronska mikroskopija, dislokacije

1 INTRODUCTION

Many metallic alloys, including duplex stainless steels (DSSs), consist of austenite (γ-Fe) and ferrite (α-Fe). The two phases have different crystal lattices, austenite having a face-centred cubic lattice (fcc) and many slip-plane systems that prevent cleavage, and ferrite having a body-centred cubic lattice (bcc) that is more easily deformable than austenite, with a propensity for cleavage. The susceptibility to cleavage is greater at lower temperatures, increasing with an addition of certain alloying elements such as chromium, silicon, phosphorus, etc., and it is higher for a coarse-grained microstructure.

Nowadays, DSSs are used in a wide range of industries, especially in the oil and gas, petrochemical, paper and nuclear industries, because of their excellent combination of mechanical properties and corrosion resistance. Austenitic Fe-NiCrMo alloys have high toughness and good resistance to oxidation and scaling.[1] An addition of Ni, Cr and Mo to iron alloys suppresses the polymorphic austenite (γ) ⇔ ferrite (α) transformation. In the alloys containing high amounts of Cr, the solid solution of Cr and Ni or Co in α-Fe is not stable[2] and it decomposes with a spinodal process up to 750 °C.[3,4] The ferritic-austenitic DSS possesses a specific microstructure, where austenite and ferrite may create internal stresses during the deformation due to their elastic and plastic differences.[5]

The localization of the plastic strain is a typical feature of the fatigue of metallic materials. One of the basic classes of crystal defects is the linear defect, consisting of dislocations, where the rows of atoms are in irregular positions. There are two general types of dislocation: the edge (the Burger vector is perpendicular to the dislocation line) and the screw (the Burger vector is parallel to the dislocation line) dislocations. In 1934 Taylor and Polanyi confirmed dislocations as the carriers of plastic deformation.[6,7] Dislocations have the strain fields arising from the distortions at their cores – the strain drops radially with the distance from the dislocation core. Edge dislocations introduce compressive, tensile and shear lattice strains. Screw dislocations introduce the shear strain only. According to Roters, Raabe and Gottstein[8], there are three dislocation classes: the density of mobile dislocations travelling through a cell structure (ρ_m), the immobile dislocation density inside the cells (ρ_i), and the density of immobile dislocations in the cell walls (ρ_w).

The aim of our research was to investigate ferrite and austenite grains using transmission electron microscopy

Table 1: Average chemical composition in mass fractions (*w*/%) of duplex stainless steel (DSS), 258-alloy type
Tabela 1: Povprečna kemijska sestava v masnih deležih (*w*/%) dupleksnega nerjavnega jekla (DSS); tip zlitine 258

Average chemical composition in mass fractions (*w*/%)											
C	Cr	Ni	Mo	Mn	Si	Cu	Co	Nb	P	S	N
0.033	22.28	9.92	2.34	0.91	0.86	0.26	0.06	0.051	0.031	0.003	0.051

(TEM) or high-resolution TEM (HRTEM) with energy-dispersive X-ray spectrometry (EDXS) and to observe dislocations (the kind of dislocations and their locations in the specimens) in austenitized (non-aged) and annealed (aged at 300 °C and 350 °C for 10000 h and 30000 h) DSS, the 258-alloy type.

2 EXPERIMENTAL WORK

The specimens of DSS (the 258-alloy type) were austenitized at 1100 °C for 6 h, water quenched and then isothermally annealed (aged) at 300 °C and 350 °C for 10000 h and 30000 h. Thin foils of specimens were prepared using argon ion slicing with a JEOL EM-09100IS Ion Slicer[9,10] or electrochemical thinning with the final application of jet electropolishing.

The preparation of thin foils by means of argon ion slicing using an ion slicer is a novel method that enables a quick preparation of high-quality specimens for TEM. The specimens with a thicknesses of around 500 µm were cut out from the bulk material, having a rectangular shape of (0.5–1.0) mm × 2.8 mm (a bulk cross-section preparation), then thinned to less than 100 µm with the grinding paper SiC 800 (the grain size of around 22 µm), and further thinned with an argon ion beam. The thinning process started at the pressure of 10^{-5} Pa or 10^{-4} Pa and alternated between the front and backside of the rotating specimens. The beam was tilted between 1.0° to 2.5°. The accelerating voltage between 4.0 kV and 6 kV, the argon-gas-flow rate between 7.1 and 7.5 (arbitrary units) and the side change interval of 30 s or 60 s were chosen. After a large thin area of the specimens up to (300–500) µm × 700 µm was obtained, a small hole was made in the thinnest region of the specimens. Polishing was done at the tilt angle of 0.5°, at the accelerating voltage of 2 kV and the side change interval of 15 s or 40 s for 7 min, 10 min or 15 min. The total time of thinning was up to 9 h and 40 min.

The other method of thin-foil preparation consisted of diamond-saw cutting of about slices 0.3 mm, mechanical grinding, electrochemical thinning, punching out diameter 3 mm thin disks and final jet electropolishing with a Struers Tenupol-5 device.

After the thin-foil preparations, the non-aged and aged specimens were examined with TEM (JEOL JEM-2100) at the electron accelerating voltage of 200 kV using conventional TEM (CTEM), high-resolution TEM (HRTEM), electron diffraction (ED), and an energy-dispersive X-ray spectrometer (EDXS, JED-2300T).

The results of the inductively coupled plasma atomic emission spectroscopy (ICP-AES) bulk average chemical composition in mass fractions (*w*/%) of the starting (non-aged) material of DSS, the 258-alloy type, are shown in **Table 1**. The base metal is iron.

3 RESULTS AND DISCUSSION

Thin foils for the investigations of non-aged and aged DSS (the 258-alloy type) were studied by means of TEM in order to define ferrite and austenite phases and to observe dislocations.

Dislocations in the non-aged DSS are shown in **Figure 1**. An HRTEM image and EDXS spectra of ferrite and austenite in the same material are shown in **Figures 2** and **3**, respectively. The insets are fast Furier transforms (FFTs). The disorientation that is slightly less evident in **Figure 2** (the α-phase) may be an indication of the size of the spinodal domain. This is yet to be investigated. The elemental composition of the non-aged DSS determined with the TEM/EDS analysis is shown in **Table 2**. Ferrite has a higher content of Cr than austenite and austenite has a higher content of Ni than ferrite. The CTEM bright-field images of dislocations in the aged (annealed) DSS are shown in **Figure 4**.

An example of the interactions of electrons and elastic stresses at the grain boundary between ferrite and austenite in one of the aged DSS specimens (350 °C for 30000 h) is shown in **Figure 5**. The elemental composition of the small areas of the specimen determined with the TEM/EDS analysis is shown in **Table 3**. Compared to the non-aged specimen (**Table 2**), the aged specimen

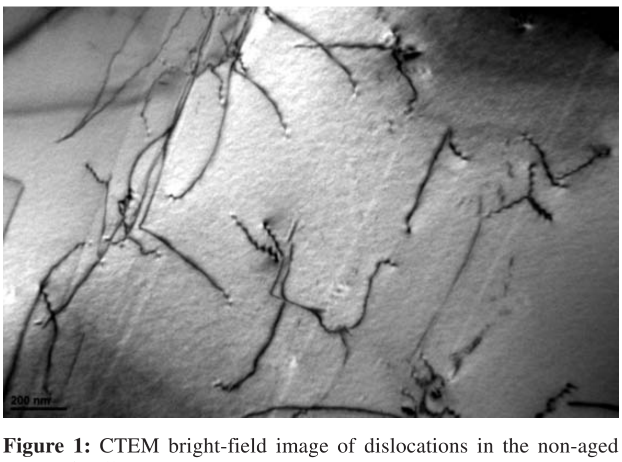

Figure 1: CTEM bright-field image of dislocations in the non-aged DSS, 258-alloy type
Slika 1: Posnetek CTEM v svetlem polju prikazuje dislokacije v nestaranem DSS, tip zlitine 258

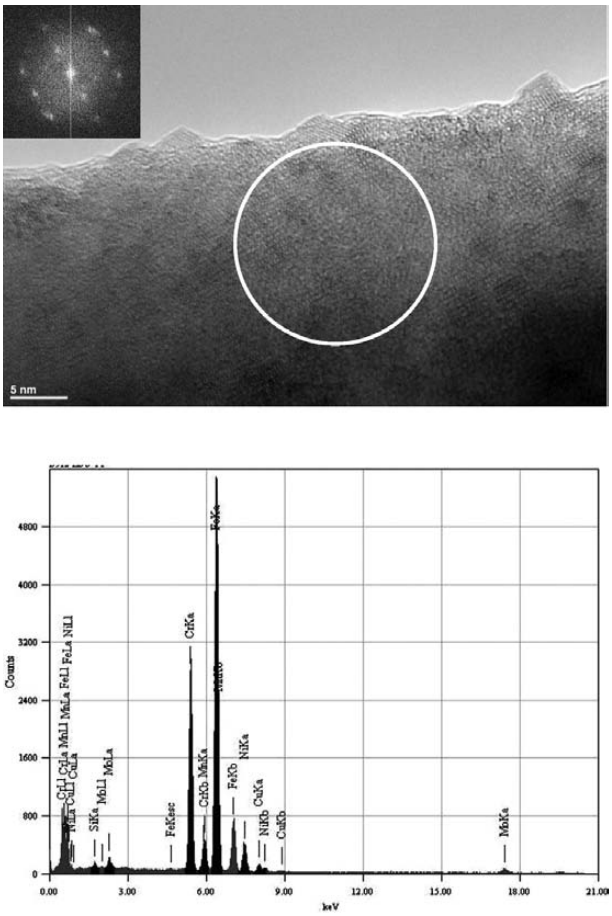

Figure 2: HRTEM image and EDXS spectrum of the indicated area of ferrite in the non-aged DSS, 258-alloy type. The inset is the fast Fourier transform (FFT).

Slika 2: Posnetek HRTEM in rentgenska spektroskopija (EDXS) označenega področja v feritu, nestaranega vzorca DSS, tip zlitine 258. Vstavljena slika prikazuje hitro Fourierjevo transformacijo (FFT).

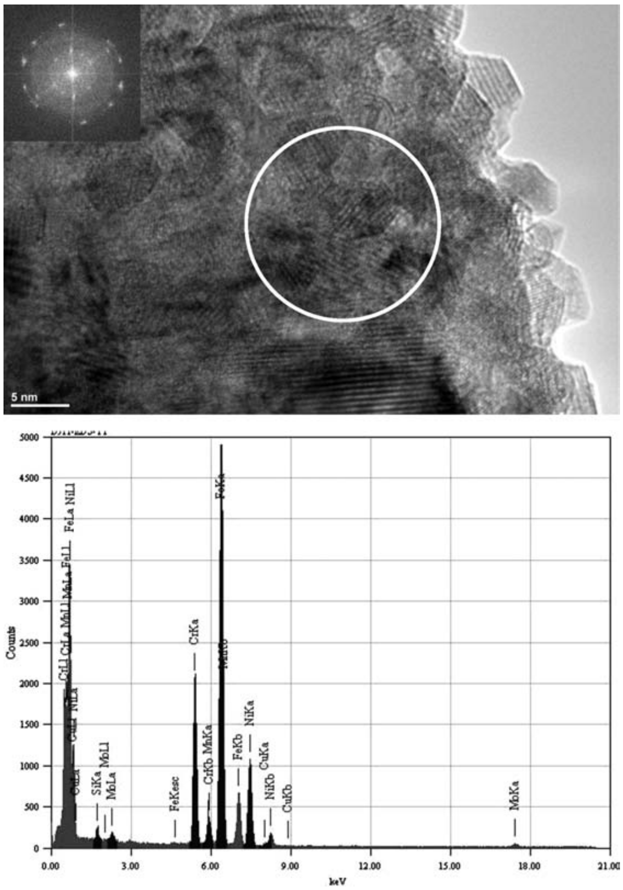

Figure 3: HRTEM image and EDXS spectrum of the indicated area of austenite in the non-aged DSS, 258-alloy type. The inset is the fast Fourier transform (FFT).

Slika 3: Posnetek HRTEM in rentgenska spektroskopija (EDXS) označenega področja v avstenitu, nestaranega vzorca DSS, tip zlitine 258. Vstavljena slika prikazuje hitro Fourierjevo transformacijo (FFT).

Table 2: Elemental composition of ferrite and austenite in the non-aged DSS, 258-alloy type, determined with the TEM/EDXS analysis

Tabela 2: Elementna sestava ferita in avstenita v nestaranem DSS, tip zlitine 258, določena z rentgensko spektroskopijo (TEM/EDXS)

Element	Energy (keV)	ferrite		austenite	
		Mass (%)	Error (%)	Mass (%)	Error (%)
Si K	1.739	0.35	0.13	0.69	0.17
Cr K	5.411	27.75	0.00	21.16	0.01
Mn K	5.894	0.38	0.20	0.69	0.28
Fe K	6.398	61.58	0.00	59.87	0.00
Ni K	7.471	5.35	0.02	14.85	0.02
Cu K	8.040	1.68	0.07	0.43	0.66
Mo L	2.293	2.90	0.06	2.30	0.20
Total		100.00		100.00	

has a slightly different composition: its ferrite has a slightly higher content of Mn, Ni, Mo and Si, and a lower content of Cr and Cu, while the austenite has a slightly higher content of Mn and Cu, and a lower content of Ni, Cr, Mo and Si.

Spinodal decomposition occurs during thermal ageing of this type of material. It is characterized by the formation of a nanocellular microstructure of ferrite domains with the austenite regions enriched with Cr and the other alphagene alloying elements as well as the regions enriched with Co, Ni and the other gammagene alloying elements. Because of the difference in the local chemical composition, the lattice parameters are modified and their accommodation creates elastic stresses that increase the hardness and change the mechanical properties (the tensile strength increases, while the ductility and toughness decrease). The change in the mechanical properties may also be related to the changes in the material's internal structure (stacking faults, the morphology and density of dislocations). It has been established that the density of dislocations may have increased during the ageing at 300 °C and that these dislocations appeared in different configurations with many of them being substantially mobile (numerous side trails and traces of dislocations escaping to the foil surface) (**Figure 4**), while many other dislocations became immobile

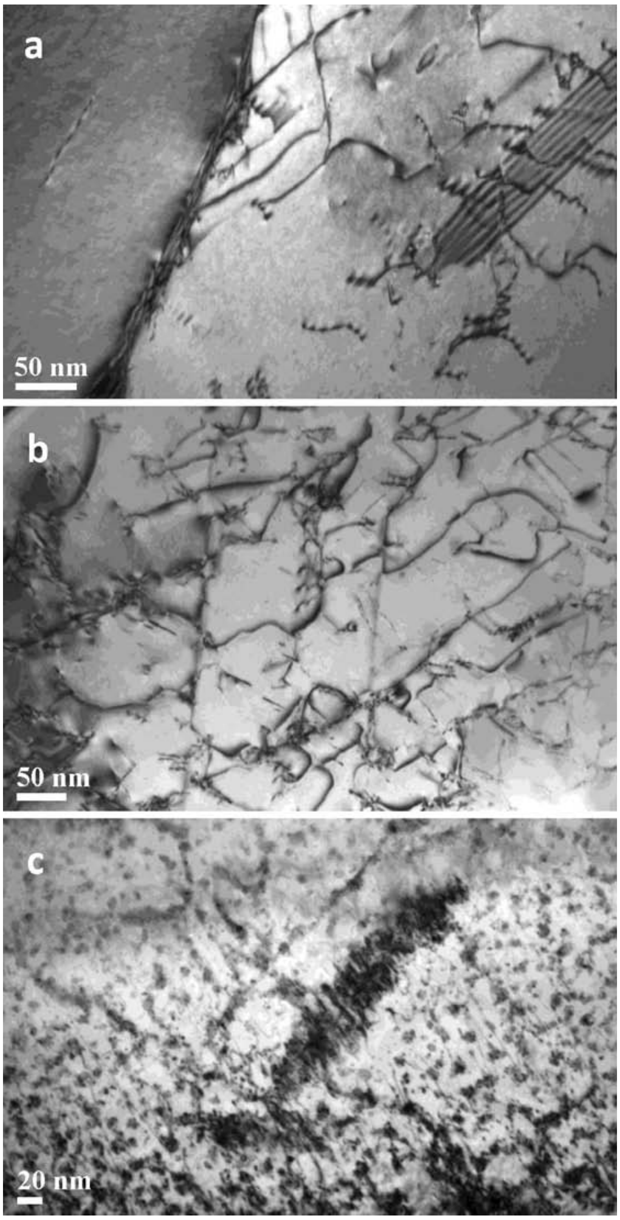

Figure 4: CTEM bright-field images of dislocations in the aged (annealed) DSS, 258-alloy type: a) 300 °C for 10000 h, b) 350 °C for 10000 h, c) 350 °C for 30000 h

Slika 4: Posnetki CTEM v svetlem polju prikazujejo dislokacije v staranem (žarjenem) DSS, tip zlitine 258: a) 300 °C in 10000 h, b) 350 °C in 10000 h, c) 350 °C in 30000 h

(or at least slowed down in their movements) after the ageing at 350 °C (**Figure 4**) when the transformation of the matrix occurred (**Figure 6**), leading to a virtually equilibrium state according to the effect of the ageing temperature on the change in the Charpy notch sharpness. Spinodal decomposition is faster at a higher temperature because of a greater diffusion rate. Due to spinodal decomposition, elastic stresses are generated at the austenite/δ-ferrite phase boundary. Dislocations may be slowed down in their movements or become immobile because of the grain (phase) boundary or obstacles. However, until now, we have not been able to detect such

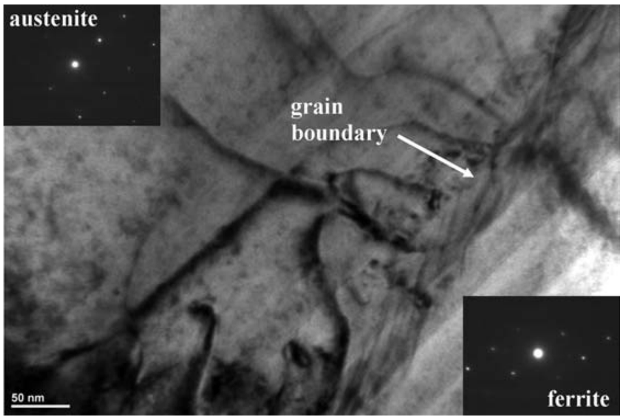

Figure 5: CTEM image of an accumulation of dislocations at the grain boundary between ferrite and austenite in the aged DSS specimen, 258-alloy type (annealed at 350 °C for 30000 h). The insets are electron-diffraction patterns of ferrite (bcc – body-centred cubic structure) and austenite (fcc – face-centred cubic structure).

Slika 5: Posnetek CTEM kopičenja dislokacij na meji zrn med feritom in avstenitom v staranem (350 °C, 30000 h) DSS, tip zlitine 258. Vstavljeni sliki prikazujeta uklonska posnetka ferita (bcc – telesno centrirana kubična struktura) in avstenita (fcc – ploskovno centrirana kubična struktura).

Table 3: Elemental composition of ferrite and austenite in the aged (annealed at 350 °C for 30000 h) DSS, 258-alloy type, determined with the TEM/EDXS analysis

Tabela 3: Elementna sestava ferita in avstenita v staranem (žarjenem pri 350 °C, 30000 h) DSS, tip zlitine 258, določena z rentgensko spektroskopijo (TEM/EDXS)

Element	Energy (keV)	ferrite		austenite	
		Mass (%)	Error (%)	Mass (%)	Error (%)
Si K	1.739	0.55	0.31	0.46	0.25
Cr K	5.411	27.13	0.01	20.31	0.01
Mn K	5.894	2.28	0.12	1.40	0.14
Fe K	6.398	59.85	0.00	63.77	0.00
Ni K	7.471	6.27	0.05	11.67	0.02
Cu K	8.040	0.63	0.64	0.56	0.48
Mo L	2.293	3.29	0.20	1.82	0.24
Total		100.00		100.00	

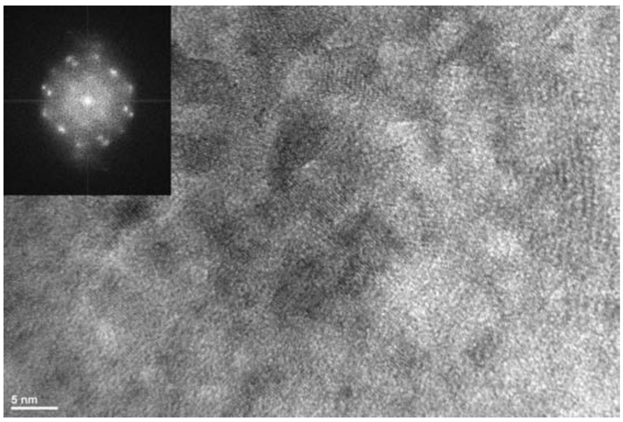

Figure 6: HRTEM image of the matrix of the aged DSS specimen, 258-alloy type (annealed at 350 °C for 30000 h). The inset is the fast Fourier transform (FFT).

Slika 6: Posnetek HRTEM matrice staranega (žarjenega pri 350 °C, 30000 h) vzorca DSS (tip zlitine 258). Vstavljena slika prikazuje hitro Fourierjevo transformacijo (FFT).

obstacles (inclusions) with TEM/EDXS. This should also be studied, in detail, in the future, possibly with a better TEM resolution. Further investigations (TEM/EDXS) will enable a better understanding of the characteristics of spinodal decomposition and the change in the compositions of both domains. They will allow us to explain the real rearrangement of the alloying elements and the formation of the eventual new phases during spinodal decomposition. As a result, we will be able to calculate the extent of the internal stresses.

4 CONCLUSIONS

A small difference caused by the change in the ageing temperature was observed. The density of dislocations in the specimens of the non-aged and aged duplex stainless steel (DSS, the 258-alloy type) increased after the ageing at 300 °C and these dislocations appeared in different configurations with many of them being substantially mobile. After the ageing at 350 °C the dislocation configurations changed and many dislocations became immobile (or at least slowed down in their movements) when the transformation of the matrix occurred.

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