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CORROSION-RESISTANT Fe – B – C ALLOYS

У роботі вивчено вплив структури евтектичних і евтектико-перитектичних сплавів Fe–B–C на їх корозійну стійкість у кислих і нейтральних середовищах. Опір корозії вивчали гравіметричним і потенціостатичним методами з наступним дослідженням зруйнованої поверхні за допомогою оптичної та електронної мікроскопії. Установлено, що швидкість корозії у водних розчинах зростає за наступною послідовністю $\text{NaCl} \rightarrow \text{Na}_2\text{SO}_4 \rightarrow \text{CH}_3\text{COOH} \rightarrow \text{HCl} \rightarrow \text{H}_3\text{PO}_4 \rightarrow \text{H}_2\text{SO}_4 \rightarrow \text{HNO}_3$. Відносно низький опір корозії досліджених сплавів пояснено переважним руйнуванням міжфазних границь поділу між первинними кристалами $\text{Fe}_2(\text{B},\text{C})$ і перитектичною фазою $\text{Fe}_3(\text{B},\text{C})$. Крім того, корозійна стійкість знижується зі збільшенням вмісту евтектики Fe– $\text{Fe}_3(\text{C},\text{B})$ у сплавах Fe–B–C. Показано, що опір корозії можна підвищити в разі збільшення вмісту бору в сплавах до 5 % за масою за рахунок зменшення об'єму евтектики і утворення боридів $\text{Fe}_2(\text{B},\text{C})$ у структурі. Бориди заліза мають підвищену корозійну стійкість завдяки появі на їх поверхні тонкої захисної плівки окислів. Збільшення вмісту бору також спричиняє зростання перенапруги катодного (водний розчин CH_3COOH) й анодного (інші розчини) процесів. Із подовженням тривалості випробувань корозія уповільнюється у зв'язку з накопиченням продуктів реакції на поверхні зразків.

Ключові слова: залізо-бор-вуглецеві залізні сплави, мікроструктура, швидкість корозії, кислі та нейтральні середовища.

В работе изучено влияние структуры эвтектических и эвтектико-перитектических сплавов Fe–B–C на их коррозионную стойкость в кислых и нейтральных средах. Сопротивление коррозии оценивали гравиметрическим и потенциостатическим методами с последующим исследованием разрушенной поверхности с помощью оптической и электронной микроскопии. Установлено, что скорость коррозии в водных растворах растет в следующей последовательности $\text{NaCl} \rightarrow \text{Na}_2\text{SO}_4 \rightarrow \text{CH}_3\text{COOH} \rightarrow \text{HCl} \rightarrow \text{H}_3\text{PO}_4 \rightarrow \text{H}_2\text{SO}_4 \rightarrow \text{HNO}_3$. Сравнительно низкое сопротивление коррозии исследованных сплавов было объяснено преимущественным разрушением межфазных границ раздела между первичными кристаллами $\text{Fe}_2(\text{B},\text{C})$ и перитектической фазой $\text{Fe}_3(\text{B},\text{C})$. Кроме того, коррозионная стойкость снижается с увеличением содержания эвтектики Fe– $\text{Fe}_3(\text{C},\text{B})$ в сплавах Fe–B–C. Показано, что сопротивление коррозии может быть повышено при увеличении содержания бора в сплавах до 5 вес. % за счет уменьшения объема эвтектики и образования боридов $\text{Fe}_2(\text{B},\text{C})$ в структуре. Бориды железа обладают повышенной коррозионной стойкостью вследствие появления на их поверхности тонкой защитной пленки окислов. Увеличение содержания бора также вызывает рост перенапряжения катодного (водный раствор CH_3COOH) и анодного (остальные растворы) процессов. С увеличением времени испытаний коррозия замедляется благодаря накоплению продуктов реакции на поверхности образцов.

Ключевые слова: железо-бор-углеродистые железные сплавы, микроструктура, скорость коррозии, кислые и нейтральные среды.

The paper introduces a study conducted in order to evaluate the effect of the structure of the eutectic or the eutectic-and-peritectic Fe–B–C alloys on their corrosion behavior in acid and neutral media. Corrosion resistance has been investigated using gravimetric and potentiostatic methods, followed by light and electron microscope examinations of the corroded surface. The results have shown that corrosion rates in the aqueous solutions increase in the following sequence: $\text{NaCl} \rightarrow \text{Na}_2\text{SO}_4 \rightarrow \text{CH}_3\text{COOH} \rightarrow \text{HCl} \rightarrow \text{H}_3\text{PO}_4 \rightarrow \text{H}_2\text{SO}_4 \rightarrow \text{HNO}_3$. The relatively low corrosion resistance of the alloys tested may be connected with interfaces between the primary $\text{Fe}_2(\text{B},\text{C})$ crystals and the peritectic $\text{Fe}_3(\text{B},\text{C})$ phase failure. Besides, corrosion resistance decreases with increasing Fe– $\text{Fe}_3(\text{C},\text{B})$ eutectic content of the Fe–B–C alloys. Raising the boron content of the alloys up to 5 wt.pct could increase corrosion resistance due to decrease in the eutectic volume and the formation of the iron borides $\text{Fe}_2(\text{B},\text{C})$. Iron borides owe their corrosion resistance to a relatively thin surface oxide that provides a barrier between the borides and the aggressive environment. Increase in boron content also enhances cathode (CH_3COOH aqueous solution), or anode (the rest) process overvoltages. With testing time prolonging, corrosion slows due to the accumulation of reaction products on the specimen surfaces.

Keywords: boron-and-carbon-containing iron alloys, microstructure, corrosion rate, acid and neutral media.

Introduction

Fe – B – C alloys are commonly used because of their relatively low cost and good physical-and-chemical properties [1]. These alloys, with appropriate phase and structural composition, perform adequately at room temperature and in atmospheric conditions. However, there is a very little information available covering peculiarities in corrosion behavior of these alloys in the acid and neutral media. Although, alloys Fe – B – C, with their chemical properties taken into account, show promise as good corrosion-resistant materials that can be used as constituents of composite materials.

The present investigation aims to evaluate the corrosion resistance of Fe – B – C alloys in different aggressive environments. By evaluating the effects of their structure of on the corrosion behavior, a proper indication of the alloys performance in various applications could be obtained and, hence, their use in such applications can be considered.

Experimental procedure

The Fe – B – C alloys were cooled at 100 K/s and contained 1.2 – 5.0 wt. pct. B, 0.2 – 1.2 wt. pct. C, Fe – balance. Corrosion behavior was investigated using gravimetric and potentiostatic methods. The specimens were corroded in the following aqueous solutions: 3 pct. NaCl, 3 pct. Na₂SO₄, 2N CH₃COOH, 1N HCl, 5N H₃PO₄, 0.5N H₂SO₄, 5 pct. HNO₃. Aggressive media were chosen in order to investigate corrosion processes proceeding with oxygen and hydrogen depolarization. Tests lasting 4 hours and 5 days in the acid and neutral media, respectively, were run at 22 ± 2°C. Silver-chloride electrode was used as the reference electrode, the auxiliary electrode being one of platinum.

Table 1

Chemical, phase and structural composition of the investigated alloys

Specimen	Chemical composition, wt.pct.		Phase composition	Structural composition
	B	C		
No.1	1.2	0.9	α , Fe – Fe ₃ (C,B)	primary γ , eutectics Fe – Fe ₃ (C,B) (20 – 25 pct.)
No.2	2.0	1.2	– “–	primary γ , eutectics Fe – Fe ₃ (C,B) (40 – 45 pct.)
No.3	3.0	1.0	– “–	primary γ , eutectics Fe – Fe ₃ (C,B) (90 – 95 pct.)
No.4	5.5	1.2	α , Fe ₂ (B,C), Fe ₃ (B,C)	primary Fe ₂ (B,C) (35 pct.), peritectic Fe ₃ (B,C) (45 pct.), eutectics Fe – Fe ₃ (B,C) (20 pct.)
No.5	5.0	0.2	α , Fe ₂ (B,C)	primary Fe ₂ (B,C), eutectics Fe – Fe ₂ (B,C) (30–35 pct.)

Model boron-containing iron alloys were tested against low-carbon steel (0.22 pct. C, 0.3 pct. Cr, 0.4 pct. Mn, 0.05 pct. Si, 0.3 pct. Ni, 0.3 pct. Cu, 0.05 pct. As, 0.05 pct. P, 0.05 pct. S, Fe – balance, by weight). Corrosion rate measurements were followed by light and electron microscope examinations of the corroded surface.

Results

The following alloys have been used in experiments (Table 1). The structure of alloys No.1–No.3 consists of primary austenite crystals and ledeburite alloyed with boron (Fig. 1,a–c). Eutectics Fe – Fe₃(B,C) and primary crystals of the solid solution Fe₂(B,C) surrounded with the shell of peritectic phase Fe₃(B,C) are observed in the structure of al-

loy No.4 (Fig. 1,d). With increase in boron content up to 5 wt.pct. primary crystals $Fe_2(B,C)$ and eutectics Fe – $Fe_2(B,C)$ appear in the structure of alloy No.5 (Fig. 1,e).

The corrosion rates of most alloys under investigation are lower than those of the reference specimen (Table 2). The corrosion rates in the aqueous solutions increase in the following sequence: NaCl→ Na_2SO_4 → CH_3COOH →HCl→ H_3PO_4 → H_2SO_4 → HNO_3 . Alloys No.1 – No.3 show maximum increase in the corrosion resistance in 1N HCl and 5N H_3PO_4 solutions. The corrosion rates of alloys No.2 – No.4 increase, especially, while testing in 5N H_3PO_4 , 0.5N H_2SO_4 , and 5 pct. HNO_3 solutions. Those in 3 pct. NaCl medium only slightly decrease. Alloy No.5 is characterized by the minimum corrosion rates, which are about 2 times (5 pct. HNO_3) to 5.5 times (5N H_3PO_4) lower than those of the reference specimen. Besides, for alloy No.5 the corrosion rates decrease in all the corrosive media.

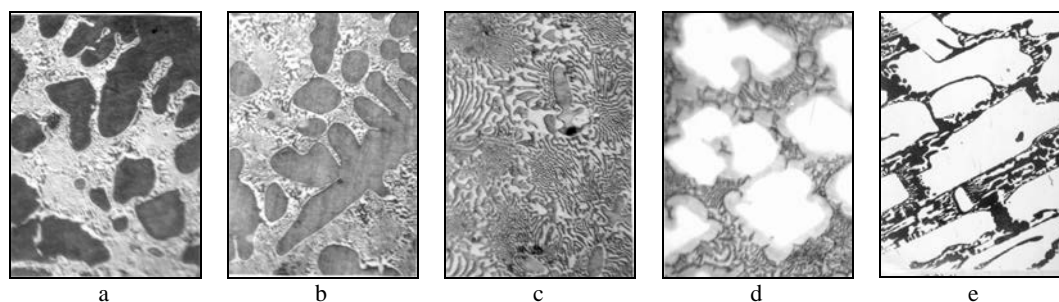


Fig. 1. Microstructure of the investigated Fe–B–C alloys, x300:
a – No.1; b – No.2; c – No.2; d – No.4; e – No.5

Table 2

Corrosion rates of Fe–B–C alloys, g/sq m-hr

Solution	No.1	No.2	No.3	No.4	No.5	ref.specimen
0.5 N H_2SO_4	75.6	91.9	113.5	221.6	48.6	140.5
1 N HCl	8.1	2.7	2.7	13.5	4.1	18.9
5 N H_3PO_4	32.4	70.2	102.1	129.1	27.0	151.4
2N CH_3COOH	4.1	2.05	4.8	14.1	1.8	5.0
5 pct. HNO_3	91.8	127.0	118.9	118.7	81.1	172.9
3 pct. NaCl	0.115	0.065	0.085	0.09	0.034	0.12
3 pct. Na_2SO_4	0.26	0.20	0.31	0.61	0.19	0.3

The corrosion effect is the most severe in 5 pct. HNO_3 and 0.5 N H_2SO_4 solutions. Virtually, corrosion resistance enhances with decreasing Fe– $Fe_3(C,B)$ eutectics content of the Fe–B–C alloys. The increase in boron content raises cathode (CH_3COOH), or anode (the other solutions) process overvoltages (Fig. 2).

More intensive corrosion processes proceed in the solutions 0.5N H_2SO_4 , 5N H_3PO_4 , and 3 pct. Na_2SO_4 , and less – in the solutions 1N HCl, 2N CH_3COOH , 5 pct. HNO_3 , and 3 pct. NaCl. Evidently, corrosion slows due to the accumulation of reaction products on the specimen surface, which separate the specimens from the aggressive environment.

Discussion

The minimum corrosion rate shows Fe–B–C alloy (No.5). The corrosion resistance of alloy No.1 is also quite high. Both No.1 and No.5 alloys are of less amount of the eutectics (20–25 pct. and 30–35 pct. respectively) and, hence, of austenite in the structure, as compared with No.3 and No.2 (95 pct. and 45 pct., accordingly) (Table 1). Besides, austenite of Fe– $Fe_2(B,C)$ eutectics corrodes less than that of Fe– $Fe_3(C,B)$ eutectics. The point is that the latter differs in a higher iron content and hoarser differentiation. The rela-

tively low corrosion resistance of specimen No.4 may be connected with interfaces between the primary $\text{Fe}_2(\text{B,C})$ crystals and the peritectic $\text{Fe}_3(\text{B,C})$ phase failure.

Thus, raising boron content of the Fe–B–C alloys up to 5 wt.pct. can increase corrosion resistance due to the decrease in the eutectics volume and the formation of solid solutions based on the iron boride Fe_2B . Iron boride owes its corrosion resistance to relatively thin surface oxide that provides a physical barrier between the boride and the aggressive environment. Boron also has positive effect on the corrosion resistance of cementite, which is particularly strong in the acid service environments.

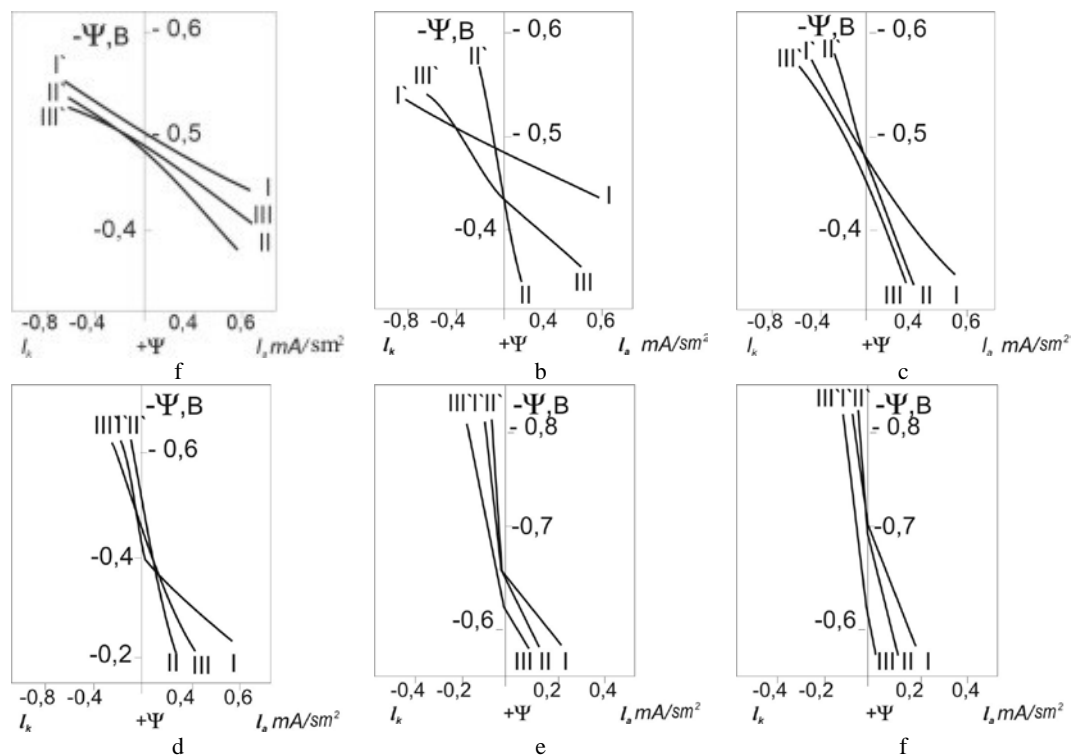


Fig. 2. Anode (I–III) and cathode (I'–III') polarization curves for reference specimen (I, I'), specimen No.3 (II, II'), and specimen No.4 (III, III') in the following media: a – $0.5 \text{ N H}_2\text{SO}_4$; b – $5 \text{ N H}_3\text{PO}_4$; c – 1 N HCl ; d – $2 \text{ N CH}_3\text{COOH}$; e – 3 pct. NaCl ; f – $3 \text{ pct. Na}_2\text{SO}_4$

Conclusion

Finally, the Fe–B–C alloys resist to nitric, sulphuric, hydrochlorine, phosphoric acids. They are also resistant to organic acids and acid salts. These materials combine corrosion resistance with high mechanical properties: hardness and compressive strength; they resist abrasive wear up to 400°C . These alloys are particularly suitable when used as protective coatings in the iron and steel, mining, chemical and allied industries where extremes of corrosion and abrasion must be withstood.

1. **Sukhova O.** Fe–B–C alloys for high temperature application / O. Sukhova // Bulletin of DU. Physics. Radioelectronics. – 2010. – V.18(2), No.17– P. 56 – 60.

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