

ON THE MATERIALS OF THE INTERNATIONAL
CONFERENCE "SCIENTIFIC AND PRACTICAL
SCHOOL FOR YOUNG METALLURGISTS" – 2023ПО МАТЕРИАЛАМ МЕЖДУНАРОДНОЙ
КОНФЕРЕНЦИИ «НАУЧНО-ПРАКТИЧЕСКАЯ
ШКОЛА ДЛЯ МОЛОДЫХ МЕТАЛЛУРГОВ» – 2023

UDC 620.193:669.1.017

DOI 10.17073/0368-0797-2024-2-229-236



Original article

Оригинальная статья

APPROACHES TO THE SELECTION OF MATERIAL DESIGN OF INFRASTRUCTURE FACILITIES FOR TRANSPORT AND INJECTION OF CO₂

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Abstract. The article is devoted to the study of dependence of carbon dioxide corrosion rate on the microstructure of material design of the pipeline for CO₂ transport and injection. Today there is a task of choosing such material design. For pipeline construction the most cost-effective materials are carbon steels, but for their application it is necessary to pay increased attention to the problem of carbon dioxide corrosion, which is intensified in wet, undrained CO₂ flows. At the same time, the choice of material should be made reasonably, taking into account the balance between corrosion resistance, mechanical characteristics and economic aspect of the issue. In this paper, the influence of microstructural state features on the corrosion rate of low-alloy mild steels for CO₂ transport and injection was investigated. The authors studied the features of steels with ferritic-bainitic, bainitic-ferritic-perlitic and ferritic-perlitic microstructures. Tests on corrosion resistance were carried out on the bench autoclave complex, which allows to recreate conditions of high pressure and temperature and to simulate real environments. It was determined that the microstructural state of steel has a significant effect on the corrosion rate, which increases with increasing volume fraction of pearlite. Understanding the relationship between the microstructural characteristics of steels and corrosion rates can simplify material selection for infrastructure facilities and contribute to more efficient and reliable use of low-alloy carbon steels in carbon capture, use, and storage projects. This study will be useful in selecting favorable microstructures for low-alloy mild steels that can be used for CCUS (Carbon Capture, Use and Storage) infrastructure projects.

Keywords: carbon capture, carbon storage, CCUS, decarburization, carbon dioxide corrosion, structure–property relationship, microstructure, chemical composition, corrosion rate

Acknowledgements: The research was supported by the Ministry of Science and Higher Education of the Russian Federation under the World Class Research Centre Programme: Advanced Digital Technologies (agreement No. 075-15-2022-311 dated 20.04.2022).

For citation: Rovbo A.S., Golubev I.A., Shaposhnikov N.O., Penigin A.V., Fedorov A.S. Approaches to the selection of material design of infrastructure facilities for transport and injection of CO₂. *Izvestiya. Ferrous Metallurgy*. 2024;67(2):229–236.

<https://doi.org/10.17073/0368-0797-2024-2-229-236>

ПОДХОДЫ К ВЫБОРУ МАТЕРИАЛЬНОГО ИСПОЛНЕНИЯ ИНФРАСТРУКТУРНЫХ ОБЪЕКТОВ ТРАНСПОРТА И ЗАКАЧКИ CO₂

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Аннотация. Работа посвящена исследованию зависимости скорости углекислотной коррозии от микроструктуры материального исполнения трубопровода для транспорта и закачки CO₂. На сегодняшний день существует задача выбора материального исполнения инфраструктурных объектов транспорта и закачки CO₂. Для строительства трубопроводов наиболее экономически эффективными материалами являются углеродистые стали, однако для их применения необходимо уделять повышенное внимание проблеме углекислотной коррозии, которая интенсифицируется во влажных неосушенных потоках CO₂. При этом выбор материала должен проводиться обоснованно, учитывая баланс между коррозионной стойкостью, механическими характеристиками и экономической стороной вопроса. В данной работе проведено исследование влияния особенностей микроструктурного состояния на скорость коррозии низколегированных малоуглеродистых сталей для транспорта и закачки CO₂. В ходе исследования изучены особенности сталей с ферритно-бейнитной, бейнитно-ферритно-перлитной и ферритно-перлитной микроструктурой. Испытания на стойкость к коррозии проведены на стендовом автоклавном комплексе, позволяющем воссоздавать условия высокого давления и температуры и моделировать реальные среды. Показано, что микроструктурное состояние стали оказывает значительное влияние на скорость коррозии, которая возрастает при увеличении объемной доли перлита. Понимание взаимосвязи микроструктурных особенностей сталей и скорости коррозии может значительно облегчить выбор материала для инфраструктурных объектов и способствовать более эффективному и надежному использованию низколегированных углеродистых сталей в проектах по улавливанию, использованию и хранению углерода. Данное исследование будет полезно при выборе благоприятной микроструктуры для низколегированных малоуглеродистых сталей, которые могут применяться для строительства инфраструктурных объектов CCUS (Carbon Capture, Use and Storage).

Ключевые слова: улавливание углерода, хранение углерода, CCUS, декарбонизация, углекислотная коррозия, взаимосвязь структура – свойства, микроструктура, химический состав, скорость коррозии

Благодарности: Исследование выполнено при финансовой поддержке Министерства науки и высшего образования Российской Федерации в рамках программы Исследовательского центра мирового уровня: Передовые цифровые технологии (соглашение № 075-15-2022-311 от 20.04.2022).

Для цитирования: Ровбо А.С., Голубев И.А., Шапошников Н.О., Пенигин А.В., Федоров А.С. Подходы к выбору материального исполнения инфраструктурных объектов транспорта и закачки CO₂. *Известия вузов. Черная металлургия*. 2024;67(2):229–236.

<https://doi.org/10.17073/0368-0797-2024-2-229-236>

INTRODUCTION

Carbon capture, use, and storage (CCUS) is a research area aimed at reducing CO₂ emissions and combating climate change. In the CCUS process (*Carbon Capture, Use and Storage*) [1; 2], CO₂ emitted into the atmosphere from various sources such as industrial enterprises, power plants, and motor vehicles is captured and subsequently stored in underground formations [3; 4]. This allows for the isolation of carbon dioxide from the atmosphere and prevents its negative impact on the climate.

Currently, there is a challenge in selecting the material design for infrastructure objects used for CO₂ transport and injection under increased environmental and economic risks [5; 6]. The selection of material should strike a balance between effectiveness in preventing intensive carbon dioxide corrosion [7] and the cost of the final solution [8].

A review of open sources on the topic of material selection for CCUS facilities [3; 9] has shown

that carbon steels are the most economically advantageous materials for pipeline construction [10]. However, their application necessitates increased attention to the problem of carbon dioxide corrosion [11], which intensifies in wet CO₂ flows [12]. Additionally, there is no consensus in the literature regarding the influence of steel microstructure and thermomechanical treatment modes on the mechanism and kinetics of corrosion processes [13 – 16]. This is because conditions can vary from one facility to another in terms of mineralization, component composition of environments, partial pressure, and temperature. Consequently, corrosion product deposits of varying morphology form on the steel surface, which can either be protective or accelerate the corrosion process. Therefore, the selection of materials must consider the operational conditions and actual environments at the facility. In this context, the goal of the present work is to investigate the influence of microstructural state features on the corrosion rate of low-alloy mild steels for CO₂ transport and injection, based on the conditions of a specific facility.

MATERIALS AND METHOD

To recreate the conditions of actual facilities, various bench setups are used, such as closed-loop flow stands or autoclave setups that replicate conditions of high pressure and temperature. In this work, an autoclave setup with a 3-liter capacity vessel was used. Currently, there are no standard methodologies for conducting corrosion tests in autoclaves, so the methodology used in this experiment is described below. The test conditions were selected based on the situation at the actual facility.

The essence of the corrosion testing method is to determine the mass loss of samples during their exposure to the corrosive environment. In the gravimetric method, the corrosion rate is determined by the mass parameter ρ , expressed in g/m²·h:

$$\rho = \frac{m_1 - m_2}{S\tau}, \quad (1)$$

where m_1 is the mass of the sample before testing, g; m_2 is the mass of the sample after testing, g; S is the surface area of the sample, m²; τ is the duration of the test, h.

If the change in mass is directly proportional to the depth of corrosion penetration under uniform corrosion conditions, the corrosion rate is recalculated into the depth parameter ν , expressed in mm/year. This parameter characterizes the uniform corrosion loss (thinning) of the sample per unit time:

$$\nu = \frac{8760\rho}{7.85 \cdot 10^3}, \quad (2)$$

where ν is the depth parameter of the corrosion rate, mm/year; 8760 is the number of hours in a year; 7.85 is the density of the investigated steel, g/cm³.

The gravimetric method allows for highly accurate results, as weighing is one of the most precise operations in quantitative analysis. The confidence interval for determining measurement error was 95 %.

Before testing, the samples were degreased using an ultrasonic cleaner in acetone, air-dried, and placed on a suspension in the autoclave, which was then sealed

and deaerated for 60 min with an inert gas flow rate of 100 ml/min per liter of capacity. The deaerated test solution was then saturated with CO₂. The total pressure in the autoclave was 6 MPa, with a partial pressure of CO₂ at 0.3 MPa. The temperature was maintained constant at 25 °C. The test duration was 96 h. For corrosion tests, three samples were selected from each steel.

The test solution consisted of 133 g/l CaCl₂, 31 g/l MgCl₂, 0.5 g/l NaHCO₃, 0.1 g/l Na₂SO₄ in distilled water. The total mineralization was 164.6 g/l. This composition corresponds to the fluid composition in the well being injected with CO₂ into underground formations. After testing, the samples were washed and air-dried, then cleaned of corrosion products using an eraser. The investigated steels correspond to the strength class K52, with their chemical composition presented in Table 1.

The microstructure of the steels was evaluated using a Reichert-Jung MEF3A optical microscope. To perform a quantitative assessment of the phase components, etching was selected to provide a contrasting image of the phases without revealing grain boundaries for subsequent automatic recognition by the Thixomet Pro image analyzer [17]. For this purpose, etching with a 4 % alcoholic solution of picric acid was used to reveal pearlite. For overall microstructure identification, a 3 % nitric acid solution in alcohol was used.

The traditional method for grain size assessment is described in GOST 5639 – 82, which, however, does not allow for the assessment of the heterogeneity of the grain structure. Nowadays, many methods for evaluating the grain structure of a material are known [18; 19]. For instance, in [20], a method for calculating the grain size variation factor F_z is proposed by the formula

$$F_z = \frac{f_{\max} Z_{\max}}{\sum f_i Z_i}, \quad (3)$$

where $f_{\max}$ is the fraction of the grain occupying the maximum area on the cross-section, %; $Z_{\max}$ is the grade of the grain occupying the maximum area on the cross-section; f_i is the fraction of the grain with a specific grade, %; Z_i is the grade of the grain.

Table 1. Chemical compositions of the studied steels

Таблица 1. Химический состав исследуемых сталей

Steel	Quantity, wt. %							
	C	Cr	Cu	Mn	Ni	P	S	Si
1	0.039	0.66	0.50	0.98	0.22	0.0074	0.0011	0.22
2	0.062	0.51	0.10	0.50	0.12	0.0055	0.0015	0.17
3	0.080	0.62	0.34	0.49	0.38	0.0037	0.0014	0.24
4	0.050	0.65	0.14	0.75	0.07	0.0031	0.0018	0.24
5	0.056	0.63	0.16	0.64	0.21	0.0042	0.0019	0.28

RESULTS OF THE QUANTITATIVE ASSESSMENT

OF STRUCTURAL COMPONENTS AND CORROSION TESTING

The materials investigated in this study were obtained from various domestic metallurgical enterprises using a technology that includes converter smelting, ladle treatment, continuous casting, followed by thermomechanical processing. The microstructures of the steels were examined in cross-section (Fig. 1).

The microstructure of steel 1 is characterized as ferritic-bainitic. The pearlite content in this steel is the lowest among all the steels studied, at 2.20 vol. %, and the grain structure (by the grain number occupying more than 10 % of the cross-section area) is evaluated as G_{10} (30 %) and G_{11} (28 %). The microstructure of steel 2 is characterized as ferritic-pearlitic with predominantly non-polygonal ferrite, with the grain structure evaluated as G_9 (13 %) and G_{10} (21 %). The pearlite content in this steel is 3.57 vol. %. The microstructure of steel 3 is also characterized as ferritic-pearlitic. The structure is evaluated as G_{11} (32 %) and G_{12} (32 %), and the pearlite content is 6.72 vol. %. The distribution of pearlite colonies is uneven, appearing as separate clusters with coarse morphology, similar to steel 2 (Fig. 2). The microstructure of steel 4 is characterized as ferritic-pearlitic-bainitic, with a pearlite content of 7.51 vol. %. The distribution of pearlite in this steel is fairly uniform, and the structure is evaluated as G_9 (14 %), G_{10} (28 %), G_{11} (29 %),

and G_{12} (18 %). The microstructure of steel 5 is characterized as ferritic-pearlitic. This steel has the highest pearlite content, 13.80 vol. %, after etching with picric acid. The structure is evaluated as G_{10} (21 %), G_{11} (32 %), and G_{12} (25 %).

RESULTS AND DISCUSSION

In ferritic-pearlitic steels, pearlite consists of a lamellar structure composed of alternating layers of ferrite and iron carbide (cementite). When exposed to aggressive media containing CO₂, the ferrite in the pearlite becomes the anode and dissolves quickly, while the cementite remains intact (Fig. 4). The carbon content is directly proportional to the pearlite content. The results of the corrosion tests shown in Fig. 3, *a* demonstrate that as the pearlite fraction in the microstructure increases, the overall corrosion resistance of the steels decreases.

The study [21] indicates that the most vulnerable areas are the boundaries between ferrite and cementite, where corrosion processes initially begin. It appears that increasing the number of pearlite colony areas leads to an increase in the number of vulnerable ferrite-cementite interphase boundaries and ferrite plates, which subsequently become anodes and dissolve quickly.

It is also worth noting the positive effect of copper on corrosion resistance – increasing the copper content from ~0.12 to 0.50 wt. % led to a reduction in the corrosion rate

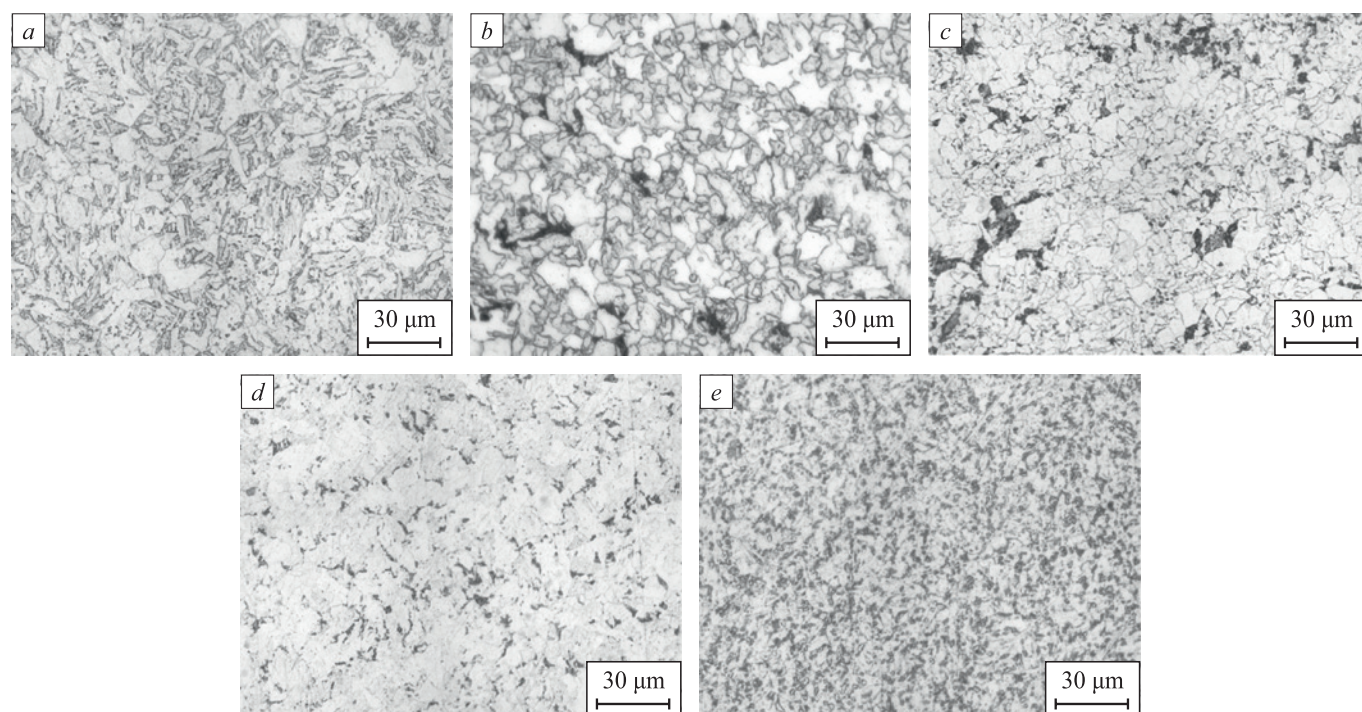


Fig. 1. General view of microstructures of the studied steels: composition 1 (*a*); composition 2 (*b*); composition 3 (*c*); composition 4 (*d*); composition 5 (*e*)

Рис. 1. Общий вид микроструктур исследуемых сталей: состав 1 (*a*); состав 2 (*b*); состав 3 (*c*); состав 4 (*d*); состав 5 (*e*)

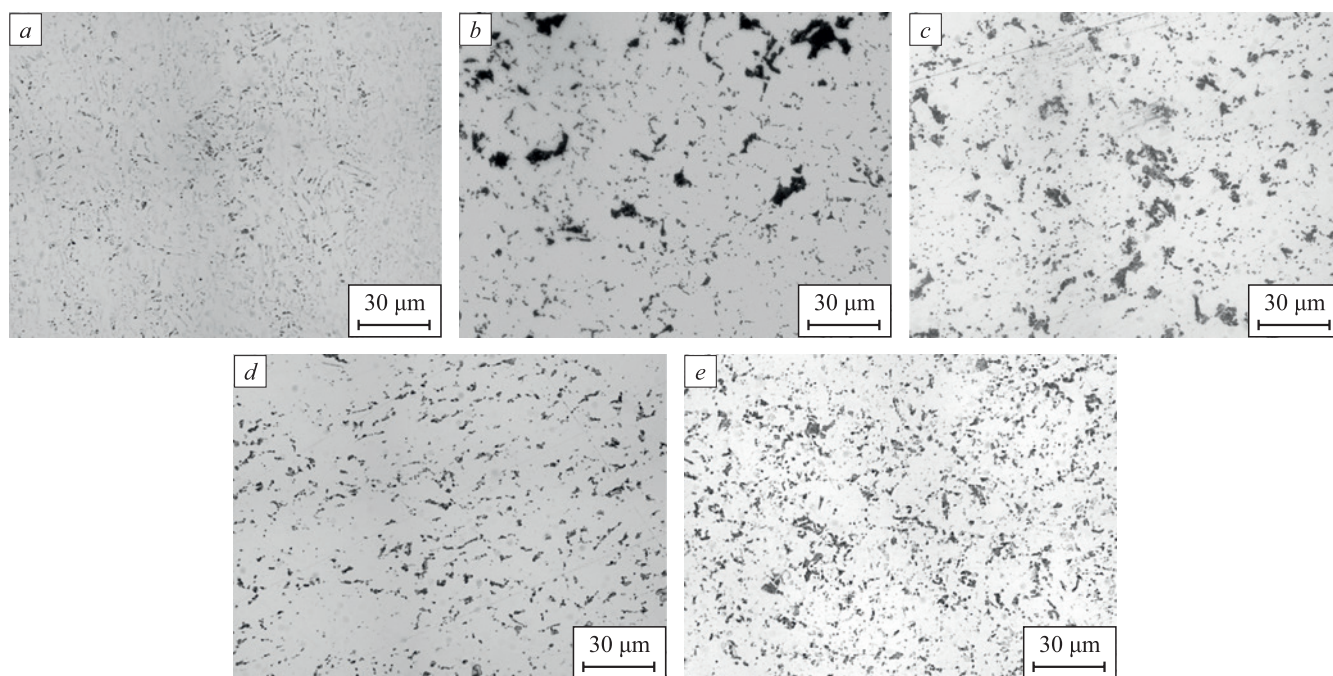


Fig. 2. Detection of perlite in the studied steels:
composition 1 (a); composition 2 (b); composition 3 (c); composition 4 (d); composition 5 (e)

Рис. 2. Выявление перлита в исследуемых сталях:
состав 1 (a); состав 2 (b); состав 3 (c); состав 4 (d); состав 5 (e)

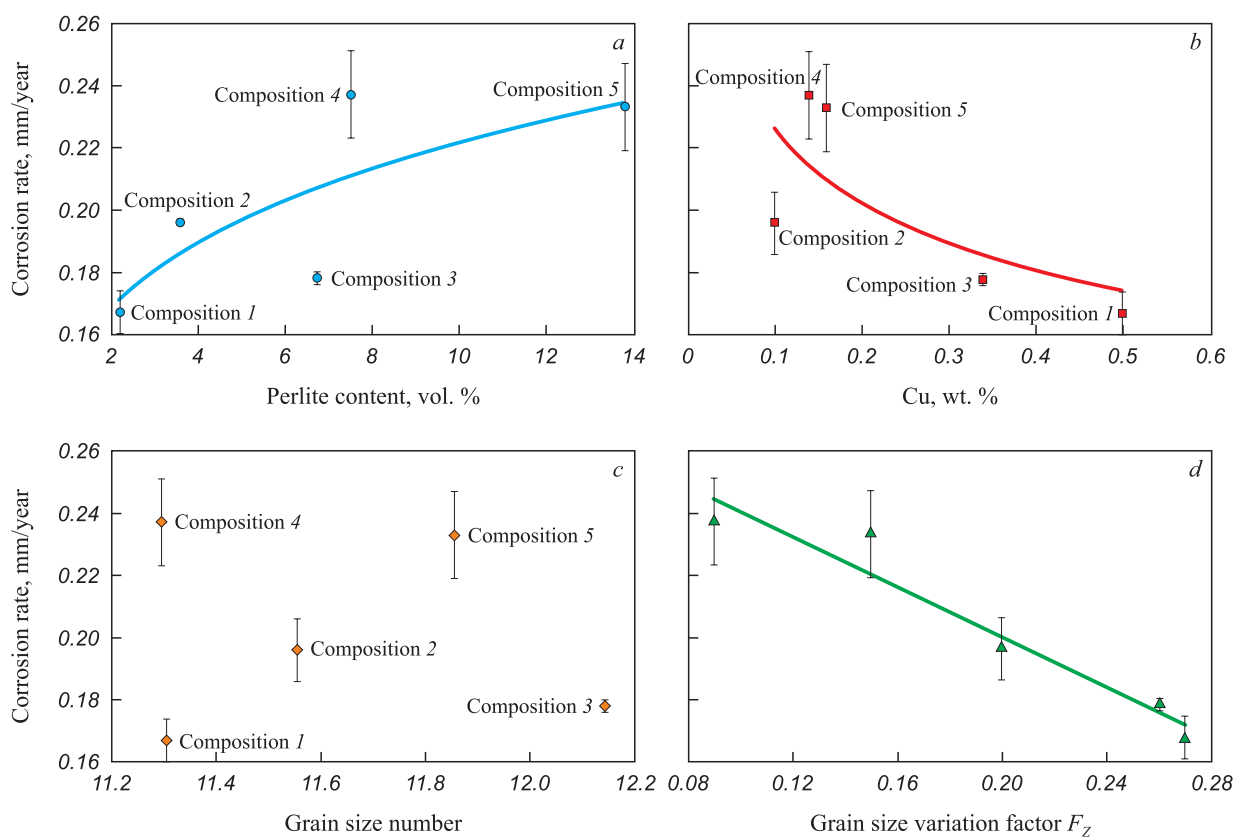


Fig. 3. Dependence of corrosion rate of the studied steels on:
perlite content (a); content of Cu in the steel (b); grain size number G (c); grain size variation factor F_z (d)

Рис. 3. Зависимость скорости коррозии исследуемых сталей от:
содержания перлита (a); содержания Cu в стали (b); номера зерна G (c); фактора разнотерности F_z (d)

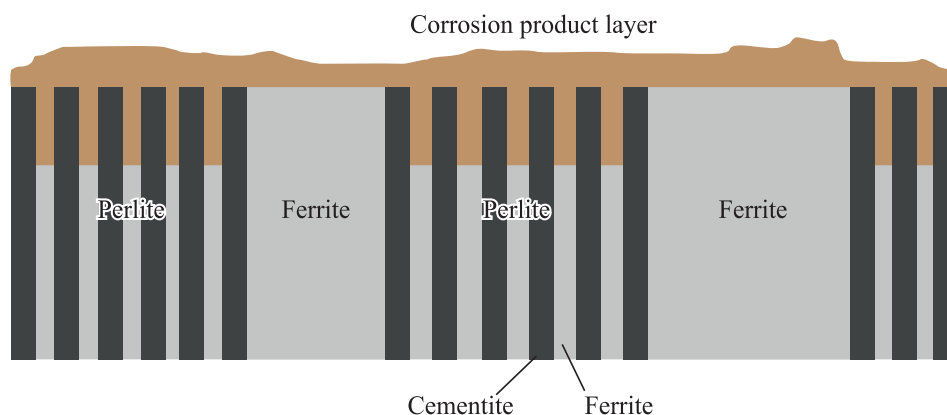


Fig. 4. Mechanism of corrosion of ferritic-pearlitic steels in CO₂-containing environments [22]

Рис. 4. Механизм коррозии ферритно-перлитных сталей в CO₂-содержащих средах [22]

from 0.237 to 0.167 mm/year (Fig. 3, *b*). The beneficial effect of copper on the corrosion properties of steels is noted in many studies. For instance, in [23], it was found that the introduction of a small amount of copper (usually up to 1 %) significantly enhances the corrosion resistance of low-carbon steels. Moreover, in high-strength low-alloy steels, copper is an alloying element that provides high toughness and good weldability. However, despite the advantages of adding copper to steel composition and the corrosion characteristics of ferritic-pearlitic microstructures demonstrated in this work, low-alloy mild steels should be used cautiously for the material design of CO₂ transport and injection infrastructure objects, and only with strict control over the presence of free water in the transported gas – its amount should be minimal. Otherwise, corrosion-resistant materials must be used.

Based on the evaluation of the microstructural parameters of the investigated steels presented in Table 2, it can be concluded that grain size does not have a determining influence on the corrosion resistance of the investigated steels (Fig. 3, *c*). However, the grain size variation, assessed by equation (3), significantly affects corrosion resistance (Fig. 3, *d*). Therefore, it can be concluded that the higher the uniformity of the structure (and, accordingly, the value of the F_z factor), the higher the corrosion resistance of the material.

CONCLUSIONS

A study was conducted on the influence of microstructural state features on the corrosion rate of low-alloy mild steels for CO₂ transport and injection (CCUS). It was shown that in ferritic-pearlitic steels, ferrite is primarily susceptible to corrosion processes, becoming an anode and dissolving quickly within pearlite. As a result, increasing the number of pearlite colony areas in the microstructure leads to a decrease in the overall corrosion resistance of the steel. The positive effect of copper on corrosion resistance was established – increasing the copper content in the investigated compositions from 0.12 to 0.50 wt. % led to a 1.5-fold reduction in the corrosion rate. It was noted that corrosion resistance is significantly influenced not by grain size, but primarily by the heterogeneity of the structure.

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Table 2. Results of assessment of the steels microstructure parameters

Таблица 2. Результаты оценки параметров микроструктуры сталей

Steel	Microstructure	[Cu], wt. %	Pearlite content, vol. %	Corrosion rate, mm/year	Ferrite grain number G	Grain size variation factor F_z
1	Ferritic-bainitic	0.50	2.20	0.167 ± 0.007	11.31	0.27
2	Ferritic-pearlitic	0.10	3.57	0.196 ± 0.010	11.56	0.20
3	Ferritic-pearlitic	0.34	6.72	0.178 ± 0.002	12.15	0.26
4	Ferritic-pearlitic-bainitic	0.14	7.51	0.237 ± 0.014	11.30	0.09
5	Ferritic-pearlitic	0.16	13.80	0.233 ± 0.014	11.86	0.15

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Received 10.10.2023

Revised 07.03.2024

Accepted 15.03.2024

Поступила в редакцию 10.10.2023

После доработки 07.03.2024

Принята к публикации 15.03.2024