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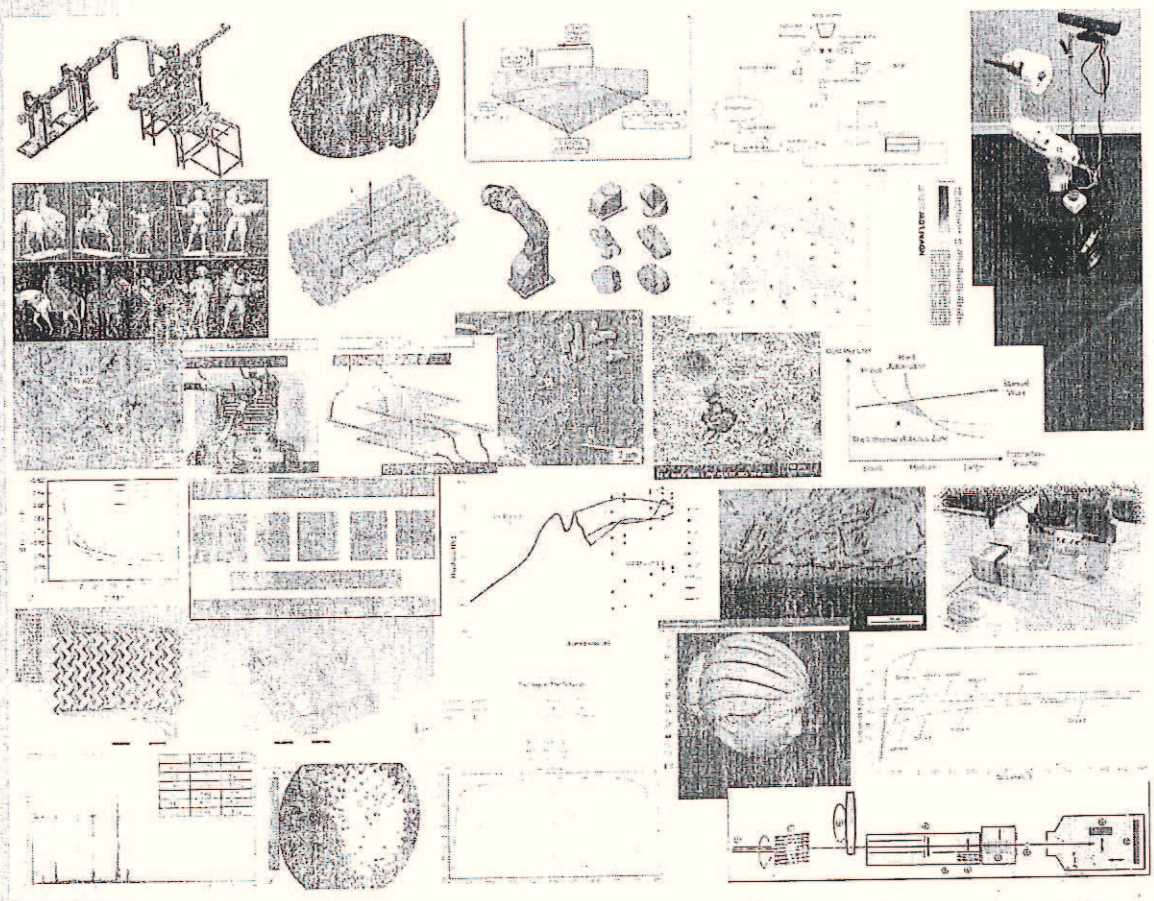

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The influence of copper content on corrosion behavior of ductile iron and austempered ductile iron

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Abstract: The effect of copper content on corrosion behavior of ductile iron and austempered ductile iron was investigated in 0.5 mol dm^{-3} NaCl solution at T = 20°C by open circuit potential measurements, linear and potentiodynamic polarisation methods. Ductile iron specimens used in this paper had: 0.031 wt.% Cu and 0.91 wt.% Cu. Specimens were austenitised at 850°C for 60 min and then austempered at 420°C for 60 min in 50% $NaNO_3$ and 50% KNO_3 salt bath. The mechanism of the corrosion attack developed on the material surface was analysed by light microscopy, scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDX).The results of the electrochemical investigations indicated that corrosion rate generally decrease with the increase in copper content in alloy. Also, higher corrosion resistance showed austempered ductile iron samples compared to ductile iron samples with the same chemical composition.

Utjecaj sadržaja bakra na korozijsko ponašanje žilavog lijeva i izotermički poboljšanog žilavog lijeva

Izvorni znanstveni rad

Sažetak: Utjecaj sadržaja bakra na korozijska ponašanje žilavog lijeva i izotermički poboljšanog žilavog lijeva ispitano je u 0.5 mol dm^{-3} NaCl otopini pri T = 20 °C mjerenjem potencijala otvorenog strujnog kruga, metodom linearne i potenciodinamičke polarizacije. Uzorci žilavog lijeva korišteni u ovom radu su imali: 0,031 wt.% Cu and 0,91 wt.% Cu. Uzorci su austenitizirani na 850°C i držani 60 min te potom izotermički poboljšani na 420°C i držani 60 min u solnoj kupki sastava 50% $NaNO_3$ i 50% KNO_3. Mehanizam korozijskog napada analiziran pomoću svjetlosnog mikroskopa, pretražnog elektronskog mikroskopa i energetsko disperzivnom *analizom* X-zrakama (EDS). Rezultati elektrokemijskih mjerenja pokazali su da dolazi do smanjenja brzine korozije s povećanjem sadržaja bakra u leguri. Također, veću korozijsku otpornost pokazali su uzorci izotermički poboljšanog lijeva u odnosu na uzorke žilavog lijeva istog kemijskog sastava.

1. Introduction

Ductile (nodular) irons are high carbon cast ferrous materials with the composition similar to grey iron [1, 2]. Ductile irons are widely used in various industrial applications such as production of machine parts, tubes, automotive parts etc. [3-5]. The reason for its great use is its advantages over steel castings and grey iron castings. The strength, hardness and wear resistance of ductile iron can be increased by appropriate heat treatment and alloying. Through austempering treatment, ductile iron can be unique material in which acicular ferrite and retained austenite are both in its microstructure [6]. Austempered ductile iron (ADI) was introduced in the 1970s, and since then its application has been growing steadily because of its high tensile strength, good fatigue resistance under dynamic loading conditions and high wear resistance [5-9]. Most studies have focused on the investigations of mechanical properties of ductile and austempered irons but the related information on the corrosion behavior of these materials appears to be limited. This paper deals with the investigations of the influence of Cu content on corrosion behaviour of the ductile iron and austempered ductile iron in 0.5 mol dm^{-3} NaCl solution. The as-cast specimens of ductile iron were first austenitised at 850°C for 60 min and then austempered in 50% $NaNO_3$ - 50% KNO_3 salt bath at 420°C for 60 min to produce ADI.

2. Experimental procedure

2.1. Sample preparation

The working electrodes were made from ductile iron cylindrical samples Ø10 x 8 mm which were soldered on insulated copper wire and then protected by two-component epoxy resin leaving a surface area of 0.5 cm^2

to contact the solution. The chemical composition of the used ductile iron samples is shown in Table 1.

The electrochemical cell was a three-electrode glass cell, with a platinum counter electrode and saturated calomel reference electrode. Before each experiment, the working electrode was polished mechanically using successive grades of emery papers up to 1200 grit, degreased ultrasonically in ethanol, washed with deionised water and transferred quickly to the electrolytic cell. Electrochemical measurements were carried out in a stagnant, naturally aerated chloride solution (0.5 mol dm^{-3} NaCl, T = 20 °C). The electrochemical polarization measurements were performed using the Princeton Applied Research PAR M 273A potentiostat/galvanostat. The potentials were referred to the saturated calomel electrode (SCE).

The evaluation of corrosion behaviour of ductile iron and austempered ductile iron in 0.5 mol dm^{-3} NaCl solution were performed by open circuit potential measurements (E_{OC}) in 60 min time period, linear polarization method in the potential region of ±20 mV around corrosion potential, with the scanning rate of 0.2 mV s^{-1} and potentiodynamic polarization method in the potential region of −0.250 V to 0.600 V towards open circuit potential, with the scanning rate of 0.5 mV s^{-1}.

After the polarization measurements the surface of the electrode were washed in deionized water, dried in the desiccator and then visualized by Canon IXUS1000 camera in macro mode and the light microscope MXFMS-BD, Ningbo Sunny Instruments co.. A more detailed surface analysis was performed with Scanning Electron Microscope Tescan Vega 5136 MM paired with Energy Dispersive Spectroscopy Microscopy (SEM/EDS).

Table 1. Chemical composition of ductile iron samples

wt.%	C	Si	Mn	Cu	S	P	Cr	V	Ni	Mo	Al	Ti	Sn	W	Mg
	3.63	2.61	0.135	0.031	0.0035	0.022	0.005	0.004	0.085	0.003	0.017	0.013	0.033	0.017	0.041
	3.63	2.61	0.135	0.91	0.0035	0.022	0.005	0.004	0.085	0.003	0.017	0.013	0.033	0.017	0.041

2.2. Electrochemical measurements

Open-circuit potentials of ductile iron and austempered ductile iron were followed over 60 min in 0.5 mol dm^{-3} chloride solution at 20 °C and the results were shown in Fig. 1 for samples that contain 0.031% and 0.91% Cu.

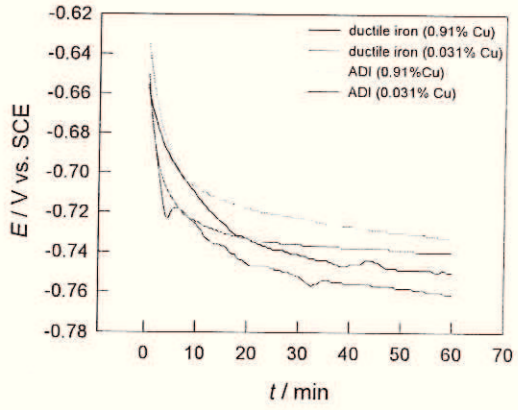

Figure 1. Variation of the open-circuit potentials of ductile iron and austempered ductile iron (ADI) with time in 0.5 mol dm^{-3} NaCl solution, at 20 °C

The electrode potentials for all investigated samples shifts to the negative values after immersion into the electrolyte solution due to the adsorption of chloride ions on the electrode surface. This change is most noticeable in the first 20 minutes of electrode immersion, after which potential changes with time become less pronounced and the stabilization of the open circuit potential values occurred. It can be seen that higher content of Cu in samples leads to the evolution of the positive values of E_{oc} of ductile iron and austempered ductile iron. Also, austempered ductile iron samples showed more positive E_{oc} values which indicate higher corrosion resistance compared with ductile iron samples.

Linear polarization measurements were performed in order to determine the values of polarization resistance, which represent the resistance of materials to corrosion. Polarization resistance is defined as the resistance of the specimen to oxidation during the application of an external potential. Registered R_p values are contrariwise proportional to the corrosion current (higher polarization resistance means lower corrosion current). Results of the examination were presented in Fig. 2 for the samples of ductile iron and austempered ductile iron which contains 0.031% Cu.

Linear polarization resistance is defined by the slope of the polarization curve near the corrosion potential, by the equation (1):

$$R_p = \frac{\Delta E}{\Delta i} \ (\Omega \ cm^2) \qquad (1)$$

Values of polarization resistance for ductile iron samples and austempered ductile iron samples were presented in Table 2. The austempered ductile iron sample has higher values of polarization resistance which means that have higher corrosion resistivity.

Final electrochemical method which was used in this investigation was potentiodymamic polarization method which was performed in wide potential area from -250 to 600 mV versus E_{oc}. Results of the examination were presented in Fig. 2 for the samples of ductile iron and austempered ductile iron which contains 0.031% Cu.

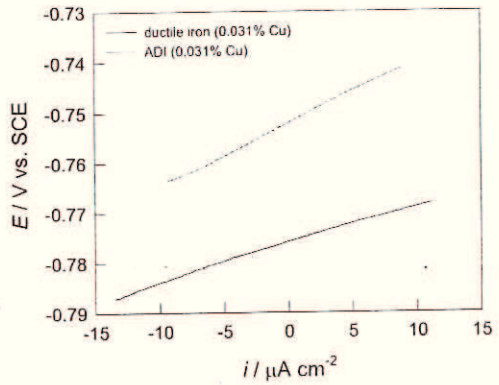

Figure 2. Linear polarization curves for ductile iron and austempered ductile iron in 0.5 mol dm^{-3} NaCl solution, at 20 °C

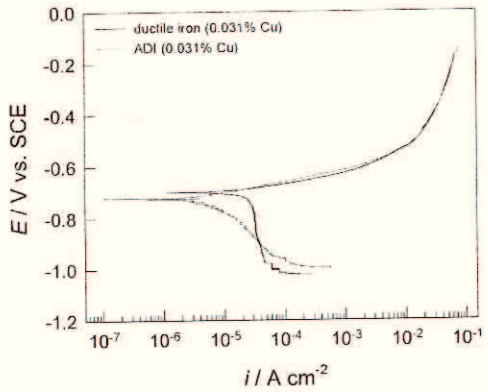

Figure 3. Potentiodynamic polarization curves for ductile iron and austempered ductile iron in 0.5 mol dm^{-3} NaCl solution, at 20 °C

The differences in corrosion behaviour between ductile iron and austempered iron are visible in the cathodic part of the polarization curve in which austempered iron samples show lower chatodic current density values, which result with the less value of the corrosion current density. Corrosion parameters for ductile iron, and austempered ductile iron as obtained by polarization measurements, are given in Table 2.

Table 2. Corrosion parameters for ductile iron and austempered iron in 0.5 mol dm^{-3} NaCl solution

Sample	E_{corr} / V	i_{corr} / μA cm^{-2}	R_p / kΩ cm^2
ductile iron (0.91% Cu)	-0.670	9.27	1.3505
ductile iron (0.031% Cu)	-0.693	21.78	0.771
ADI (0.91% Cu)	-0.672	6.34	1.7095
ADI (0.031% Cu)	-0.715	6.96	1.275

From the Table 2 it can be seen that higher Cu content in ductile and austempered ductile iron lead to the lower values of corrosion current density and to higher values of polarization resistance values, which means the higher corrosion resistance of the alloy.

After polarization measurements, electrode surfaces were cleaned ultrasonically in deionized water, dried in desiccator and whereupon electrodes were photographed in macro mode with digital camera Canon Ixus 1000 and also examination of their surfaces were done with light microscope.

Figure 4 shows the results of this surface examination for ductile iron and austempered ductile iron with Cu content of 0.031%.

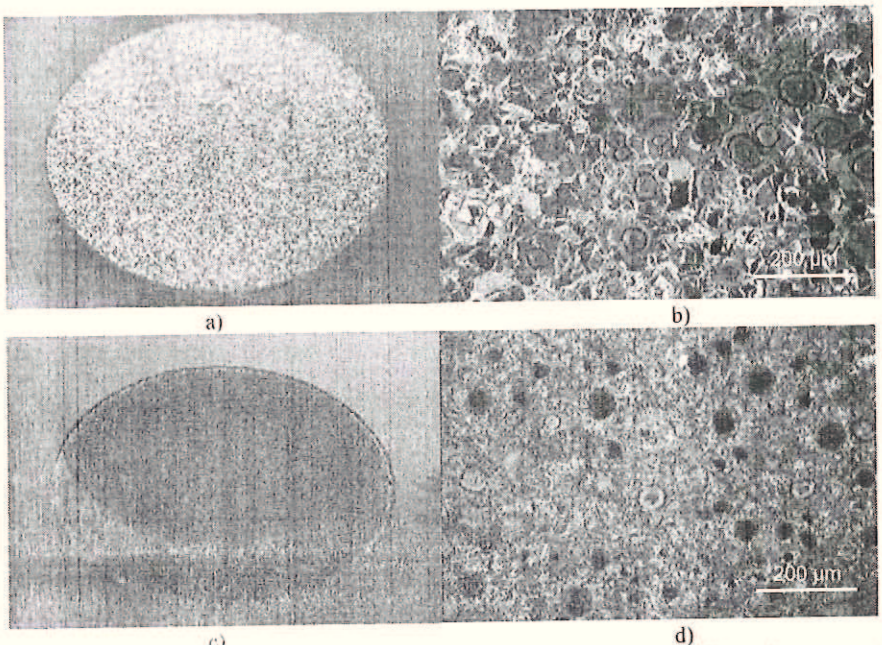

Figure 4. Macro images and optical micrographs of corroded surfaces of ductile iron a) and b) and austempered ductile iron c) and d)

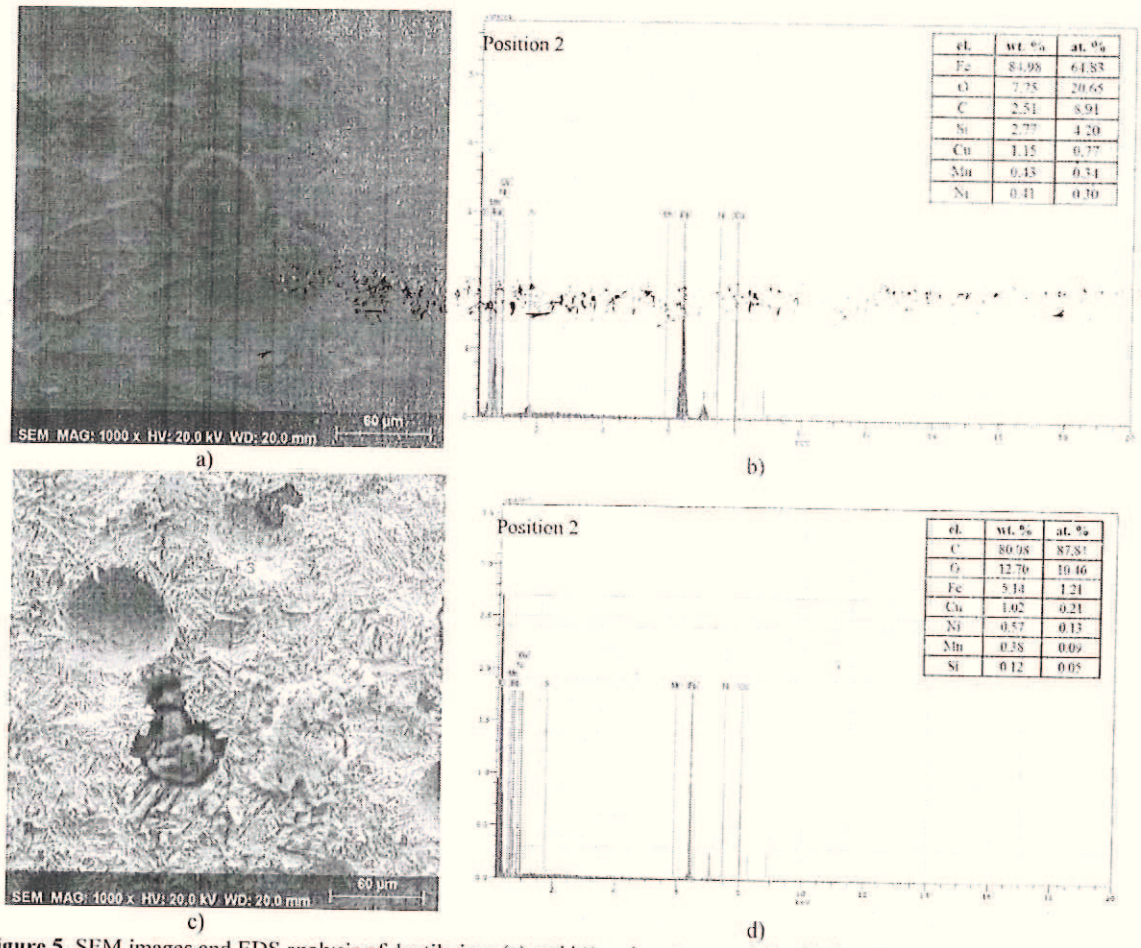

Figure 5. SEM images and EDS analysis of ductile iron (a) and b)) and austempered ductile iron (c) and d)) with Cu content of 0.031 %, after potentiodynamic polarization measurements

Table 3. EDS elemental analysis in different position on the electrode surface

Sample	Ductile iron			Austempered ductile iron		
Element	Position 1 wt. %	Position 2 wt. %	Position 3 wt. %	Position 1 wt. %	Position 2 wt. %	Position 3 wt. %
C	87.49	2.51	0.93	74.69	80.08	7.18
O	8.69	7.75	1.77	18.40	12.70	7.51
Fe	2.02	84.98	92.85	5.02	5.14	82.64
Cu	0.91	1.15	1.21	0.79	1.02	0.82
Ni	0.38	0.41	0.59	0.58	0.57	0.27
Mn	0.35	0.43	0.70	0.38	0.38	0.55
Si	0.15	2.77	1.95	0.15	0.12	1.03

From the Figure 4 it can be seen significant differences in the appearance of the surface between corroded ductile iron and austempered ductile iron. On the Figure 4 b) it is clearly visible corroded matrix (anode) around the graphite (cathode) which results in corrosive cracks. This corrosive appearance was indicative of graphite corrosion and uniform attack. Corroded surface of ADI have significant less corrosive cracks on surface which can be explained due to occurrence of the retained austenite in the microstructure [7].

Detail surface morphology examinations of the corroded samples were examined by scanning electron microscope (SEM). The quantitative analysis of the elements on the electrode surface was determined by energy dispersive spectroscopy (EDS). Results of SEM/EDS analysis of ductile and austempered iron surface after were shown in Figure 5. EDS elemental analysis of electrode surfaces were presented in Table 3:

Figure 5 shows SEM micrographs of the ductile iron and austempered ductile iron after polarization test. As shown in Figures 5 a) and c), the matrix (anode) around the

graphite (cathode) was corroded to form the corrosive cracks, and peel-off of the graphite was observed on the surfaces of the both specimens. This corrosive appearance was indicative of graphite corrosion and uniform attack. In the cases of ADI and the phenomenon of peel-off of the graphite still took place, but uniform attack was reduced due to the occurrence of the retained austenite in the microstructure [10]. The published research about corrosion of ductile and austempered ductile iron in literature indicated that the corrosion behaviour of ductile iron depends on the nodular graphite quantity as well as the retained austenite content in the microstructure, and that the corrosion resistance is related to the interface of the graphite/matrix [7,11]. A lower nodular graphite quantity and more retained austenite content which were achieved by thermal processing and conversion of ductile iron in austempered ductile iron could provide better corrosion resistance which were confirmed in this investigations. The EDS analysis was performed on 3 different sites on the sample surface and the results of the analysis are shown in Figure 5 b) and d) and Table 3. Surface analysis have confirmed that round particle represent graphite nodules with highest content of carbon along with significantly less quantity of oxygen and iron. Matrix have the highest quantity of iron but the percentage of alloying elements, which have noble potential compare to iron, are higher than in the produced alloy before polarization measurements. This can be explained by dominant dissolution of iron from the matrix, which leads to increase the content of alloying elements on the surface.

3. Conclusion

- Higher content of Cu in samples leads to the evolution of the positive values of open circuit potential of ductile iron and austempered ductile iron. Also, austempered ductile iron samples showed more positive E_{oc} values which indicate higher corrosion resistance compared with ductile iron samples.
- Higher Cu content in ductile and austempered ductile iron lead to the lower values of corrosion current density and to higher values of polarization resistance values, which means the higher corrosion resistance of the alloy. Austempered ductile iron shows higher values of polarization resistance and lower values of corrosion current density which means higher corrosion resistance compared to ductile iron.
- Macro images and microscopic images of electrode surfaces after polarization measurements showed significant differences between ductile iron and austempered ductile iron samples which manifests in intensive graphite corrosion for ductile iron samples and significant less corrosive cracks on surface of ADI, due to retained austenite in ductile iron structure which mitigate corrosion rate.
- Results of SEM/EDS analysis have shown that the surface of the samples was significantly damaged by corrosion. The corrosive appearance was indicative of graphite corrosion and uniform attack. In the cases of ADI and the phenomenon of peel-off of the graphite still took place, but uniform attack was reduced due to the occurrence of the retained austenite in the microstructure. EDS analysis have confirmed that round particle represent graphite nodules with highest content of carbon while around matrix have the highest quantity of iron, and the higher percentage of alloying elements than in the produced alloy before polarization measurements. This can be explained by dominant dissolution of iron from the matrix, which leads to increase the content of alloying elements on the surface.

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