ISSN 1848-0071
UDC 669.14.018.291+620.193=111
Recieved: 2011-11-09
Accepted: 2012-03-06
Original scientific paper

THE INFLUENCE OF MEDIUM AND MICROSTRUCTURE ON CORROSION RATE OF DUAL PHASE HIGH-STRENGTH STRUCTURAL STEELS

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The corrosion damages significantly reduce the use-value and shorten the life time of various constructions. As a result of corrosion damages occur enormous costs, and sometimes major disasters which can lead to the material costs and also dangerous consequences for human life. With proper selection of structural material and its corrosion protection these unpleasant consequences can be avoided or significantly reduced. Every material has a different corrosion behavior depending on the physical conditions and medium in which it is located.
In this work the influence of medium and microstructure on corrosion rate of dual phase high-strength structural steels was studied. The electrochemical measurements revealed that both examined dual phase steels showed lower corrosion rate in the medium of 5 % NaOH, than in the medium of 5 % H_2SO_4. The metallographic analysis of investigated materials indicated the fact that the amount of martensite phase and morphology of microstructural constituents have a significant effect on the corrosion behavior of dual phase steels. Namely, with decreasing the amount of martensite in dual phase steels corrosion rate increases in both examined media.
Key words: dual phase steel, corrosion rate, corrosion behavior, microstructure.

Utjecaj medija i mikrostrukture na brzinu korozije dvofaznih visokočvrstih konstrukcijskih čelika. Korozijska oštećenja znatno smanjuju uporabnu vrijednost i skraćuju vijek trajanja različitih konstrukcija. Kao posljedica korozijskih oštećenja javljaju se ogromni troškovi, a katkad i velike havarije koje osim materijalnih mogu dovesti do opasnih posljedica po ljudski život. Uz pravilan odabir konstrukcijskog materijala i njegove antikorozijske zaštite ove neugodne posljedice mogu se u znatnoj mjeri izbjeći ili smanjiti. Svaki materijal različito se korozijski ponaša ovisno o fizikalnim uvjetima i mediju u kojem se nalazi.
U ovom radu proučavan je utjecaj medija i mikrostrukture na brzinu korozije dvofaznih visokočvrstih konstrukcijskih čelika. Elektrokemijskim mjerenjima je ustanovljeno da oba ispitana dvofazna čelika pokazuju manju brzinu korozije u mediju 5 % NaOH, nego u mediju 5 % H_2SO_4. Metalografska analiza ispitanih materijala ukazala je na činjenicu da udio martenzitne faze i morfologija mikrostrukturnih konstituenata ima značajan utjecaj na korozijsko ponašanje dvofaznih čelika. Naime, smanjenjem udjela martenzita dolazi do povećanja brzine korozije dvofaznih čelika u oba ispitana medija.
Ključne riječi: dvofazni čelik, brzina korozije, korozijsko ponašanje, mikrostruktura.

INTRODUCTION

The corrosion processes that we meet every day are accidental destruction of structural materials due to mechanical, chemical or biological action of the environment [1-3]. In other words, corrosion processes are spontaneous processes between the metal and environmental components in which metal passes into thermodynamically stable state. Corrosion reduces the use-value of the metal, causing production losses, delays in operation, various disasters, etc.

Considering steel is the material that is mostly used for producing various structures, it is necessary to be familiar with its corrosion behavior in contact with different corrosive media. It should be noted that the electrochemical corrosion of steel is especially pronounced in the energy and metallurgical plants and in the chemical, food, textile and metal industry processing [4].

Nowadays, one of the main trends of car producers is towards weight reduction to decrease consumption and gas emission, along with increasing in passenger safety. Although use of lightweight materials has gained some applications in autobody, steel still represents the main choice.

Due to the demands of automotive industry for simultaneously increasing strength and ductility of structural steels and above mentioned facts, in the last two decades, new families of high-strength steel, so called advanced high-strength steel have been developed. These new steel grades include DP (dual phase), TRIP (transformation induced plasticity), CP (complex phase), martensite and TWIP (twinning induced plasticity) steels [5-8].

DP steel is characterized by two-phase microstructure composed mainly of ferrite and a small quantity of martensite, where high strength of martensite phase and high plasticity of ferrite phase at the same time increased strength and ductility („the microstructural engineering“) [9]. Therefore, this steel shows better mechanical properties compared to conventional high-strength steels, which has prompted researchers to study its applicability for other structural purposes [10].

Although a good combination of mechanical properties of DP steels is well known in the literature [5,11-13], further research is needed to determine the influence of phase constituents on corrosion resistance of dual phase steels. General insight into the corrosion behavior of certain material can be obtained on the basis of data on its corrosion in several typical aggressive media.

Therefore, in this paper the influence of different media and microstructure on the corrosion behavior of dual phase steels was studied.

EXPERIMENTAL

In this work the samples of cold-rolled steel strips of commercial dual phase high-strength structural steel marked HCT450X and HCT600X were used. Due to the high absorption of impact energy and a good combination of high strength and high ductility, these cold-rolled dual phase steels are primarily designed for production of automotive structural and safety components.

However, their application has spread to the manufacturing of tanks and pressure vessels. Chemical composition and mechanical properties of examined dual phase steels in delivered condition were shown in Tables 1 and 2.

Table 1. Chemical composition of examined dual phase steels (mass. %)
Tablica 1. Kemijski sastav ispitanih dvofaznih čelika (mas. %)

Chemical element	Sample	
	HCT450X	HCT600X
C	0.056	0.077
Mn	1.250	1.48
Si	0.14	0.12
P	0.01	0.018
S	0.0018	0.0061
Al	0.052	0.038
Cr + Mo	-	0.51
Nb + Ti	-	0.003
V	-	0.001
B	-	0.0002

Table 2. Mechanical properties of examined dual phase steels [14]
Tablica 2. Mehanička svojstva ispitanih dvofaznih čelika [14]

Sample	Yield strength R_e/MPa	Tensile strength R_m/MPa	Elongation A/%
HCT450X	280-340	450-530	≥ 27
HCT600X	330-410	600-700	≥ 21

In order to study electrochemical corrosion behavior of dual phase steels, the samples in shape of plate dimensions (height×width×thickness) = (3×2×0.15) cm were grounded with emery paper to a 600 grit finish, rinsed in distilled water and degreased in ethanol.

Then the sample as working electrode was partially immersed in the tested medium in three-electrode glass cell where saturated calomel electrode-SCE (reference electrode) and Pt-mesh (auxiliary electrode) were found [9].

After that, stabilization of open circuit potential E_{ocp} was followed using a computer controlled potentiostat/galvanostat (Parstat 2273), at room temperature T = (19 ± 2) °C during 30 minutes.

After stabilization E_{ocp} potentiodynamic polarization was performed in the narrow field of potential from -250 mV to +250 mV vs E_{corr}, with the scan rate of 5 mV/s. Upon the completion of measurements, the specimen surface immersed in the tested medium was measured. Corrosion parameters were determined using Tafel's extrapolation method, while v_{corr} was determined from I_{corr} using Faraday's law. Two measurements were carried out for both dual phase steels in two different media: 5 % NaOH and 5 % H_2SO_4.

For the purpose of metallographic investigations of microstructural characteristics of non-hydrogenated steels, the samples of cold-rolled steel strips dimensions (height×width×thickness) = (1.5×0.75×0.15) cm were cut in rolling direction and pressed in conductive mass by machine for hot pressing of samples (SimpliMet® 1000).

The samples were then grounded (emery paper No. 400, 500, 600 and 800 grit) and polished with the water suspension of Al_2O_3 by the automatic device for grounding and polishing (Buehler). For the purpose of finding inclusions thus prepared samples have been observed "in white" by optical microscope with digital camera (Olympus GX 51) and a system for automated picture analysis (AnalySIS® Materials Research Lab).

After the micrography of inclusions the samples were etched by nital (5 % HNO_3 in ethanol) and their microstructures were recorded.

RESULTS AND DISCUSSION

Potentiodynamic polarization in a narrow field potentials from -250 mV to +250 mV vs E_{corr} was performed in order to determine the polarization curve of typical indicators of general corrosion: corrosion potential E_{corr}, anode slope β_a, cathode slope β_c, corrosion current density I_{corr} and corrosion rate v_{corr}.

There is a number of graphical and numerical methods where the values of corrosion parameters are determined by polarization measurements [1,2]. One of the most commonly used methods is the Tafel's graphical method which is applied in this paper. Voltamogramms registered in the Tafel's area are given as E = f (log I) views of polarization curves (Figure 1 and 2).

Using software PowerCorr™ the straight lines in linear area of the curves were drawn, where the intersection of straight lines had abscissa log I_{corr} and ordinate E_{corr}. Corrosion parameters of examined dual phase steels were determined as arithmetic mean of two measurements for each tested material and listed in Table 3.

From Figure 1 and 2 and Table 3 it can be noticed that both examined steels have significantly lower corrosion current density I_{corr} and corrosion rate v_{corr} in the medium of 5 % NaOH.

On the other hand, dual phase steel HCT600X showed a lower corrosion rate in both media, which means that it is more resistant to general corrosion than sample HCT450X.

Furthermore, the corrosion potential E_{corr} of tested samples, and the open circuit potential E_{ocp} showed a more positive value in the medium of 5 % NaOH, than in the medium of 5 % H_2SO_4.

That can be seen from Figure 3 and 4 which show the time dependence of the open circuit potential for investigated dual phase steels.

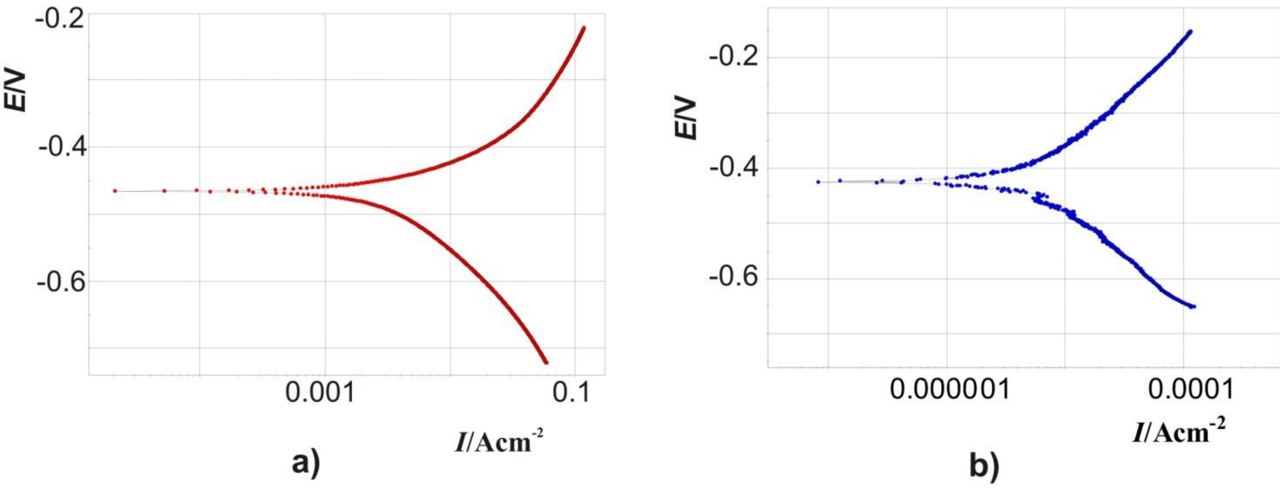

Figure 1. Polarization curve of HCT450X dual phase steel in medium:
a) 5 % H_2SO_4, b) 5 % NaOH
Slika 1. Polarizacijska krivulja dvofaznog čelika HCT450X u mediju:
a) 5 % H_2SO_4, b) 5 % NaOH

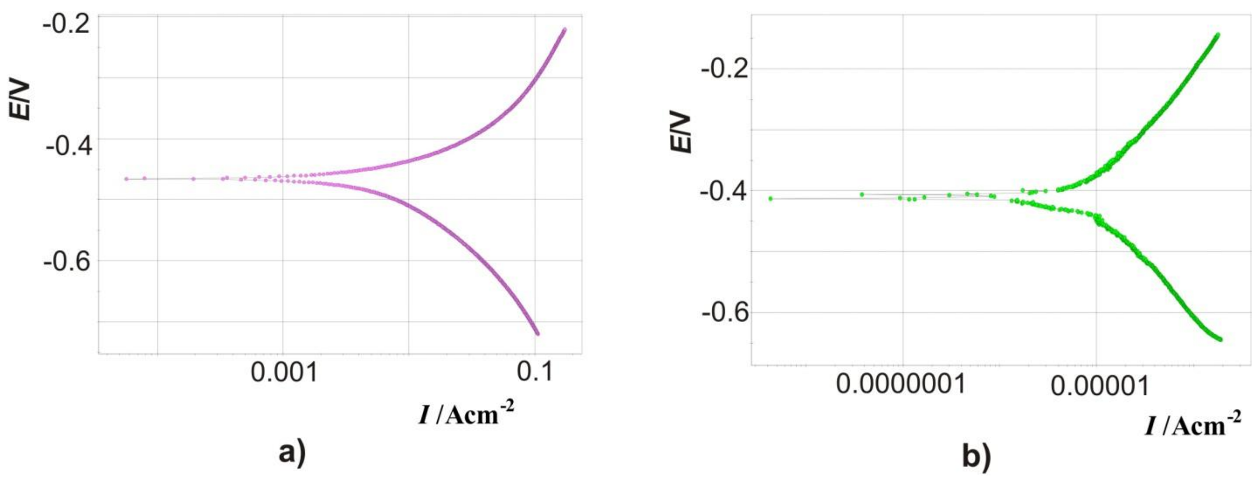

Figure 2. Polarization curve of HCT600X dual phase steel in medium:
a) 5 % H_2SO_4, b) 5 % NaOH
Slika 2. Polarizacijska krivulja dvofaznog čelika HCT600X u mediju:
a) 5 % H_2SO_4, b) 5 % NaOH

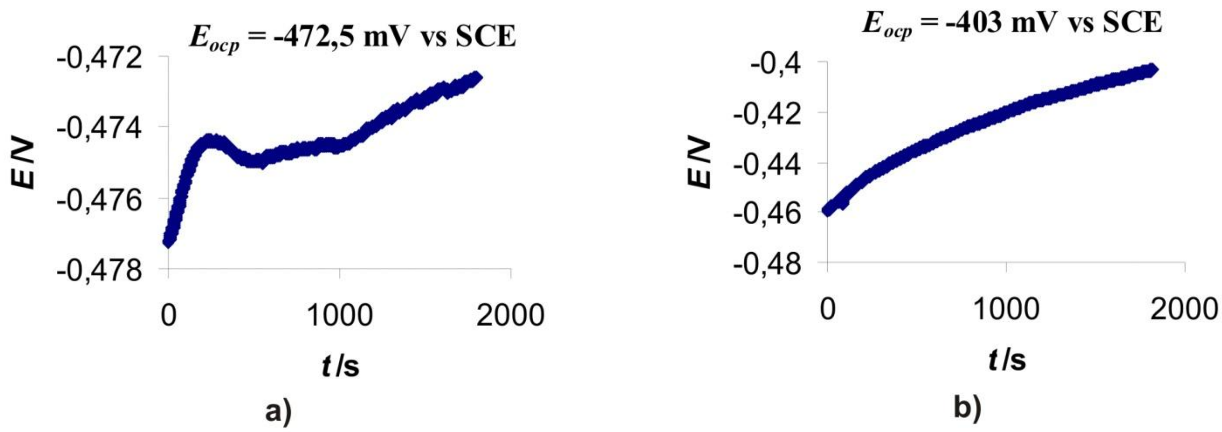

Figure 3. Time dependance of open circuit potential for HCT450X dual phase steel in medium: a) 5 % H_2SO_4 and b) 5 % NaOH

Slika 3. Ovisnost mirujućeg potencijala o vremenu za dvofazni čelik HCT450X u mediju: a) 5 % H_2SO_4 i b) 5 % NaOH

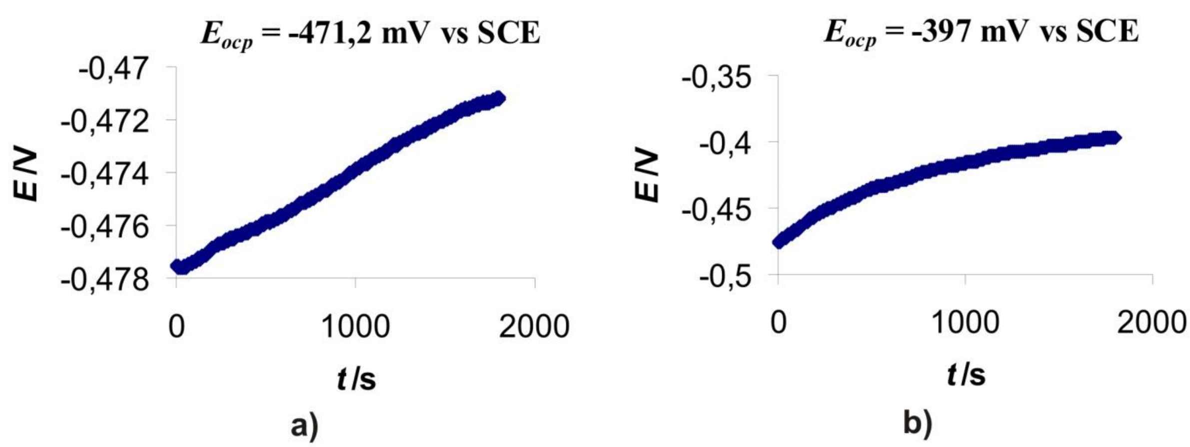

Figure 4. Time dependance of open circuit potential for HCT600X dual phase steel in medium: a) 5 % H_2SO_4 and b) 5 % NaOH

Slika 4. Ovisnost mirujućeg potencijala o vremenu za dvofazni čelik HCT600X u mediju: a) 5 % H_2SO_4 i b) 5 % Na

Table 3. Corrosion parameters of examined dual phase steels
Tablica 3. Korozijski parametri ispitanih dvofaznih čelika

Sample	MEDIUM: 5 % NaOH					MEDIUM: 5 % H_2SO_4				
	E_{corr} vs SCE	β_a	β_c	I_{corr}	v_{corr}	E_{corr} vs SCE	β_a	β_c	I_{corr}	v_{corr}
	mV	mV	mV	Acm^{-2}	mm y^{-1}	mV	mV	mV	Acm^{-2}	mm y^{-1}
HCT450X	-422	178.2	159.2	5.6×10^{-6}	0.012	-467	79.6	153.2	4.0×10^{-3}	8.42
HCT600X	-411	170.1	157.9	4.0×10^{-6}	0.008	-465	74.7	129.6	2.5×10^{-3}	7.99

Namely, since the steels before performing potentiodynamic polarization were exposed to 30 minutes of action a particular media, in an acidic medium of 5 % H_2SO_4 the potential managed to stabilize after a specified time (Figures 3a and 4a). However, in alkaline medium of 5 % NaOH, the potential is constantly growing and in 30 minutes becomes more positive by approximately 80 mV (Figures 3b and 4b).

The potential increase in alkaline medium can be related to the fact that during the interaction of samples and the media it probably began to create an oxide layer on the dual phase steels, which hinders the penetration of aggressive ions from the media through the metal, and in some way shows a protective effect [15].

As a result, the lower corrosion rate in 5 % NaOH was obtained for both investigated steels. The cause of such corrosion behavior of examined dual phase steels can be found in the chemical composition of investigated materials [15].

Since both tested steels are very pure materials with a low content of phosphorus and sulphur, and they belong to a group of low-carbon steels, the creation of carbides and other inclusions is unlikely. Namely, metallographic analysis revealed only globular inclusions to a lesser extent in examined dual phase steels (Figures 5 and 6). Exactly because of the reduced presence of inclusions, the presence of microgalvanic couples is eliminated, which leads to the increasing of corrosion resistance of examined samples [15].

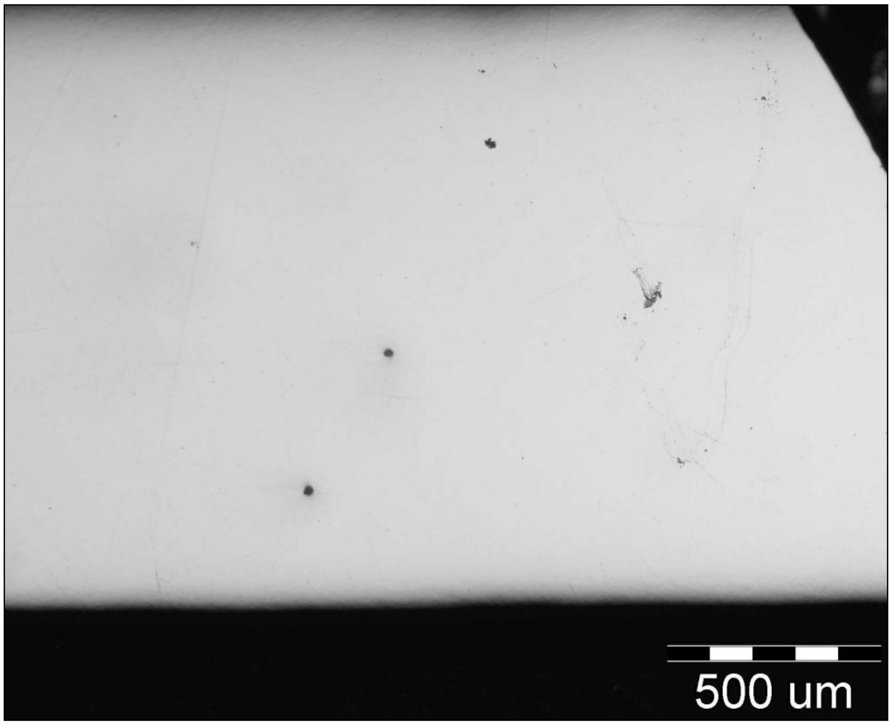

Figure 5. Optical micrograph of globular inclusions in HCT450X dual phase steel
Slika 5. Metalografski snimak globularnih uključaka u dvofaznom čeliku oznake HCT450X

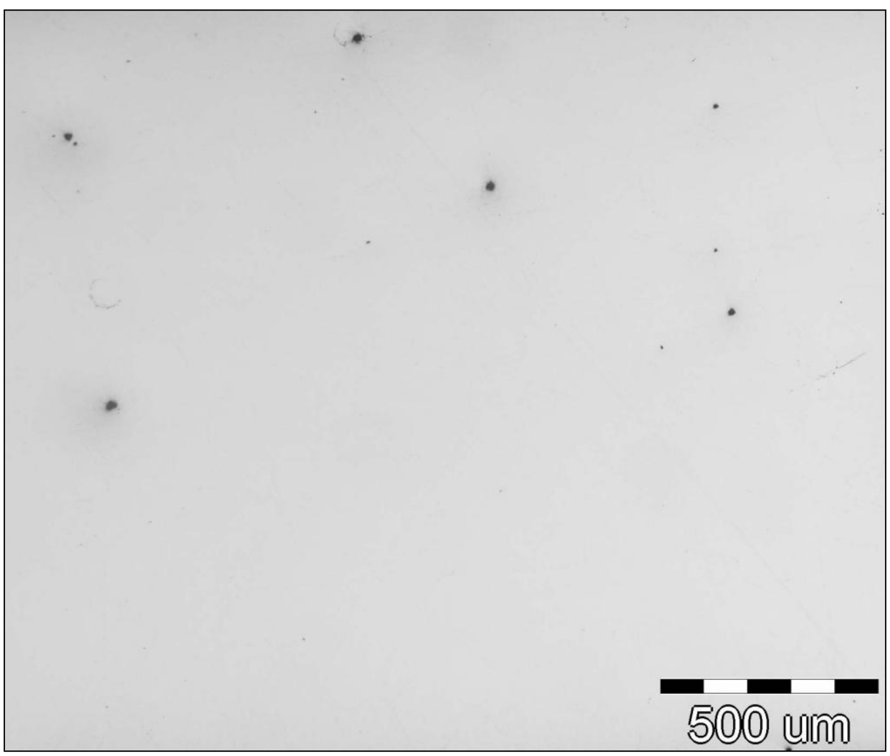

Figure 6. Optical micrograph of globular inclusions in HCT600X dual phase steel
Slika 6. Metalografski snimak globularnih uključaka u dvofaznom čeliku oznake HCT600X

It is assumed that the reason for the creation of these globular inclusions in dual phase steels is caused by calcium treatment in ladle furnace [16], which leads to their increased hardness and maintains their globular shape through the forming process. On the other hand, elongated MnS inclusions with bigger dimensions which increase anisotropic properties were not registered in examined dual phase steels.

Factors of corrosion resistance can be found in the microstructure of the investigated materials (Fig. 7 and 8).

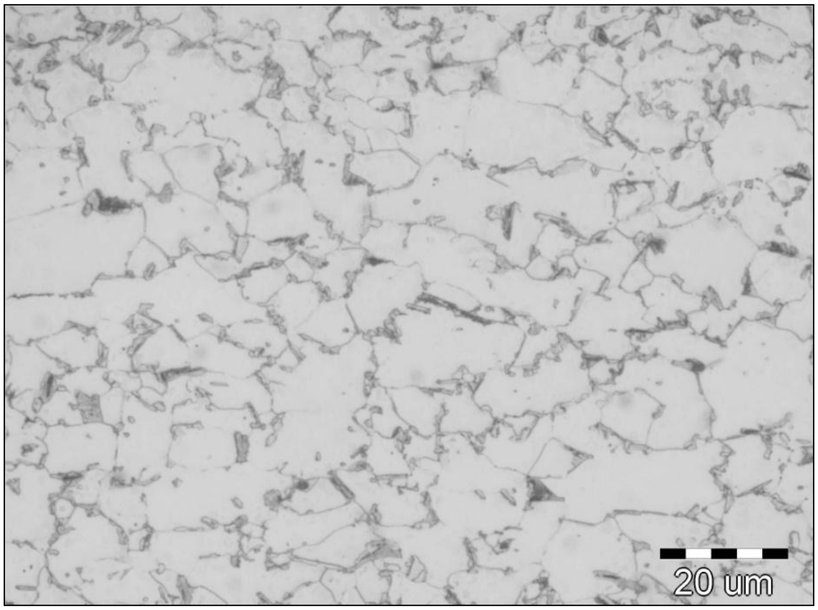

Figure 7. Optical micrograph of microstrucure of HCT450X dual phase steel
Slika 7. Metalografski snimak mikrostrukture dvofaznog čelika oznake HCT450X

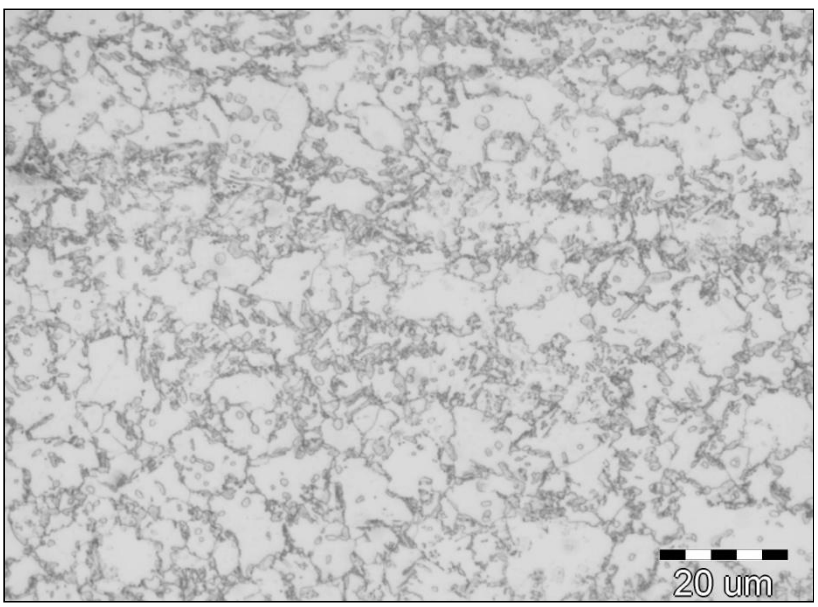

Figure 8. Optical micrograph of microstrucure of HCT600X dual phase steel
Slika 8. Metalografski snimak mikrostrukture dvofaznog čelika oznake HCT600X

Both tested materials are dual phase steels with extremely fine-grained microstructure consisting of ferrite and martensite.

DP steels are produced by intercritical annealing (producing an α + γ microstructure) and then severe cooling/quenching, resulting in a soft ferrite matrix containing hard martensite particles, and often small amounts of retained austenite or other phases [17]. The intercritical anneal can follow either finish rolling for hot strip product or cold rolling for CRA (cold-rolled-and-annealed) or HDG (hot-dip galvanized) product.

The crucial role in the production of dual phase steels has microalloying which is tasked to enable getting as much as possible fine-grained microstructure and precipitates hardening [5]. It is important to notice that the hardening mechanism of HCT600X dual phase steel, unlike HCT450X dual phase steel has been achieved by increased content of chromium and manganese. Chromium usually has a stabilizing effect on the austenite and decreases the critical cooling rate required for transformation without diffusion, which helps the formation of martensite [5].

From Figures 7 and 8 it is obvious that HCT600X dual phase steel has a higher amount of martensite in its microstructure than HCT450X dual phase steel. The electrochemical studies revealed that the amount of martensite and morphology of microstructural constituents have a significant impact on the corrosion behavior of investigated materials [15], because the sample HCT600X, which has a higher amount of martensite showed a lower corrosion rate in both tested media. In other words, corrosion rate decreases with increasing the amount of martensite in dual phase steels.

It can be concluded that because of better mechanical properties, lower corrosion rate and increasing amount of martensite, the examined dual phase steel HCT600X in relation to HCT450X can be classified as better structural material for production of safety parts and components in automobile industry.

CONCLUSION

- The electrochemical measurements revealed that examined dual phase steels show significantly lower corrosion rate in the medium of 5 % NaOH than in the medium of 5 % H_2SO_4, which may be related to the formation of a thin oxide layer of the protective effect.
- Dual phase steel HCT600X showed a lower corrosion rate than the sample HCT450X in both tested media, which may be related with the microstructure of the investigated materials.
- The microstructure of examined steels is composed of ferrite and martensite, whose quantities and morphology have a significant effect on corrosion behavior of dual phase steels.
- The metallographic analysis showed that decreasing the martensite percentage in examined dual phase steels the corrosion rate increased in both tested media.
- The summary analysis of obtained results showed that because of better mechanical properties, lower corrosion rate and increasing amount of martensite, the examined dual phase steel HCT600X in relation to HCT450X can be classified as better structural material for production of safety parts and components in automobile industry.

Acknowledgement

This work was supported by the Ministry of Science, Education and Sport of the Republic of Croatia within the project 124-1241565-1524.

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