

CORROSION BEHAVIOUR OF TEMPERED 42CrMo4 STEEL

KOROZIJSKO OBNAŠANJE POBOLJŠANEGA JEKLA VRSTE 42CrMo4

Sunčana Smokvina Hanza^{1*}, Lovro Štic¹, Lovro Liverić¹, Vedrana Špada²

¹University of Rijeka, Faculty of Engineering, Vukovarska 58, 51000 Rijeka, Croatia

²METRIS Materials Research Centre of Region of Istria, Zagrebačka 30, 52100 Pula, Croatia

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Low-alloy 42CrMo4 steel (AISI 4140) is a medium carbon steel, commonly used as a quenched and tempered steel. Because of its good mechanical properties, high tensile strength and toughness, 42CrMo4 is one of the widely used and investigated steels. To increase ductility even more, in addition to standard quenching and tempering, the steel is often hardened by double quenching and tempering and austempering. The aim of this paper was to investigate the corrosion behaviour of 42CrMo4 steel after quenching and tempering, double quenching and tempering and austempering. For this purpose, microstructural characterization and electrochemical investigation after different hardening processes were performed. The microstructure of the specimens was observed using optical microscopy and scanning electron microscopy. Open circuit potential and potentiodynamic polarization measurements of the tempered specimens were carried out using a computer-controlled potentiostat with a three-electrode set-up in 0.6 M NaCl naturally aerated solution. It was concluded that applied heat treatment processes increase the corrosion resistance of the 42CrMo4 steel in comparison to normalized steel. In comparison to quenched and tempered steel, double quenching and tempering, as well as austempering, do not significantly change the corrosion resistance of the steel.

Keywords: quenching, tempering, characterization, corrosion

Malo legirano jeklo vrste 42CrMo4 (AISI 4140) je jeklo s srednjo vsebnostjo ogljika, ki se običajno uporablja v poboljšanem (kaljenem in popuščnem) stanju. Zaradi svojih dobrih mehanskih lastnosti; to je predvsem visoke natezne trdnosti, je jeklo 42CrMo4 eno od najbolj uporabljenih in preiskovanih jekel. Jeklu pogosto izboljšajo duktilnost tako, da izvedejo dvojno kaljenje in popuščenje ter postopek austempranja. Avtorji v članku opisujejo raziskavo, v kateri primerjajo korozijsko obnašanje poboljšane, dvakratno poboljšane in austemprane jekla 42CrMo4. V ta namen so izvedli mikrostrukturno in elektrokemično karakterizacijo različno toplotno obdelanega jekla po različnih postopkih njegove obdelave. Mikrostrukture jekla so opazovali pod optičnim in vrstičnim elektronskim mikroskopom. Meritve potenciala odprtega tokokroga in potenciodinamične polarizacije so izvajali na preizkušanjih s postavitvijo treh elektrod v 0,6 M naravno prezračeni raztopini NaCl z računalniško vodenim potenciostatom. Avtorji ugotavljajo, da je v raziskavi uporabljena toplotna obdelava izbranega jekla 42CrMo4 povečala njegovo korozijsko obstojnost. Dvojno poboljšanje in austempranje jekla ni bistveno izboljšalo njegove korozijske obstojnosti v primerjavi s standardnim enojnim postopkom poboljšanja.

Ključne besede: kaljenje in popuščenje jekla (poboljšanje), karakterizacija, korozija

1 INTRODUCTION

Low-alloy 42CrMo4 steel (AISI 4140) is a medium carbon, chromium molybdenum alloy steel. The higher carbon content of 42CrMo4 steel gives greater heat treatment capabilities, making it suitable for components that must be able to withstand dynamic loading or impact. Therefore, it is commonly used as a quenched and tempered steel in various applications where high tensile strength and toughness are required.

The standard heat treatment of 42CrMo4 steel consists of austenitizing, quenching and tempering. Austenitizing includes heating the steel above the critical temperature and holding the steel at that temperature for a period of time, long enough for the transformation to occur. Quenching is the rapid cooling of steel from the austenitizing temperature when the diffusionless martensite transformation takes place. The carbon content in martensite corresponds to that in austenite. Martensite is

hard, but very brittle, due to the lattice distortion caused by carbon atoms trapped in the octahedral sites of the martensite, impurity atom segregation at the austenite grain boundaries, carbide formation during quenching, and residual stresses produced during quenching.¹ The hardness of martensite in medium carbon, low-alloy steels, which depends on strengthening of the ferrite by interstitial carbon atoms, can be calculated according to the empirical formula.²

Tempering is the subsequent heat treatment of quenched steel that decreases the hardness and reduces the brittleness (increases toughness) of steel components, and also reduces the tensile residual stresses produced during quenching. The hardness after tempering is a linear function of the tempering temperature and a logarithmic function of the tempering time.³ Any temperature, up to the lower critical, can be used for tempering. Therefore, different mechanical properties can be obtained, depending on the requirements in service. The tempering range from 260 °C to 370 °C is avoided because of tempered martensite embrittlement.¹

*Corresponding author's e-mail:
suncana@riteh.hr (Sunčana Smokvina Hanza)

A relatively novel heat treatment of 42CrMo4 steel is double quenching and tempering. It is used for achieving better toughness at the same hardness level, due to the refining effect on the size of the prior austenite grains.⁴⁻⁶

Austempering is another hardening treatment of 42CrMo4 steel. It is used for greatly improving the toughness relative to tempered martensite, and to reduce the distortion and cracking during rapid cooling in single and double quenching and tempering processes. In the austempering process, tempering is not required. The resulting microstructure of austempering is bainite, rather than tempered martensite.

Although the main purpose of the heat treatment is to change the mechanical properties⁷⁻¹¹, heat treatment also changes the corrosion properties of the material.¹²⁻¹⁵

Electrochemical corrosion is the destructive attack of a metal material by electrochemical reaction with the environment, that negatively affected the crucial mechanical properties of the components. Seawater is an almost a universal fluid to evaluate the corrosion resistance of metal materials. Any material showing a good resistance to corrosion in seawater is considered satisfactory for major aqueous applications.

Corrosion is driven by external and internal factors. External factors are the corrosive medium parameters, such as the composition of the corrosive medium, pH, temperature and velocity, while the internal factors are materials parameters. Microstructural constituents are the most important material parameters that can affect the corrosion resistance of steels for quenching and tempering. A heterogeneous ferrite-pearlite microstructure of normalized steels for quenching and tempering forms anodic and cathodic sites which lead to corrosion. A homogenised microstructure after quenching and tempering is the cause of the better corrosion properties of quenched and tempered steels. Alloying additions of less than 5 % have little effect on the seawater corrosion.

In this paper, the corrosion behaviour of 42CrMo4 steel subjected to different hardening processes has been investigated. The aim of this paper was to extend the knowledge on the corrosion resistance of 42CrMo4 steel after quenching and tempering (QT), double quenching and tempering (DQT) and austempering (AT) processes. The main goal was to investigate which process of hardening gives the best corrosion resistance of 42CrMo4 steel.

For this purpose, microstructural characterization and electrochemical investigation were performed after QT, DQT and AT. The microstructure of the specimens was observed using optical microscopy and scanning electron

microscopy. Open circuit potential and potentiodynamic polarization measurements of the tempered specimens were carried out using computer-controlled potentiostat with a three-electrode set-up in 0.6 M NaCl naturally aerated solution.

2 EXPERIMENTAL INVESTIGATIONS

2.1 Material and heat treatment

Investigated specimens were prepared by cutting $\phi 16$ steel bars of normalized 42CrMo4 steel into smaller pieces measuring 4 mm in length. Glow discharge optical emission spectrometer LECO GDS 500 A was used to determine the chemical composition of the steel (Table 1).

The hardening processes applied in this research are schematically compared in Figure 1: quenching and tempering (QT), double quenching and tempering (DQT) and austempering (AT). The heat treatment parameters are shown in Table 2. The hardness of the specimens achieved after the hardening processes was measured for the purpose of verification of the heat treatment processes. The obtained hardness after tempering is similar to the experimental literature data.⁶

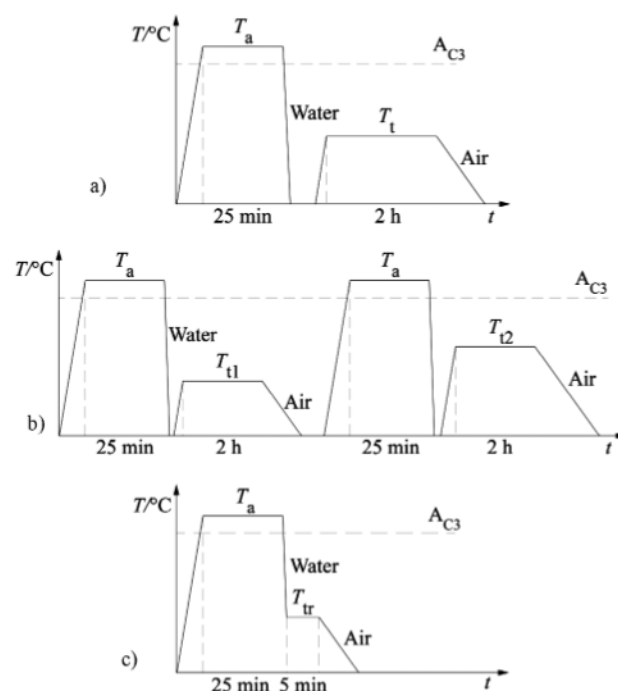


Figure 1: Hardening processes: a) QT, b) DQT, c) AT

Table 1: Chemical composition of 42CrMo4 steel (balance Fe)

Chemical composition, w/%											
C	Si	Mn	P	S	Ni	Cr	Mo	Cu	Al	Ti	V
0.427	0.214	0.846	0.0056	0.0173	0.0407	1.07	0.183	0.167	0.0386	0.0089	0.0106

Table 2: Heat treatment parameters

Specimen no.	Heat treatment	Parameters	Hardness
		Temperature / time / cooling medium	
1	Normalizing	870 °C / – / air	90 HRB
2	QT	Q: 850 °C / 25 min / water; T: 400 °C / 2 h / air	45 HRC
3		Q: 850 °C / 25 min / water; T: 500 °C / 2 h / air	37 HRC
4		Q: 850 °C / 25 min / water; T: 600 °C / 2 h / air	30 HRC
5	DQT	Q1: 850 °C / 25 min / water; T1: 200 °C / 2 h / air Q2: 850 °C / 25 min / water; T2: 400 °C / 2 h / air	44 HRC
6		Q1: 850 °C / 25 min / water; T1: 250 °C / 2 h / air Q2: 850 °C / 25 min / water; T2: 500 °C / 2 h / air	38 HRC
7		Q1: 850 °C / 25 min / water; T1: 300 °C / 2 h / air Q2: 850 °C / 25 min / water; T2: 600 °C / 2 h / air	30 HRC
8	AT	850 °C / 25 min / salt bath (325 °C / 5 min) → air	42 HRC
9		850 °C / 25 min / salt bath (375 °C / 2 min) → air	36 HRC
10		850 °C / 25 min / salt bath (400 °C / 8 min) → air	30 HRC

The identical austenitizing temperature ($T_a = 850\text{ °C}$) and time ($t_a = 25\text{ min}$) were selected in all the hardening processes so that all the specimens had the same initial austenite microstructure. The DQT heat treatment consisted of two stages of austenitizing, quenching and tempering. The first tempering stage was performed at the temperature T_{t1} , twice as low as that of the second tempering stage, T_{t2} , to achieve a more refined prior austenite grain.⁴⁻⁶ Tempering temperature in the second tempering stage of DQT, T_{t2} , corresponded to the tempering temperature of a single QT process, T_t . To study only the influence of the tempering temperature on the microstructure of tempered martensite, the same tempering time of 2 h was selected in the QT and DQT processes. Austempering was performed by cooling specimens in a hot salt bath AS 140 with a chemical composition of 50 % NaNO_3 and 50 % KNO_3 . The salt-bath temperature, T_{tr} , and the holding time at this temperature were obtained experimentally, to achieve precisely determined hardnesses of (42, 36, 30) HRC.

2.2 Microstructural characterization

The importance of microstructure on the properties of metal materials has long been recognized. Therefore, microstructural characterization after hardening processes has been done to obtain the connection between the microstructure and the corrosion resistance of the 42CrMo4 steel. The microstructure of the normalized specimen and the hardened specimens was observed using an OLYMPUS BX51 optical microscope and scan-

ning electron microscope FEG QUANTA 250 SEM FEI with EDS OXFORD detector.

Metallographic samples were prepared by grinding and polishing with a STRUERS LABOPOL device, with first stage grinding MD-Piano 220 resin bonded diamond disc, followed by MD-Allegro composite disc with diamond suspension. After grinding, the samples were polished with MD-Dac polishing cloth with DiaPro Dac 3 diamond suspension, followed by MD-Chem polishing cloth with OP-U NonDry colloidal silica suspension. After grinding and polishing, samples have been etched using a nital 3 % solution for 20 seconds.

2.3 Electrochemical investigation

Electrochemical investigations were performed using a computer-controlled Princeton Applied Research potentiostat Parstat 2263. A three-electrode set-up was used: the working electrode with an exposed area of 1 cm^2 , a saturated calomel electrode (SCE) placed in a Luggin capillary as the reference electrode and graphite counter electrode. Before electrochemical investigations, specimens were ground and polished with the sandpapers P320, P600, P800, P1200 and P2400, and afterwards degreased in ethanol and rinsed with deionized water.

All the measurements were conducted at room temperature ($20 \pm 2\text{ °C}$), in the 0.6-M NaCl naturally aerated solution, prepared from analytical grade NaCl and deionized water.

Open circuit potential, E_{OC} , measurements were performed as a function of time for a period of 2 h. Potentiodynamic polarization was performed at a scan rate of 0.166 mVs^{-1} , over a potential range of $E_{OC} \pm 250\text{ mV}$, starting from the most negative potential.

The corrosion rate was calculated from polarization curves, based on the corrosion current density, i_{corr} , known equivalent weight ($EW = 18.558\text{ g}$) and density

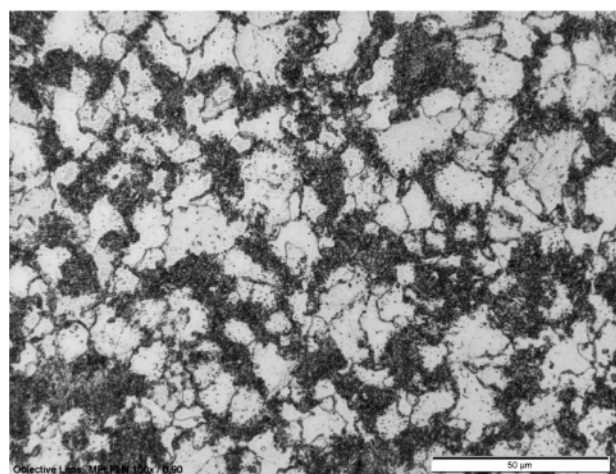


Figure 2: Ferrite-pearlite microstructure of specimen no.1. Optical microscope. Etchant: nital 3 %

($\rho = 7.85 \text{ g/cm}^3$) of 42CrMo4 steel, according to the expression:

$$v_{\text{corr}} = \frac{0.0033 \cdot i_{\text{corr}} \cdot EW}{\rho} \text{ [mmpy]} \quad (1)$$

3 RESULTS AND DISCUSSION

The heterogeneous microstructure of normalized 42CrMo4 steel comprised of ferrite crystals among the colonies of pearlite is shown in **Figure 2**.

Figure 3 and **Figure 4** show the microstructures of 42CrMo4 steel after different heat treatment processes: quenching and tempering, double quenching and tempering and austempering. Micrographs in **Figure 3** were obtained by optical microscopy, while **Figure 4** shows scanning electron micrographs.

Figures 3a to 3c and **4a to 4c** show tempered martensite, the microstructure of quenched and tempered steel, which is a result of the decomposition of martensite upon heating during tempering. Tempered martensite

consists of uniformly dispersed cementite particles within a continuous ferrite matrix. A higher tempering temperature led to coarsening of the cementite particles.

The microstructure of double quenched and tempered steel is also tempered martensite (**Figures 3d to 3f, 4d to 4f**), which consists of refined, uniformly dispersed cementite particles within a continuous ferrite matrix. A higher tempering temperature also leads to coarsening of the cementite particles. However, due to the structure refining by double quenching and tempering, coarsening of the structure with increasing the tempering temperature is less noticeable.

The microstructure of austempered steel (**Figures 3g to 3i, 4g to 4i**) consists of bainite. Higher temperatures of isothermal transformation favour an upper bainite structure resulting in a lower hardness.

Potentiodynamic polarization curves presented in the semi-logarithmic plot (**Figure 5**) are composed of cathodic and anodic branches, resulting from the electrochemical reactions in the system. The anodic branch of

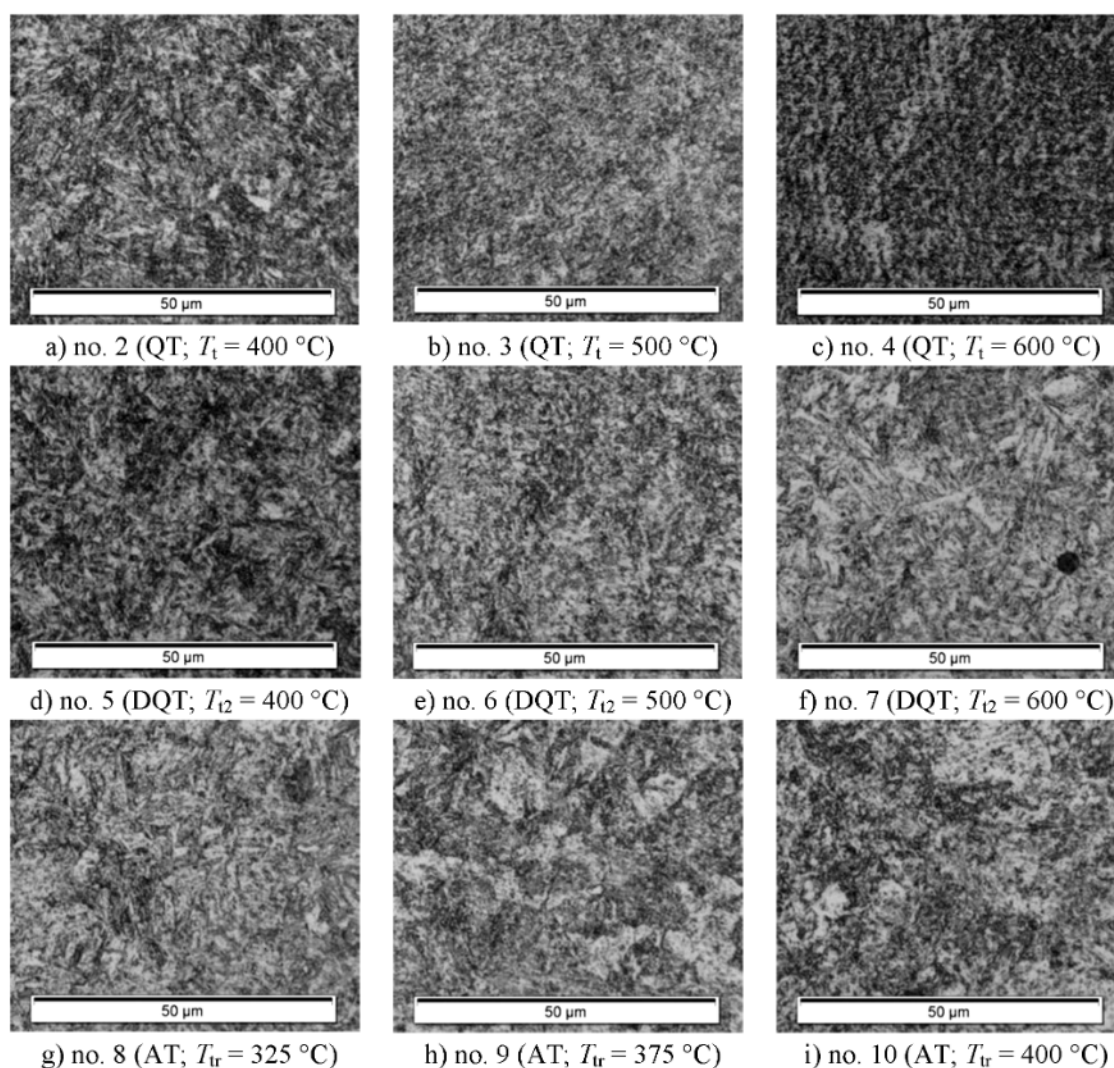


Figure 3: Microstructure of hardened specimens. Optical microscope. Etchant: nital 3 %

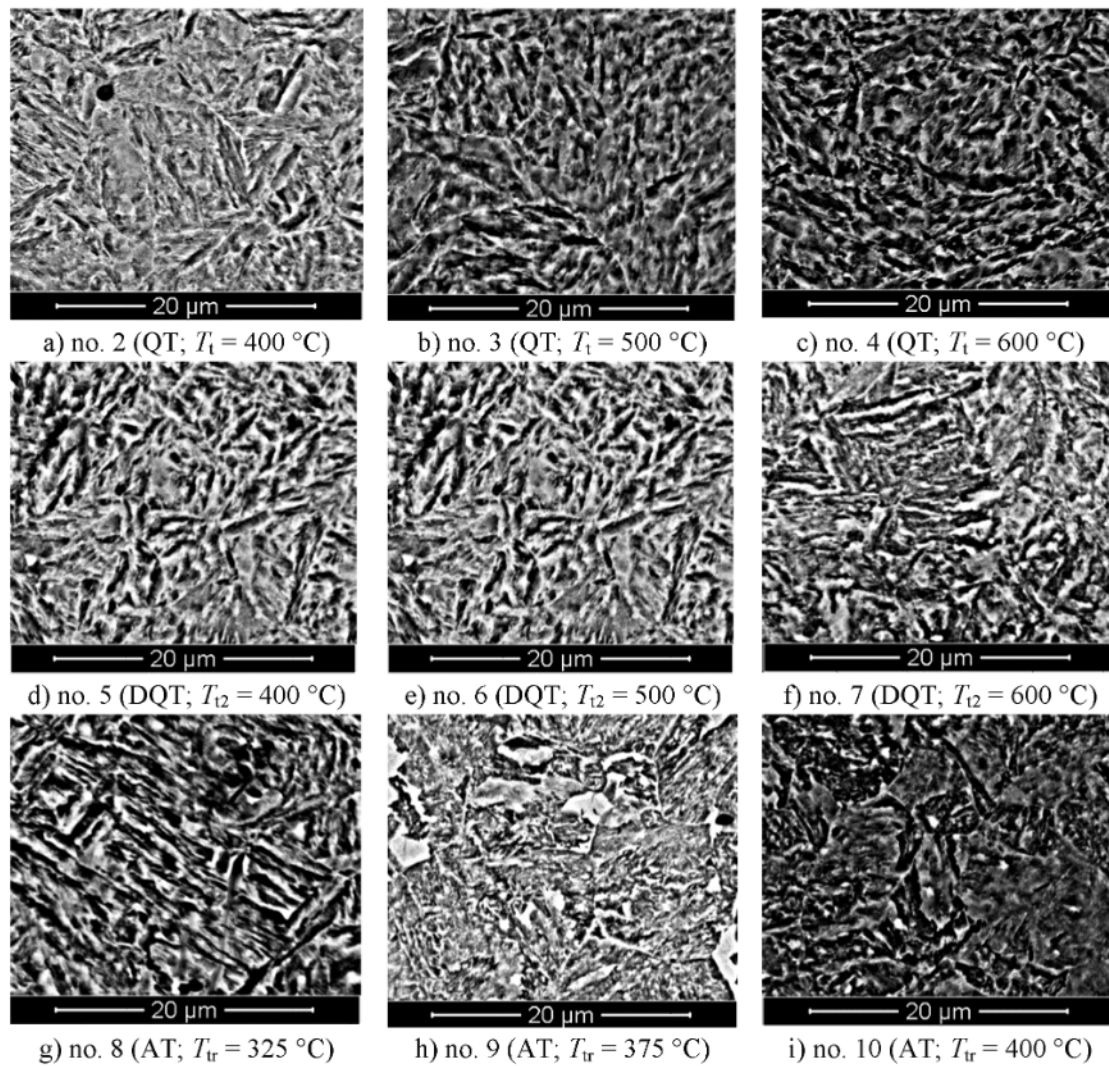
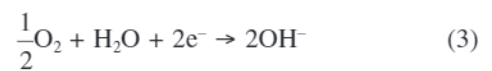


Figure 4: Microstructure of hardened specimens. SEM, BSE

the polarization curve describes the anodic dissolution of iron in NaCl solution, which can be expressed by the Equation:



The cathodic part of the polarization curve represents the oxygen reduction reaction expressed by the equation:



In comparison to normalized steel, for all the hardened specimens, the anodic current density increases much faster with the potential indicating an active dissolution, while the cathodic current density increases much

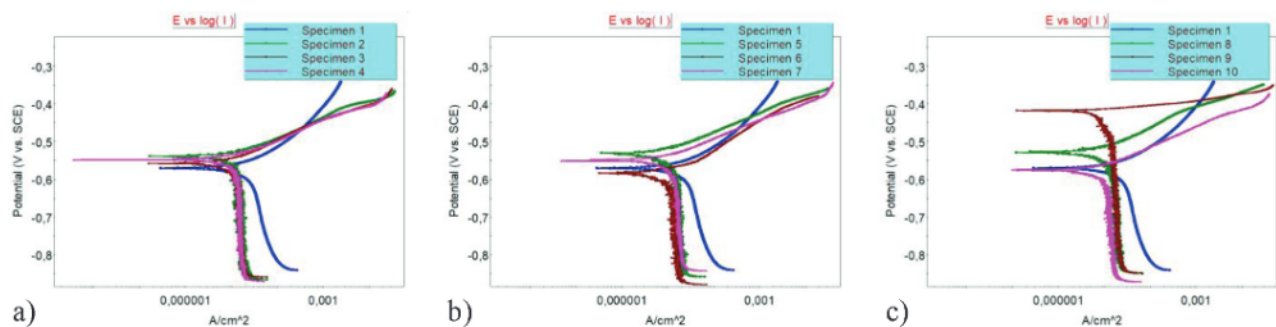


Figure 5: Potentiodynamic polarization curves for specimens in 0.6 M NaCl solution: a) QT, b) DQT, c) AT. The blue curve corresponds to normalized 42CrMo4 steel

Table 3 Corrosion parameters of the specimens taken from potentiodynamic polarization curves

Specimen no.	$E_{\text{corr}}/\text{mV}$	$i_{\text{corr}}/\mu\text{A cm}^{-2}$	$^{[1]}\beta_c/\text{mV dec}^{-1}$	$^{[2]}\beta_a/\text{mV dec}^{-1}$	$v_{\text{corr}}/\text{mmpy}$	Potential range /mV
1 (N)	-570.90	41.72	-1009.339	119.967	0.32240	-841, -341
2 (QT; $T_1 = 400\text{ }^\circ\text{C}$)	-539.67	13.17	-1771.798	53.188	0.10180	-866, -366
3 (QT; $T_1 = 500\text{ }^\circ\text{C}$)	-557.08	10.75	-1046.199	56.195	0.08307	-860, -360
4 (QT; $T_1 = 600\text{ }^\circ\text{C}$)	-546.28	8.55	-1632.979	52.322	0.06609	-870, -370
5 (DQT; $T_2 = 400\text{ }^\circ\text{C}$)	-531.86	11.10	-992.362	53.858	0.08580	-859, -359
6 (DQT; $T_2 = 500\text{ }^\circ\text{C}$)	-584.55	14.84	-1229.696	73.565	0.11470	-872, -379
7 (DQT; $T_2 = 600\text{ }^\circ\text{C}$)	-549.46	9.38	-886.627	72.925	0.07250	-842, -342
8 (AT; $T_3 = 325\text{ }^\circ\text{C}$)	-529.01	11.73	-919.045	62.728	0.09068	-849, -349
9 (AT; $T_3 = 375\text{ }^\circ\text{C}$)	-418.21	10.05	-1028.957	16.603	0.07763	-850, -350
10 (AT; $T_3 = 400\text{ }^\circ\text{C}$)	-575.57	9.73	-1024.331	55.735	0.07517	-871, -371

^[1] Cathodic Tafel Slope; ^[2] Anodic Tafel Slope

slower in a manner characteristic to a diffusion-controlled process.^{16,17} The values of anodic current, i_a , are much higher than the cathodic current, i_c , at high overpotential values. This indicates that the reduction process occurs at a slower rate than the oxidation process, and therefore, cathodic reaction controls the electrochemical corrosion of the 42CrMo4 steel.

The corrosion parameters obtained from polarization measurements are shown in **Table 3**. All the hardened specimens have a lower corrosion current density, i_{corr} , which means a lower corrosion rate, v_{corr} , up to five times, in comparison to normalized steel. A similar observation is found in the literature for quenched and tempered steel.^{13,14} Better corrosion resistance of the hardened specimens is due to the more homogeneous microstructure of the tempered martensite and bainite in comparison to that of the normalized steel. Among the hardened specimens, a corrosion rate lower than 0.8 mmpy was consistently obtained for the specimens quenched and tempered at 600 °C, as well as for the specimens austempered at 375 °C and 400 °C. The specimen austempered at 375 °C showed a pronounced corrosion potential shift in the positive direction upon heat treatment. The overall shift of the corrosion potential on all but two specimens may indicate the influence of surface passivation due to the presence of chromium and molybdenum in the steel.¹⁸ It can be concluded that the tempering temperature influences the corrosion resistance of tempered martensite. This may be explained by the effect of the tempering temperature on the coarsening and spheroidization of cementite that are more pronounced at higher temperatures leading to a smaller cathodic reactivity and to the reduction of the cementite to ferrite area.¹⁸ The holding temperature during austempering has a small influence on the corrosion rate of bainite. In general, the investigated heat treatments lower the corrosion rate of 42CrMo4 steel from moderate to low according to the standard practice NACE SP0775-2013.

5 CONCLUSIONS

The corrosion behaviour of low-alloy 42CrMo4 steel after different hardening processes was analysed by potentiodynamic polarization, as well as by optical and scanning electron microscopy examination. The following conclusions can be drawn:

1. Applied heat treatment processes (quenching and tempering, double quenching and tempering and austempering) increase the corrosion resistance of 42CrMo4 steel up to five times in comparison to the normalized steel.
2. For the steel tempered at 600 °C, double quenching and tempering, as well as austempering, have no impact on the corrosion resistance of steel.
3. For the steel tempered at 400 °C, double quenching and tempering, as well as austempering, increase the corrosion resistance of steel.
4. For the steel tempered at 500 °C, double quenching and tempering decrease the corrosion resistance of steel.
5. Diffusion-limited cathodic oxygen reduction controls the corrosion rate of 42CrMo4 steel.
6. The homogenisation of the cementite distribution within a continuous ferrite matrix beneficially influences the corrosion resistance of 42CrMo4 steel.
7. As the tempering temperature increases, the effects of coarsening and spheroidization of cementite become greater, leading to the smaller cathodic reactivity.
8. The selection of 42CrMo4 steel heat treatment parameters should be based on achieving the required mechanical properties, without taking into account the corrosion behaviour.

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