

INHIBITION OF THE PITTING CORROSION OF GREY CAST IRON USING CARBONATE

RAZISKAVE INHIBIRANJA JAMIČASTE KOROZIJE SIVIH LITIN Z UPORABO KARBONATNE MEŠANICE

Aleksandra Kocijan, Monika Jenko

Institute of Metals and Technology, Lepi pot 11, 1000 Ljubljana, Slovenia
aleksandra.kocijan@imt.si

Prejem rokopisa – received: 2005-09-27; sprejem za objavo – accepted for publication: 2005-12-20

We studied the electrochemical characteristics of grey cast iron in Upon, a commercial alkaline cleaning agent. The influence of a chloride solution was also studied. The passive region narrows with increasing chloride concentration, with the breakdown potential shifting to more negative values. The influence of a temperature increase is shown in a higher current density in the passive region due to a lower corrosion resistance. The mechanisms of pitting formation under various experimental conditions were studied using the cyclic potentiodynamic polarization technique. The ability of bicarbonate and carbonate salts to inhibit the pitting corrosion was also studied. The proposed solution exhibited excellent inhibition characteristics to prevent the pitting corrosion of grey cast iron, irrespective of the temperature and the chloride concentration gradient.

Key words: grey cast iron, alkaline, bicarbonate, carbonate, corrosion

Raziskovali smo elektrokemijske lastnosti sive litine za izdelavo centralnega ohišja avtomobilskih motorjev v raztopini komercialnega alkalnega pralnega sredstva Upon, ki se uporablja za čiščenje omenjenih materialov. Raziskovali smo tudi vpliv kloridnih ionov na vedenje sive litine. Z višanjem koncentracije klorida se pasivno območje oži, potencial preboja se pomika k bolj negativnim vrednostim in pri višjih koncentracijah klorida skoraj ne moremo več govoriti o pasivnem območju, saj gostota toka stalno narašča. Vpliv povišanja temperature na vedenje sive litine je izrazit, tok je nekoliko višji, kar pomeni slabšo korozijsko odpornost pri višjih temperaturah. S ciklično potenciodinamsko polarizacijo smo raziskovali mehanizem tvorbe jamic v pasivni plasti pri različnih pogojih in vpliv dodatka raztopine karbonata in bikarbonata na inhibiranje jamičaste korozije. Karbonatna mešanica se je izkazala kot odličen inhibitor jamičaste korozije sive litine, ne glede na temperaturo in koncentracijo klorida.

Ključne besede: sive litine, alkalna raztopina, bikarbonat, karbonat, korozija

1 INTRODUCTION

Aqueous-based cleaning systems are widely used for industrial cleaning. They are effective and often have environmental and worker-safety advantages over cleaning systems based on organic solvents. In aqueous cleaning systems, however, conditions can exist that increase the possibility of corrosion. The temperature of the cleaning bath, for example, is often well above ambient in the range from 40 °C to 70 °C. There is significant aeration caused by agitation, which can promote corrosion, depending on the metal. The bath can be made with distilled or deionised water, but many applications use tap water, and therefore, metal parts in the bath may come into contact with species that could promote corrosion. Other aggressive species will be present in the dirt washed from the part. Localised attack can be promoted by the surface roughness as a result of machining¹.

Most importantly, the pH of the wash bath is often a determining factor in corrosion. For a number of metals, high pH values will significantly reduce the overall corrosion rates; this occurs with ferrous metals. Generally, the overall corrosion is reduced significantly at pH values of 11 or greater². Ferrous-based alloys are often washed, inadvertently or purposely, at pH values

less than the optimum for corrosion protection. Industrial cleaning agents based principally on hydroxide lack any buffering capacity. The presence of acidic soils can cause the pH of these highly alkaline systems to fall below 11.

In addition to general overall corrosion, localised corrosion can occur. Because of the inclusion of bicarbonate and carbonate salts in some cleaning compositions, it is of particular interest to study the effect of these salts on localised corrosion. Much work has been done on investigating this particular problem; however, the studies were made under different experimental conditions³⁻¹⁰.

In the present work, the electrochemical characteristics of grey cast iron in the commercial alkaline cleaning agent Upon were studied. The influence of the chloride, the temperature and the pitting inhibitors was also studied.

2 EXPERIMENTAL

The grey cast iron UNS F12101 was studied electrochemically. The composition of the material was: 3.1 % C, 2 % Si, 0.8 % Mn, 0.1 % S, 0.1 % P, 0.3 % Cr and the remainder Fe. Experiments were carried out in 10 g/L of the cleaning solution P3-Upon 5800, pH 12

(Henkel, Slovenia), at 65 °C and room temperature. The influence of the chloride in concentrations of 0.5 mM, 1 mM, 1.5 mM and 3 mM was also studied. Experimental solutions composed of Upon with KHCO_3 and K_2CO_3 (Merck, Darmstadt, Germany) in a molar ratio 1: 5 were studied in terms of the enhanced pitting corrosion characteristics with and without the additions of chloride ions.

The test specimens were cut from automobile parts (Cimos, Koper, Slovenia) into discs of 15 mm diameter. The specimens were abraded with SiC emery paper down to 1000 grit prior to the electrochemical studies and rinsed with distilled water. The specimens were then embedded in a Teflon PAR holder and employed as a working electrode. The reference electrode was a saturated calomel electrode (SCE, 0.242 V vs. SHE) and the counter electrode was a high-purity graphite rod.

The electrochemical measurements were recorded using an EG&G PAR PC-controlled potentiostat/galvanostat Model 263 with M252 and Softcorr computer programs. The specimens were immersed in the solution 1 hour prior to the measurement in order to stabilize the surface at the open-circuit potential. The potentiodynamic curves were recorded, starting 250 mV more negative than the open-circuit potential. The potential was then increased, using a scan rate of 1 mV s^{-1} , until the transpassive region was reached. In the cyclic polarisation measurements the working electrode was polarised until the current density reached a value of 10^{-3} A/cm^2 and the potential was turned to more negative values.

3 RESULTS AND DISCUSSION

Figure 1 shows potentiodynamic curves for grey cast iron in a commercial alkaline cleaning agent Upon ($c = 10 \text{ g/L}$), with and without the addition of NaCl to concentrations of 0.5 mM, 1 mM, 1.5 mM and 3 mM.

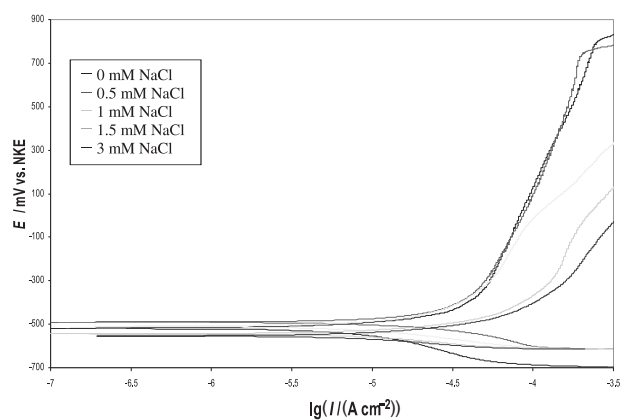


Figure 1: Comparison of potentiodynamic curves for grey cast iron in a commercial alkaline cleaning agent Upon in the presence of different concentrations of chloride.

Slika 1: Primerjava potenciodinamskih krivulj za sivo litino v Upon-u z dodatkom različnih koncentracij NaCl

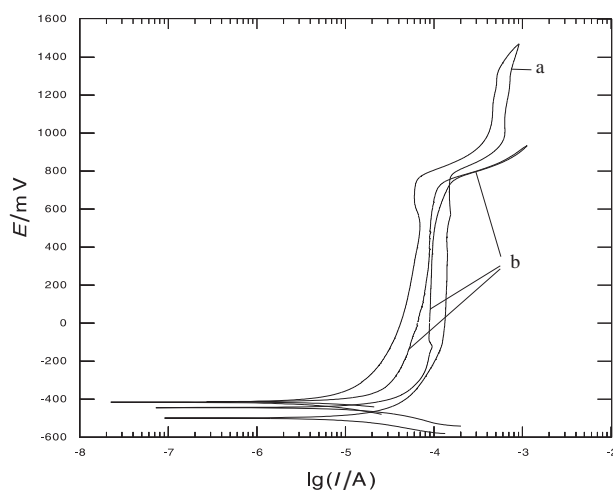


Figure 2: Comparison of cyclic polarisation curves for grey cast iron in a commercial alkaline cleaning agent Upon at room temperature (a) and at 65 °C (b).

Slika 2: Primerjava cikličnih potenciodinamskih polarizacijskih krivulj za sivo litino v Upon-u pri sobni temperaturi (a) in pri 65 °C (b)

After 1 h of stabilization at the open-circuit potential, the corrosion potential (E_{corr}) for grey cast iron in the commercial alkaline cleaning agent Upon is -0.520 V . The values of E_{corr} for the tested material are not significantly changed by the addition of NaCl. Following the Tafel region, the grey cast iron exhibits passive behaviour. The extent of the passive range decreases with the addition of chloride. The passive range is limited by the breakdown potential (E_b), which is defined as the potential at which the current density in the passive range starts to increase abruptly. The breakdown potential for the grey cast iron in Upon solution is approximately 0.80 V. In the presence of chloride, the

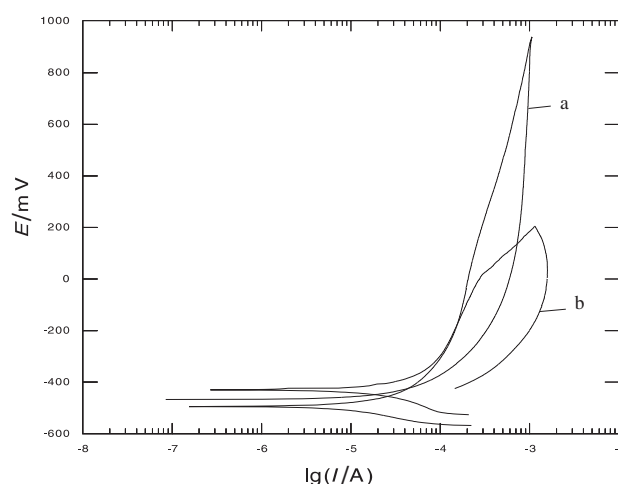


Figure 3: Comparison of cyclic polarisation curves for grey cast iron in a commercial alkaline cleaning agent Upon with the addition of 1.5 mM NaCl at room temperature (a) and at 65 °C (b).

Slika 3: Primerjava cikličnih potenciodinamskih polarizacijskih krivulj za sivo litino v Upon-u z 1,5 mM NaCl pri sobni temperaturi (a) in pri 65 °C (b)

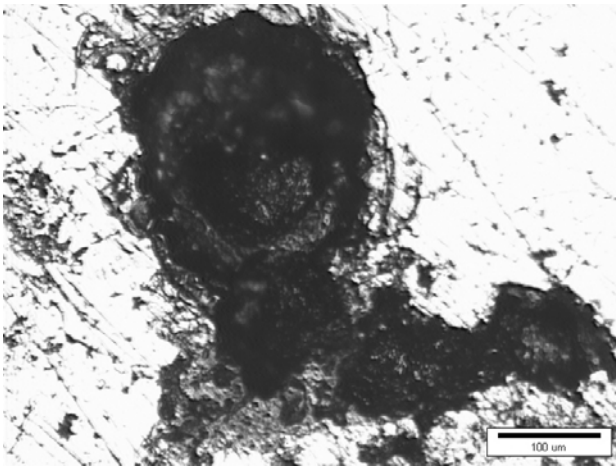


Figure 4: Photograph of grey cast iron after cyclic polarisation in Upon solution with the addition of chloride ions, magnification 150-times. The formation of a pit is visible.

Slika 4: Posnetek vzorca sive litine po ciklični polarizaciji v raztopini Upona z dodatkom kloridnih ionov, povečava 150-kratna. Viden je nastanek jamice.

breakdown potentials are moved to more negative values.

Cyclic polarisation techniques can characterise the tendency of the material to pit. A sample is exposed to a large anodic polarisation, after which the polarisation scan is reversed. The return scan on the cyclic polarisation retraces the path of the forward scan if the surface has been unaffected by the forward scan. If pitting has occurred, the scan will show a large degree of hysteresis, with the reverse scan remaining at high current values until the applied potential is appreciably low. The influence of the temperature on the electrochemical behaviour of grey cast iron is presented in **Figure 2**. The cyclic polarisation curve for grey cast iron in a commercial alkaline cleaning agent Upon ($c =$

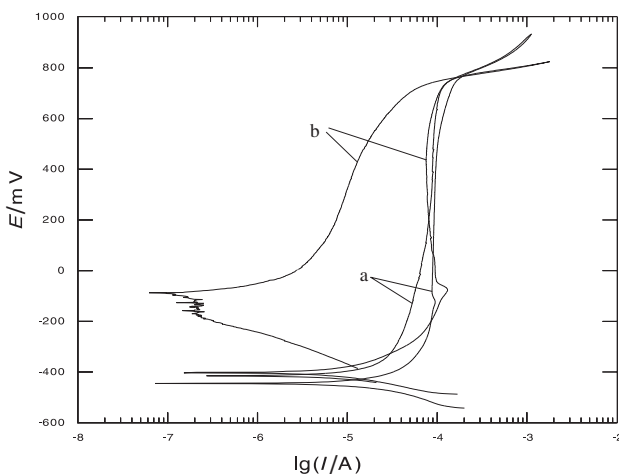


Figure 5: Comparison of cyclic polarisation curves for grey cast iron in a commercial alkaline cleaning agent Upon with (a) and without the addition of 0.06 M $\text{NaHCO}_3/\text{Na}_2\text{CO}_3 = 1/5$ (b) at 65 °C.

Slika 5: Primerjava cikličnih potenciodinamskih polarizacijskih krivulj za sivo litino v 10 g/L Upona, brez dodatka 0,06 M $\text{NaHCO}_3/\text{Na}_2\text{CO}_3 = 1/5$ (a) in z njim (b) pri 65 °C

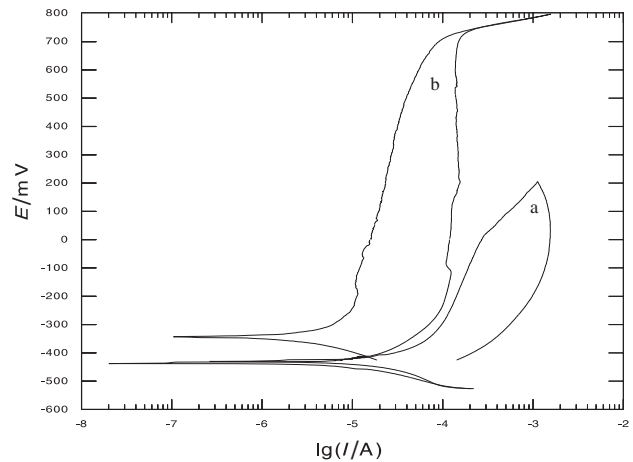


Figure 6: Comparison of cyclic polarisation curves for grey cast iron in a commercial alkaline cleaning agent Upon containing 1.5 mM NaCl with (a) and without the addition of 0.06 M $\text{NaHCO}_3/\text{Na}_2\text{CO}_3 = 1/5$ (b) at 65 °C.

Slika 6: Primerjava cikličnih potenciodinamskih polarizacijskih krivulj za sivo litino v 10 g/L Upona z 1,5 mM NaCl, brez dodatka 0,06 M $\text{NaHCO}_3/\text{Na}_2\text{CO}_3 = 1/5$ (a) in z njim (b) pri 65 °C

10 g/L) at room temperature showed no tendency for pitting corrosion since the current density in the reverse scan is somewhat lower than in the forward scan. In contrast, at 65 °C the current-density values were a bit higher in the reverse scan than in the forward scan. The influence of temperature was more pronounced in the presence of chloride ions (**Figure 3**). The addition of chloride ions drastically reduced the resistance to pitting corrosion of the grey cast iron at higher temperatures. The polarisation scan was already reversed at 0.5 V, the hysteresis was extremely broad, the current density values were distinctly higher in the reverse scan than in the forward scan, and pits were visible on the surface of the sample (**Figure 4**). When 0.06 M $\text{NaHCO}_3/\text{Na}_2\text{CO}_3 = 1/5$ was incorporated into the solution of Upon the current-density values in the reverse scan at 65 °C were much higher than in the solution without the addition of carbonate/bicarbonate salts, suggesting that $\text{NaHCO}_3/\text{Na}_2\text{CO}_3$ provided even better protection against pitting (**Figure 5**). In the presence of chloride the $\text{NaHCO}_3/\text{Na}_2\text{CO}_3$ mixture again exhibited a great inhibiting effect on the pitting corrosion of grey cast iron (**Figure 6**). The breakdown potential values shifted to 0.8 V, like for the measurements without the presence of chloride, and in the reverse scan the current-density values were much higher than without the $\text{NaHCO}_3/\text{Na}_2\text{CO}_3$ mixture, indicating better resistance to pitting. In fact, visually, the electrode did not display any obvious pitting.

4 CONCLUSION

The corrosion characteristics of grey cast iron in an alkaline environment at 65 °C were studied using electrochemical methods. At pH 12 the potentiodynamic measurements showed that the material was fairly

resistant to general corrosion. The addition of chloride to the solution drastically diminished the resistance to pitting corrosion. The inclusion of $\text{NaHCO}_3/\text{Na}_2\text{CO}_3$ inhibited this pitting.

While it has been determined that the addition of carbonate significantly inhibited the occurrence of pitting when the samples were severely polarised, more work is needed to clearly establish the mechanisms that explain how carbonate protects the surface of the metal.

5 REFERENCES

- ¹ S. T. Adamy, F. R. Cala, Inhibition of pitting in ferrous materials by carbonate as a function of temperature and alkalinity, *Corrosion*, 55 (1999), 825
- ² W. Whitman, R. Russell, V. Altieri, Effect of hydrogen-ion concentration on the submerged corrosion of steel, *Ind. Eng. Chem.* 16 (1924), 665
- ³ J. G. H. Thomas, T. J. Nurse, R. Walker, Anodic passivation of iron in carbonate solutions, *Brit. Corros. J.* 5 (1970), 87
- ⁴ J. M. Sutcliffe, R.R. Fessler, W. K. Boyd, R. N. Parkins, Stress corrosion cracking of carbon steel in carbonate solutions, *Corrosion* 28 (1972), 313
- ⁵ R. W. Revie, R. R. Ramsingh, Effects of potential on stress corrosion cracking of grade 483 (X-70) HSLA line pipe steels, *Can. Metall.* 22 (1983), 235
- ⁶ J. Stikma, S. A. Bradford, Stress corrosion cracking of dual-phase steel in carbonate/bicarbonate solutions, *Corrosion* 41 (1985), 446
- ⁷ R. N. Parkins, P. M. Singh, Stress corrosion crack coalescence, *Corrosion* 46 (1990), 485
- ⁸ X. Mao, X. Liu, R. W. Revie, Pitting corrosion of pipeline steel in dilute bicarbonate solution with chloride ions, *Corrosion* 50 (1994), 651
- ⁹ A. K. Pilkey, S. B. Lambert, A. Plumtree, Stress corrosion cracking of X-60 pipeline steel in a carbonate-bicarbonate solution, *Corrosion* 51 (1995), 91
- ¹⁰ L. J. Qiao, J. L. Luo, X. Mao, Hydrogen evolution and enrichment around stress corrosion crack tips of pipeline steels in dilute bicarbonate solution, *Corrosion* 54 (1998), 115