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Increasing the corrosion resistance of ferrosilide in hot sulfuric acid by alloying with chromium, nickel and molybdenum

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Підвищення корозійної стійкості феросиліду у гарячій сірчаній кислоті при легуванні хромом, нікелем та молібденом

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Abstract. *The corrosion resistance of ferrosilides of the Fe-Si-Cr-Ni-Mo-Mn system in concentrated sulfuric acid in the temperature range of 25-200°C was investigated. The corrosion rate was calculated based on electrochemical parameters using passivation and temperature dependence models of the Arrhenius type. It was confirmed that the main factor determining corrosion resistance is the silicon content. The existence of a critical Si content threshold was shown, upon reaching which a continuous passive* SiO_2 *film is formed, which provides a reduction in the corrosion rate by 1-2 orders of magnitude. Characteristic temperature ranges of the corrosion process were identified: stable passivation (25-80°C), transitional regime (80-150°C) and degradation of the passive state (150-200°C). It has been shown that Cr and Mo in Fe-Si alloys enhance the stability of the passivated state, particularly at high sulfuric acid temperatures, whereas Ni primarily affects the electrochemical characteristics, and Mn reduces the effectiveness of passivation. The effectiveness of adding chromium to Fe-Si alloys increases proportionally with the Si content; molybdenum stabilizes passivation at acid temperatures above 150°C and reduces the rate of localized corrosion; nickel is not a determining factor at high acid temperatures. The influence of operational factors (turbulence, erosion, impurities) on the corrosion rate has been determined. The expected corrosion rates for the studied alloys in sulfuric acid have been calculated, taking into account industrial operating conditions. The experimental data obtained can be used to develop new corrosion-resistant materials and optimize the composition of Fe-Si alloys for operation in high-temperature aggressive environments of concentrated sulfuric acid.*

Keywords: *Fe-Si alloys; corrosion resistance; sulfuric acid; passivation; silicon dioxide; electrochemical corrosion; high-temperature corrosion; alloying elements.*

Анотація. *Досліджено корозійну стійкість феросилідів системи Fe-Si-Cr-Ni-Mo-Mn у концентрованій сірчаній кислоті в діапазоні температур 25-200°C. Виконано розрахунок швидкості корозії на основі електрохімічних параметрів із використанням моделей пасивації та температурної залежності типу Арреніуса. Підтверджено, що основним фактором, який визначає корозійну стійкість, є вміст кремнію. Показано існування критичного порогу вмісту Si, при досягненні якого формується суцільна пасивна плівка* SiO_2*, що забезпечує зниження швидкості корозії на 1-2 порядки. Виділено характерні температурні області корозійного процесу: стабільна пасивація (25-80°C), перехідний режим (80-150°C) та деградація пасивного стану (150-200°C). Показано, що Cr і Mo у складі феросиліду підвищують стабільність пасивного стану, особливо при високих температурах сірчаної кислоти, тоді як Ni впливає переважно на електрохімічні характеристики, а Mn знижує ефективність пасивації. Ефективність введення хрому до складу феросиліду зростає пропорційно вмісту Si, молібден стабілізує пасивацію при температурах кислоти вище 150°C і знижує швидкість локальної корозії, нікель не є* *визначальним фактором при високих температурах кислоти. Визначено вплив експлуатаційних факторів (турбулентність, ерозія, домішки) на швидкість корозії. Розраховані очікувані швидкості корозії для досліджуваних сплавів у сірчаній кислоті з врахуванням умов промислової експлуатації. Отримані експериментальні дані можуть бути використані для розробки нових корозійностійких матеріалів і оптимізації складу феросилідів для роботи у високотемпературних агресивних середовищах концентрованої сірчаної кислоти.*

***Ключові слова:** феросиліди; корозійна стійкість; сірчана кислота; пасивація; діоксид кремнію; електрохімічна корозія; високотемпературна корозія; легувальні елементи.*

Introduction

Corrosion of alloys in acidic environments remains one of the key challenges in modern metallurgy and chemical engineering [1, 2]. Operating conditions are particularly challenging at elevated temperatures in concentrated sulfuric acid, where traditional corrosion-resistant materials, notably stainless steels and nickel-based alloys, demonstrate limited suitability due to the intense destruction of passive protective films and the development of localized corrosion processes [3, 4].

In this regard, there is growing interest in ferrosilicides as promising materials with enhanced corrosion resistance. Fe-Si alloys demonstrate enhanced corrosion resistance in sulfuric acid; they are capable of forming a dense passive silicon dioxide film on the surface, characterized by high chemical inertness in strong acids [4, 5]. At the same time, the effectiveness of the passivation film's preservation significantly depends on the silicon content, the acid temperature, and the presence of alloying elements in the alloy, such as chromium, molybdenum, nickel, and manganese [6, 7]. The issue of determining the critical silicon content and the effect of complex alloying of ferrosilicide on the kinetics of corrosion processes and the stability of the passive film, at which a stable passive state is ensured over a wide operating temperature range, remains insufficiently studied.

It is also important to take into account not only laboratory conditions but also real-world operating conditions, including flow turbulence, erosion wear, and the presence of impurities, which can significantly alter corrosion mechanisms and lead to an increase in the rate of material degradation [8].

Classical studies [1, 4] have shown that even at silicon contents in the range of 14-16%, ferrosilicides undergo a transition from Fe-oxide to SiO_2-controlled passivation, which is accompanied by a sharp decrease in corrosion current density and explains the high corrosion resistance of high-silicon cast irons and intermetallides. According to the phase diagram [9], at a Si content >14.37% Si, the Fe_3Si intermetallic phase forms, and a Si content in the alloy exceeding 15% defines a region where a mixture of iron and Fe_3Si predominates; in this region, upon cooling of the melt, the formation of ordered intermetallics and a significant decrease in ductility are expected.

During crystallization, the main final phases in an alloy containing >15% Si up to 99% of the total mass will be FeSi, Fe_3Si, and Fe_5Si_3 (Fig. 1), with only up to 1% of unbound Si (in the form of fine crystals and/or inclusions). The brittleness of such an alloy is explained by the virtually complete absence of ferrite and the acquisition of ceramic properties. At the same time, such an alloy acquires properties of thermal-oxidative stability and corrosion resistance due to the formation, under appropriate heat treatment conditions, of a protective layer of SiO_2.

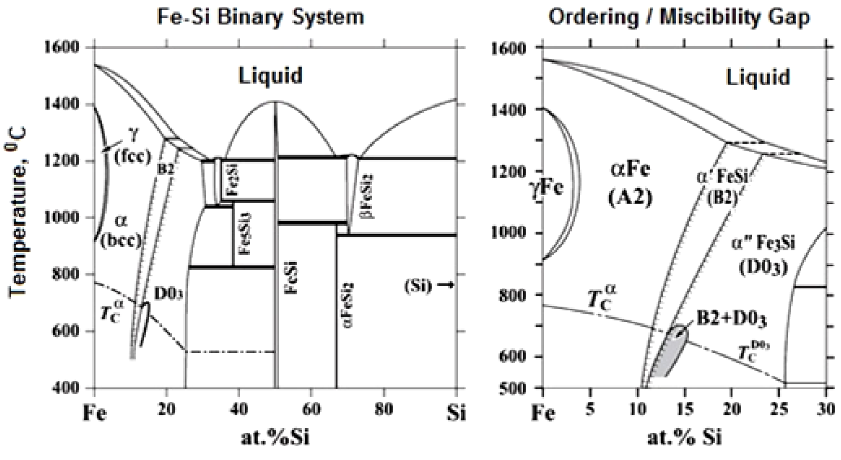


Fig. 1. Fe-Si phase diagram at 1 atm from Numakura and Tsugawa (1972).

A mixture of FeSi, Fe_3Si, and Fe_5Si_3 in sulfuric acid performs better than the individual phases, ensuring a long-lasting passive state of ferrosilicide [9-11]. The synergistic effect of resistance to H_2SO_4 is achieved through the following mechanism: Fe_3Si (with an optimal Fe/Si ratio) promotes the formation of a passivation film (SiO_2 + Fe oxides), Fe_5Si_3 promotes the formation of amorphous SiO_2, and FeSi promotes less stable passivation. The formation of SiO_2, which is poorly soluble in H_2SO_4, prevents ion diffusion.

The interaction of Fe-Si with sulfuric acid over time is accompanied by active corrosion in the initial period due to the anodic dissolution of iron:

$$Fe \rightarrow Fe^{2+} + 2e^- \quad (1)$$

followed by oxidation

$$Fe^{2+} \rightarrow Fe^{3+} + 2e^- \quad (2)$$

cathodic reactions in acidic media

$$2H^+ + 2e^- \rightarrow H_2\uparrow \quad (3)$$

Corrosion reaction upon contact with acid

$$Fe + H_2SO_4 \rightarrow FeSO_4 + H_2\uparrow \quad (4)$$

this, in turn, is accompanied by the enrichment of the ferrosilicon surface with silicon (Si) and the formation of a passivation film of silicon dioxide (SiO_2) during its oxidation

$$Si + 2H_2O \rightarrow SiO_2 + 4H^+ + 4e^- \quad (5)$$

or films of hydrated silicon dioxide

$$Si + 2H_2O \rightarrow SiO_2 \cdot nH_2O + 2H_2\uparrow \quad (6)$$

chemically inert in H_2SO_4, followed by a transition to a passive state.

When casting products from such Fe-Si alloys, it is necessary to cool them slowly along with the mold. Rapid cooling can cause metastable states to “freeze,” and the formation of the Fe_3Si intermetallic compound may be partially suppressed. In this case, part of the Si will remain in the solid solution (in α-Fe) or nanometric intermetallic precipitates will form. An excessive metastable structure can affect phase distribution, and there is a risk of hot or cold cracks forming in cast parts due to internal stresses. Conditions for machining are created by thermal tempering or controlled recrystallization, which in turn can lead to the formation of brittle intermetallides and an increase in brittleness over time or under the influence of temperature.

The presence of impurities (Al, Mn, C, P, S, etc.) in Fe-Si alloys promotes the formation of secondary phases and the incorporation of some Si into complex complexes, which alters the phase distribution and structure of the alloy. At the same time, low S and P content (< 0.05%) prevents brittleness and intergranular corrosion of the alloy.

Recent studies [1-7, 9, 11] have confirmed that ferrosilicides are one of the most promising classes of materials for use in aggressive acidic environments. However, the lack of comprehensive studies comparing the corrosion resistance of pure and economically alloyed ferrosilides under high-temperature operating conditions in concentrated H_2SO_4 underscores the relevance of further research in this area.

The purpose of the work.

The aim of this study is to investigate the corrosion resistance of Fe-Si-Cr-Ni-Mo-Mn ferrosilicides in concentrated sulfuric acid over a temperature range of 25-200°C, to determine the effect of silicon content and alloying elements on the corrosion rate, and to examine the characteristics of passive film degradation.

Analysis of recent studies and publications.

The optimal composition of an Fe-Si alloy, in terms of casting properties, is as follows: 12-16% Si, up to 2.5% C (S, P < 0.05%), with the remainder being Fe. The typical structure of such an alloy consists of a ferritic matrix (Fe + Si solid solutions), free graphite inclusions (fine plates or globules), and a minimum of cementite. Due to the silicon content of up to 16%, hardness increases (~250-350 HB and higher), with a simultaneous decrease in ductility, and corrosion resistance in acids (especially in H_2SO_4) increases due to the formation of a SiO_2 film during heat treatment [12].

Obtaining more ductile alloys is possible by reducing the silicon content to 6-10% Si or by alloying with elements that increase ductility. This approach is based on addressing the fundamental issue - the presence of an intermetallic, brittle Fe_3Si matrix. The improvement in ductility is also partially achieved through process modifications or changes in the alloy’s chemical composition and structure.

In the Fe-Si-C system, silicon sharply reduces the solubility of carbon in liquid and solid iron. For example, at a silicon content of >15%, the solubility of carbon in liquid Fe decreases to 0.1-0.2% at 1500°C. Excess carbon from the melt is converted into graphite (silicon “displaces” carbon from the metal into the graphite phase). When the alloy contains more than 12–13% Si, the carbon activity a_C increases, and the activity coefficient f_C at 15% Si will be >10 (carbon becomes energetically “excessive”); the system’s attempt to minimize energy leads to the formation of a solid phase - graphite. The primary graphitizer in Fe-Si alloys is silicon itself. Already at >4% Si, silicon stimulates graphitization - it reduces the stability of cementite Fe_3C and promotes the precipitation of carbon as graphite. An excess of graphite reduces acid resistance but improves casting properties.

To prevent graphite precipitation, it is advisable to reduce the carbon content in the charge (< 0.05% C), use $CaO\text{-}SiO_2$ slag, and raise the melting temperature to 1580-1620°C, which temporarily increases the solubility of C, and deoxidize with Al. The effects of high S content on graphitization are mitigated by preliminary desulfurization of the melt.

The addition of Ni, Mo, Co, and Cr to the ferrosilicide composition in limited quantities (1-5% Ni, 1-2% Mo, 3-6% Cr) helps reduce brittleness [4], but does not ensure full ductility of the alloy.

Nickel has high solubility in ferrite (α-Fe) and in Fe_3Si intermetallic compounds, contributing to the stabilization of the solid solution, which in turn ensures the presence of Si in supersaturated α-Fe during cooling. In addition, Ni slows down the ordering of Fe_3Si, resulting in the formation of finer intermetallic compounds and a reduction in brittleness.

Molybdenum has limited solubility in solid Fe-Si alloys, but even a small amount of Mo significantly slows down diffusion. Mo tends to form carbides and silicides ($MoSi_2$ and $FeMoSi_2$, respectively), but at concentrations up to 1% Mo in alloys with <15% Si, these compounds will promote the formation of fine precipitates. Overall, molybdenum acts as a solid solution hardener and promotes the formation of a fine-grained alloy structure and a reduction in brittle intergranular fracture. The impact toughness of such low-alloyed Fe-Si alloys can increase by ~10-20% from the base level.

The presence of chromium in Fe-Si alloys will promote the formation and stabilization [13] of a passive oxide film, but in sulfuric acid, its stability will depend on concentration and temperature. It is known [1, 2, 5, 12] that an alloy containing 20-35% Ni, 15-20% Cr, 2-5% Mo (analogous to Alloy 20) (Table 1). For high resistance in hot concentrated (90-98% H_2SO_4) acid, it is considered advisable to use high-nickel alloys with a content of ≥50-60% Ni, 12-17% Mo, and 14-16% Cr (equivalent to Hastelloy C-276 / Alloy C-276) (Table 1).

Table 1 - Chemical composition of selected H_2SO_4-resistant alloys, wt. %.

Alloys	Ni	Cr	Mo	Fe	Cu	Si	Mn	W	Co	Other / Notes
Hastelloy C-276	55-57	15-16	15-17	≤5	-	≤0.08	≤1	3-4.5	≤2.5	C≤0.01%, others Ni
Hastelloy C-22	56	20-22.5	12.5-14.5	2-6	-	≤0.08	≤0.5	2.5-3.5	≤2.5	Improved Cr/W balance
Hastelloy B-2	bal	-	26-30	≤2	-	≤0.1	≤1	-	-	Cr-free, for reducing acids
Alloy 20	32-38	19-21	2-3	35-45	3-4	≤1	≤2	-	-	Ti=0.6-1.0%, Nb≈0.1%
904L	23-25	19-23	4-5	bal	1-2	≤1	≤2	-	-	N≈0.1%, S low
Monel 400	63-70	-	-	2-3	28-34	≤0.5	≤2	-	-	High plasticity
Inconel 718*	50-55	17-21	2.8-3.3	bal	-	≤0.35	≤0.35	-	≤1	Al 0.2-0.8, Ti 0.6-1.15
Iron alloy with ~14%Si (ferrosilide)	≤1	≤0.5	-	bal	-	13–15	≤0.5	-	-	Hard Fe–Si phases, brittle

* contains additionally 4.75-5.5% Nb

It should be noted that Alloy 20 is significantly more resistant than 316L stainless steel in sulfuric acid, but this is true only for moderate concentrations of H_2SO_4; at high temperatures, degradation occurs and the corrosion rate increases significantly (M. Bazgir, K. Rahmanik, 2021).

When using Hastelloy (C-276, C-22) in concentrated sulfuric acid, corrosion is higher than in HCl, and for C-276 it can reach 0.5-2 mm/year (S. Hastuty, A. Widiatmoko, T. Sudiro et al., 2023).

Ferrosilicides (Duriron - Fe-Si alloys with 14-18% Si) have demonstrated high resistance in H_2SO_4 due to the SiO_2 surface passivation effect, and according to [9], the corrosion rate does not exceed 0.01 mm/year. At the same time, in industrial applications, hydrodynamic factors (flow velocity, destruction of the passivation film, etc.) have a negative impact on the corrosion rate.

In a study of the stability of Fe-Si (containing 6% Si) in boiling concentrated H_2SO_4, the authors [14] demonstrated a decrease in the corrosion rate (≈0.056 mm/year) over time (passivation of the alloy).

The corrosion resistance of Fe-Si alloys with 8-20% Si content in H_2SO_4 at 250°C was investigated in [15] using potentiometric polarization and potential decay analysis. It was shown that the passivity of alloys with 14% Si is controlled by the formation of a SiO_2 film with low electrical conductivity. At Si contents below 14%, the alloy’s behavior is determined by a passive iron oxide film. A restoration of passivity was observed at Si contents of 14% and 16% following a potential drop, which was explained by self-passivation after the dissolution of the iron oxide film and the saturation of the surface with Si.

A comparison of the corrosion resistance in 10% and 20% H_2SO_4 solutions of an alloyed intermetallic coating composed of Fe_3Si, applied to the surfaces of AISI420 and AISI304 stainless steels containing Cr and Ni, and to the surface of A3 carbon steel, was conducted in the study [16] using an electrochemical method and static immersion tests. It was confirmed that, due to the presence of Cr and Ni alloying elements, the Fe_3Si coating was dense, relatively thick, and had only a few defects, which helped ensure the protection of stainless steel against surface corrosion. The pronounced passivation of Fe_3Si in sulfuric acid was confirmed.

Changes in the phase composition, microstructure, and pore structure of porous pressed Fe-Si samples obtained by the synthesis of elemental powders, as well as corrosion resistance to a sulfuric acid solution (at a concentration of 160 g/l), were investigated in [17]. The following sequence of phase formation was established: α-Fe, Fe_3Si, η-Fe_5Si_3, and ε-FeSi during sintering. A two-phase nature of the corrosion kinetics of the Fe-Si alloy was revealed, with average corrosion rates of 0.00211 %/year and 0.00118 %/year, respectively.

The authors of a study on the corrosion resistance of Fe-Si alloys in boiling solutions of 95% and 50% sulfuric acid [18] found that the critical Si content for passivation lies in the range of 9-10% Si and 12-15% Si in 95% and 50% acid, respectively. The oxide film formed on the surface of passivated Fe-Si alloys was investigated using X-ray diffraction and scanning microscopy. It was found that the passivation film consisted of an amorphous oxide with an Si/O atomic ratio of approximately 0.5, and its growth rate depended on the alloy composition and acid concentration.

The feasibility of using Fe-Si alloy in boiling sulfuric acid and hydrogen iodide in the thermochemical hydrogen production process was investigated in [19]. It was confirmed that although the corrosion resistance of the Fe-Si alloy increases with increasing Si content, the material becomes brittle. Using the chemical vapor deposition method, a Fe-Si alloy with a graded composition (CG Fe-Si) was preliminarily prepared, containing 14% Si on the surface and 3% Si on the substrate. The resulting CG Fe-Si alloy exhibited corrosion resistance in boiling H_2SO_4 (at a concentration of 17.7 kmol/m^3) equivalent to that of a Fe-Si alloy with 12% Si; however, after 300 hours of immersion in the acid, the SiO_2 film on the surface became prone to delamination around areas with microcracks caused by cooling during chemical deposition.

Research results and discussion. The smelting of experimental Fe-Si alloys was carried out in an IST-016 induction furnace at the laboratory of the Department of Metallurgy at DSTU according to the following procedure.

In the first stage, in accordance with the theoretical rationale outlined above, the charge was properly prepared by refining the cast iron to remove sulfur to the specified levels (less than 0.05% S). Desulfurization of the molten cast iron was achieved by blowing dispersed magnesium (99.9% Mg, manufactured in China) through a submerged tuyere according to the method described in [20]. The resulting molten refined cast iron was poured into cast iron molds. In the next stage, by remelting the steel billet and refining the melt in the furnace, steel castings with the specified chemical composition were obtained.

After forming a single charge from refined ingots of cast iron, steel, and ferroalloy (FeSi45) -used to produce a molten metal with a silicon content of 6-15% Si - the charge was loaded into the crucible of the induction furnace. During the smelting process, slag was skimmed off the surface of the metal bath. A portion of the Fe-Si metal melt was left in the furnace crucible to form a “slurry” and increase the degree of incorporation of the alloying elements added in subsequent stages.

In the second stage of melting, the calculated amount of refined cast iron was added to the resulting Fe-Si melt, and after its incorporation, FeSi45 and alloying elements (FeCr, Mo, Ni) were added. During the absorption of the alloying elements, the melt was protected from the effects of atmospheric oxygen by blowing argon (at a flow rate of 0.05 m^3/min) onto the surface of the bath through a tube located under a graphite plug at the furnace throat.

During the melting process and prior to pouring, the bath temperature was measured. A “Smotrich-5P” partial-emission pyrometer and TS360309 immersion thermocouple blocks with a “Heraeus” Digitemp DTK 01-T-II digital temperature meter were used. The pouring temperature of the resulting melts was determined relative to the liquidus temperature of the expected composition; an excess temperature gradient of 83-96 degrees was maintained, taking into account heat losses during transfer to the ladle and during pouring into preheated (600-620°C) sand-clay molds.

Table 2 – Results of elemental analysis of experimental Fe-Si alloys.

№ alloy	Conditional marking	Contents, %					
		Fe	Mn	Si	Cr	Ni	Mo
1	FS17Cr4	75.78	1.82	17.7	3.9	0.21	0.04
2	FS19Cr3NM	72.01	2.57	18.97	3.69	1.47	1.08
3	FS24Cr6N2M	64.94	1.46	23.99	6.37	1.74	1.23
4	FS27Cr6NM	49.45	6.67	27.67	6.16	1.11	0.6
5	FS12Cr8N2	74.26	1.43	12.38	7.85	2.15	0.05
6	FS25Cr6NM	66.1	1.32	24.3	6.1	1.62	1.1
7	FS16Cr6N2M	77.2	1.2	15.9	6.2	1.9	1.05

Data on the fluidity, linear shrinkage, shrinkage cavity volume, and porosity of the alloys were obtained using standard methods. To determine the casting properties of the experimental alloys, a standardized casting test with a constant cross-section and central metal feed was used. The hardness of the alloys was determined using the Brinell method on a TSh-2M device.

Prior to testing the obtained experimental alloys for corrosion resistance [10], a SiO_2 passivation film was formed on their surfaces. According to the theory, film formation proceeds as follows: Si → SiO_2 (dense film); Fe → Fe_2O_3 (outer layer); Ni → NiO (in the presence of Ni, it reacts with Fe_2O_3); Cr → Cr_2O_3; carbon-oxidizes locally but burns off rapidly from the surface layer at 800-900°C.

In this process, Si forms a dense layer of SiO_2 that inhibits further oxidation, causing the surface to passivate rapidly, while the deeper alloy layers remain virtually unaffected by oxidation. To create a protective oxide film of SiO_2 on the surface of the castings, controlled surface oxidation was ensured rather than oxidation of the entire volume, taking into account the following conditions:

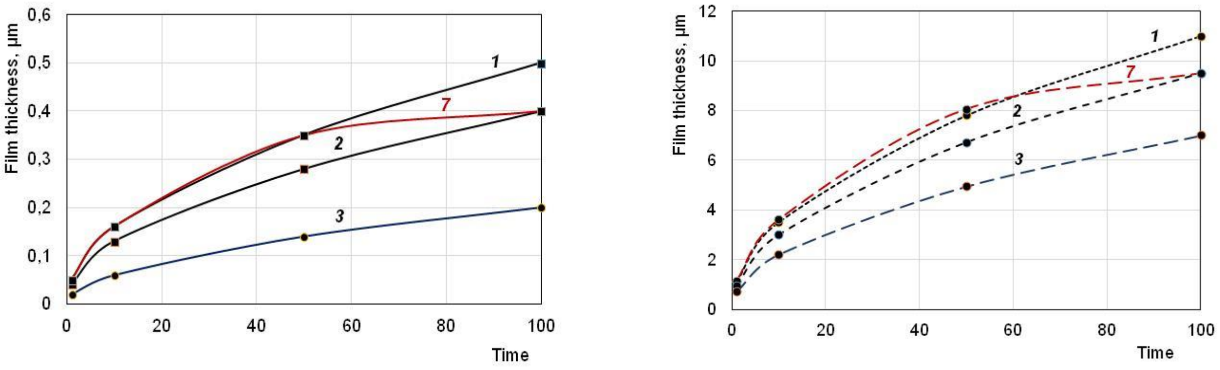
- the temperature during heat treatment in the furnace was maintained at 850-1000°C for 3-4 hours, with the castings held in the dry air atmosphere of the working space;

- a moderate heating rate (up to 5 °C/min) and cooling of the castings in the furnace to <200°C were intended to prevent cracking and destruction of the SiO_2 passivation film.

To calculate the thickness (*x*) of the SiO_2 film on Fe-Si alloys (including those doped with Cr, Ni, and Mo) for a heat treatment duration (t), the parabolic oxidation law was used, in µm:

$x^2 = k_P \cdot t$, where k_P is the parabolic rate constant (µm²/h). This is due to the fact that at high heat treatment temperatures of ferrosilicide, the film growth rate is limited by the diffusion of ions through the already formed oxide layer.

Figure 2 shows a graph of the increase in the thickness of the oxide passivation film during heat treatment for the studied alloys No. 1, 2, 3, and 7 at holding temperatures of 800°C (a) and 1100°C (b), respectively.



a b

Fig. 2. The kinetics of the growth in thickness of the oxide passivation film during heat treatment for alloys No. 1, 2, 3, and 7 at holding temperatures of 800°C (a) and 1100°C (b), respectively.

Annealing alloy No. 1 at 1100°C for 5 to 10 hours (Fig. 2, b) results in the formation of a film thick enough to protect the ferrosilicide surface. With longer aging, the film thickness reaches 11 µm, which can lead to cracking due to internal stresses in the oxide and the formation of microcracks. At temperatures of 1000-1100°C, SiO_2 begins to crystallize into α-cristobalite, which may contribute to the formation of micropores at the oxide grain boundaries.

The film growth rate slows down over time due to a diffusion barrier formed by the SiO_2 layer, which blocks the influx of oxygen atoms into the metal. The critical film thickness, at which it retains plasticity, high strength, and does not delaminate, is 5-7 µm. If the thickness exceeds 10 µm, the accumulated stress energy can lead to spontaneous delamination of the film.

The film's density is determined by its ability to block oxygen from reaching the metal and is calculated using the Pilling-Bedworth ratio (PBR) [10], which is approximately 1.88 for SiO_2. Under conditions where PBR < 2.5, the film is continuous and completely covers the metal surface without breaking away from its own volume. At heat treatment temperatures of 800-900°C, the film remains amorphous, ensuring ideal density.

A positive effect of Fe-Si alloying elements on the formation of the passivation film has been observed. Thus, Ni improves the plasticity of the metal beneath the film, partially compensating for the brittleness of the high-silicon matrix, and enhances the film's adhesion (creating an "anchor effect" at the metal-oxide in

\]terface), preventing its delamination during cooling, mechanical loading, or vibrations. Mo increases the strength of the metal substrate itself at 800-900 °C and resistance to pitting corrosion, which can occur if the acid contains chloride impurities. Cr strengthens the film itself by partially dissolving in it, which increases its fracture toughness. As a result, a multilayer structure forms instead of pure SiO_2. Directly on the metal is a dense SiO_2 film, and on the outside is a thin layer of iron chromites ($FeCr_2O_4$) or chromium oxide (Cr_2O_3), which makes the film less brittle.

However, it is not the thickness but the chemical stability of the passivation film in an acidic liquid medium that plays the key role. Upon contact with sulfuric acid, the iron on the surface begins to dissolve, but the silicon remains. It reacts with water to form hydrated silicon dioxide (6). This layer becomes extremely dense, chemically inert, and insoluble in acid.

To assess the tendency to form a stable passivation effect in Cr-, Ni-, and Mo-alloyed ferrosilicides (Table 2), the equivalent silicon content Si_{eq} was calculated, which accounts for the influence of the alloying elements:

$$Si_{eq} = Si + k_{Cr} \cdot Cr + k_{Mo} \cdot Mo + k_{Ni} \cdot Ni \qquad (7)$$

k_{Cr}, k_{Mo} та k_{Ni} - empirical equivalents adapted for SiO_2 passivation (Olssand and Landolf, 2023), which are 0.4, 0.6, and 0.2, respectively.

For example, for alloy No. 2 (Table 2), the calculated Sieq value is ≈ 22.85%, indicating a 1.2-fold "increase" in the equivalent Si content upon alloying. In general, the oxidation of 3–6% Cr introduced into Fe-Si with 15-19% Si ensures the formation of a combined protective layer of SiO_2 + Cr_2O_3 in concentrated H_2SO_4, but one that is less continuous than at >24% Si.

The corrosion rate of such complex multicomponent alloys in hot sulfuric acid depends heavily not only on its temperature but also on the acid concentration (diluted or concentrated), the presence of oxidizing agents, the formation of Fe_3Si and Fe_5Si_3 phases, and the Fe-Si structure of the products, which depends on the manufacturing method and heat treatment, as well as the flow velocity of the medium (turbulence, erosion development, etc.).

According to [9], when ferrosilicide is exposed to sulfuric acid, active corrosion is observed at $Si_{eq} < 16\%$; at 16-20% Si_{eq}, partial passivation occurs; at 20-24% Si_{eq}, an unstable passivation film forms; and as Si_{eq} increases beyond 24%, stable passivation occurs.

The characteristic temperature ranges of the corrosion process can be identified as follows: stable passivation (25-80°C), a transitional regime (80-150°C), and degradation of the passive state (150-200°C). At temperatures > 150°C, degradation of the passivation film is observed, with the corrosion rate of the Fe-Si alloy increasing by an order of magnitude compared to when Si content is > 24% and when Si < 15%.

At a concentration of 98%, sulfuric acid acts as a passivator; it is a strong oxidizing agent that instantly forms a protective layer of SiO_2 enriched with chromium oxides on the surface of the high-silicon alloy. At the same time, while the passivation film is stable at an acid temperature of 25°C, at 200°C the acid is extremely aggressive, actively dissociates, and the kinetic energy of the molecules allows them to penetrate through the SiO_2 film layer. The film undergoes “chemical erosion.” The introduced dopants (Mo, Cr) stabilize the passive state and prevent catastrophic destruction of the passivation film.

For X-ray diffraction analysis of the experimental alloys, a DRON-4M diffractometer with digital data acquisition and a Cu-Kα X-ray tube was used. The “Match! 4.2” software was used for the interpretation and calculation of the diffractogram.

The phase and elemental compositions of the surfaces of experimental alloy samples No. 1, 2, 4, and 5 are shown in Fig. 3.

Electrochemical corrosion tests were performed on samples of the experimental alloys (Table 2). Classical potential range from $E_{(ref)}$ to E_1, where $E_{(ref)} = -2.00$ V; $E_1 = 2.00$ V. V = 0.74 mV/s - scan rate; current range ±45 mA.

Using the results of the electrochemical corrosion test (corrosion current icorr, mA/cm²) and the Arrhenius equation

$$i_{corr(T)} = i_{corr} \cdot \exp(-E_a/(RT)) \quad (8)$$

to account for the effect of changes in acid temperature in the range of 25-200°C, as given by [9]

$$V_{corr} = (3{,}27 \cdot 10^{-3} \cdot i_{corr} \cdot EW)/\rho \quad (9)$$

calculated the corrosion rate, mm/year, of the experimental alloys (Table 2) taking into account operation in “passive” (immersion in 98% H_2SO_4) and “industrial” (turbulent flows of 98% H_2SO_4, erosion) modes, with consideration of the stabilizing effect of Cr and Mo. In equation (9): *EW* - equivalent weight of the alloy, g/eq; ρ - density of the alloy, g/cm³.

The dependence of the corrosion rate (material loss) on the acid temperature during operation of the alloys (Table 2) in the “industrial” mode is shown in Fig. 4.

Alloys No. 4, 3, and 6 (Table 2) exhibit the best expected corrosion resistance (Fig. 4) within the studied temperature range (25-200°C). At the same time, an increase in the Si content in ferrosilicide to >15%, as shown above, is accompanied by increased brittleness, the development of microcracks, and a disruption in the density of the passivation film, and requires the development of a special casting technology and imposes limitations on operating conditions.

Taking into account the results obtained, the following composition can be considered optimal for an economically alloyed ferrosilicon with increased resistance in H_2SO_4, suitability for machining, and “industrial” operating conditions, in %: 15.5-17.5 Si; 4.5-6.0% Cr; 1.5-2.0% Ni; 1.2-1.5% Mo; 0.1-0.4% C.

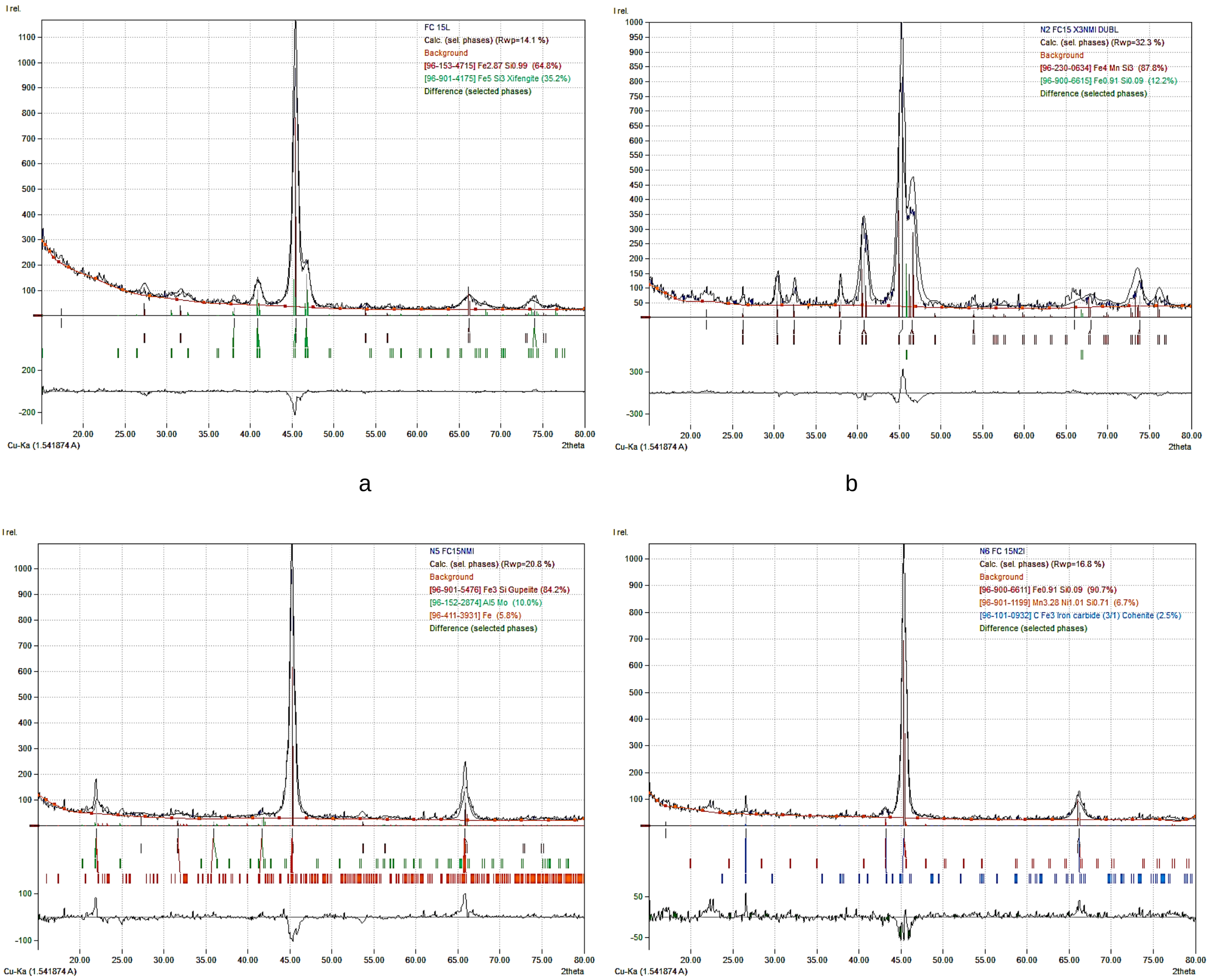
The experimental data obtained can be used to develop new corrosion-resistant materials and optimize the composition of ferrosilides for use in high-temperature, aggressive environments containing concentrated sulfuric acid.

Conclusions

(1) The casting and selected mechanical properties of experimental Fe-Si alloys containing 12-27% Si and alloyed with Cr, Ni, and Mo were investigated.

(2) It was confirmed that the silicon content in Fe-Si alloys is the primary factor determining the corrosion resistance of ferrosilicides in concentrated sulfuric acid. At Si contents below 15%, partial formation of a passivation film was observed; at 16-20% Si, a partially stable SiO_2 film layer forms; and when the Si content increases to 24% or higher, a continuous protective SiO_2 film forms, which reduces the alloy’s corrosion rate by 1-2 orders of magnitude.

(3) The following characteristic temperature regions of the corrosion process have been identified: stable passivation (25-80°C), a transitional regime (80-150°C), and degradation of the passive state (160-200°C). At temperatures >150°C, degradation of the passivation film is observed, with the corrosion rate of the Fe-Si alloy increasing by an order of magnitude when the Si content is > 24% compared to when Si < 15%. The corrosion rate was calculated based on electrochemical parameters using passivation models and Arrhenius-type temperature dependence. It was confirmed that the main factor determining corrosion resistance is the silicon content. The existence of a critical threshold for Si content was demonstrated; upon reaching this threshold, a continuous SiO_2 passive film forms, which reduces the corrosion rate by 1-2 orders of magnitude.



a

b

c

d

Fig. 3. Phase and elemental compositions of the surfaces of alloy samples No. 1 (a), No. 2 (b), No. 4 (c), and No. 5 (d) (Table 2): a) 64.8% $Fe_{2.87}Si_{0.99}$; 35.2% Fe_5Si_3 and Fe 82.3%; Si 17.7%; b) 87.8% Fe4MnSi3; 12.2% $Fe_{0.91}Si_{0.09}$ and Fe 65.7%; Si 21.0%; Mn 13.3%; c) 84.2% Fe_3Si; 10.0% Al5Mo; 5.8% Fe and Fe 77.9%; Si 12.1%; Al 5.9%; Mo 4.2%; d) 90.7% $Fe_{0.91}Si_{0.09}$; 6.7% $Mn_{3.28}Ni_{1.01}Si_{0.71}$; 2.5% Fe_3C and Fe 88.8%; Si 4.8%; Mn 4.7%; Ni 1.5%; C 0.2%, respectively.

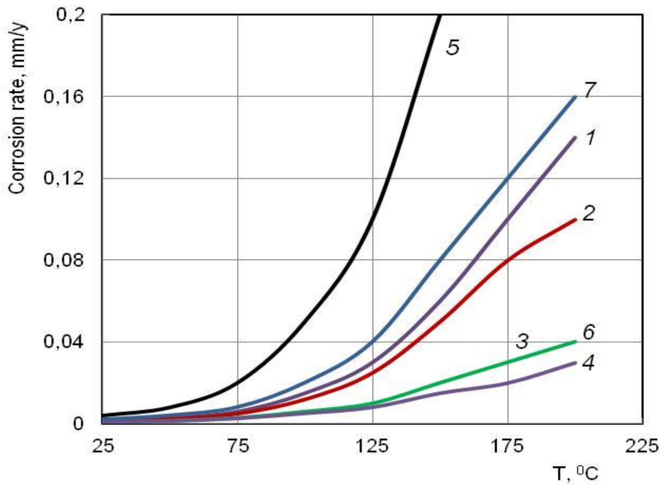


Fig. 4.. Calculated expected corrosion rates of the experimental Fe-Si alloys (Table 2) in concentrated acid (98% H_2SO_4) as a function of acid temperature. The curve for alloy No. 6 practically coincides with the curve for alloy No. 3.

(4) It has been shown that the actual corrosion rate of ferrosilicide is determined not only by composition but also by the operating conditions of the alloys, namely, medium turbulence, erosion development, and the presence of H_2O and Fe^{3+}; the difference in material mass loss between laboratory and industrial conditions can be 10-20 times.

(5) It has been established that the formation of a continuous passive SiO_2 film, as well as the formation of Fe_3Si and Fe_5Si_3, are key factors in ensuring the enhanced corrosion resistance of ferrosilicides in hot concentrated H_2SO_4. A critical silicon content of >24% Si can be identified, at which the transition to a stable passive state of the alloy occurs even when the acid temperature rises to 200°C in systems with aggressive hydrodynamics. At the same time, increasing the Si content in ferrosilicides beyond 15% is accompanied by increased brittleness, the development of microcracks with acid penetration, and a disruption of the passivation film density, and requires the development of special casting technologies and operating conditions.

(6) Obtaining more ductile ferrosilides is possible through alloying with elements that enhance ductility by addressing the underlying issue - the presence of an intermetallic brittle matrix (Fe_3Si). It is advisable to introduce Ni, Mo, and Cr into the Fe-Si alloy in limited quantities, which reduces brittleness but still does not make the alloy fully ductile.

(7) The addition of chromium to an Fe-Si alloy enhances surface passivation through the formation of Cr_2O_3, but is effective only with sufficient Si content; molybdenum stabilizes the passive state at acid temperatures above 150°C and reduces the rate of localized corrosion; nickel has a partial effect on electrochemical parameters but is not a determining factor at high acid temperatures. Oxidation of 3-6% Cr added to a Fe-Si alloy with 15–19% Si ensures the formation of a combined protective layer of SiO_2 + Cr_2O_3 in concentrated H_2SO_4, but one that is less continuous than at >24% Si

(8) Based on the experimental results, the following composition can be considered optimal for an economically alloyed ferrosilicon with increased resistance in H_2SO_4, suitability for machining, and “industrial” operating conditions: 15.5-17.5% Si; 4.5-6.0% Cr; 1.5-2.0% Ni; 1.2-1.5% Mo; 0.1-0.4% C.

References

1. Fontana, M. G. Corrosion Engineering. (1986). 3rd ed. *New York: McGraw-Hill*.
2. Uhlig, H. H., Revie, R. W. (2008). Corrosion and Corrosion Control. 4th ed. *Hoboken: Wiley*. https://doi.org/10.1002/9780470872864
3. Davis J.R. Corrosion of Nickel and Nickel Alloys. *ASM International*. 2000. https://doi.org/10.31399/asm.tb.cnia.t59290001.
4. Wranglén, G. (1985). An Introduction to Corrosion and Protection of Metals. *Chapman & Hall.*
5. Marcus, P. (Ed.). (2011). Corrosion Mechanisms in Theory and Practice. https://doi.org/10.1201/b11020
6. Olsson, C.-O.A., Landolt, D. (2003). Passive films on stainless steels-chemistry, structure and growth*. Electrochimica Acta*, 48, 1093-1104. https://doi.org/10.1016/S0013-4686(02)00841-1.
7. Frankel, G. S. (1998). Pitting corrosion of metals: A review. *Journal of The Electrochemical Society,* 145(6), 2186-2198. https://doi.org/10.1149/1.1838615
8. ASTM G31-21. Standard Practice for Laboratory Immersion Corrosion Testing of Metals. *ASTM International*. 2021.
9. Jennings, H. S. (2006). ASM Handbook, Corrosion - Environments and Industries. *ASM International,* 13C, 690-703.
10. Standard Practice for Calculation of Corrosion Rates and Related Information from Electrochemical Measurements (ASTM 102-89). https://doi.org/10.1520/G0102-89R15E01
11. Stawarz M. (2023). Crystallization of Fe_2Si and Fe_5Si_3 phases in high-alloy cast irons. *Crystals*. https://doi.org/10.3390/cryst13071033
12. Srivastava, S. K. & Crook, P. (2016). Unpublished Work. *Haynes International*.
13. Li, W., Xu,, C., Chen K., et al. (2022). Corrosion of Fe-Cr-Si alloys in oxidizing and sulphidizing environments coatings. *Coatings*. https://doi.org/10.3390/coatings12101588
14. Kwon, H.-C., Kim, D.-J., et al. (2011). Corrosion characteristics of Fe–Si, Ni–Ti and Ni alloys in sulfuric acid environments. *Korean Journal of Materials Research*.
15. Omurtag, Y., & Doruk, M. (). Some investigations on the corrosion characteristics of Fe-Si alloys. *Corrosion Science*, 10(4), 225-231.
16. Tang, C., Wen, F., Chen, H., Liu, J., Tao, G., Xu, N., & Xue, J. (2019). Corrosion characteristics of Fe3Si intermetallic coatings prepared by molten salt infiltration in sulfuric acid solution. Journal of Alloys and Compounds, 778, 972–981. https://doi.org/10.1016/j.jallcom.2018.11.198
17.Shen, B., He, Y., Wang, Z., Yu, L., Jiang, Y., & Gao, H. (2020). Reactive synthesis of porous FeSi intermetallic compound. Journal of Alloys and Compounds, 826, 154227. https://doi.org/10.1016/j.jallcom.2020.154227
18. Onuki, I., Futakawa, M., Tayama, I. Corrosion resistance of Fe-Si alloys in boiling sulfuric acid. *Materials for thermochemical processes*. https://doi.org/10.2472/JSMS.46.1041
19. Ioka, I., Mori, J., Kato, C. et al. (1999). The characterization of passive films on Fe-Si alloy in boiling sulfuric acid. *Journal of Materials Science Letters*, 18, 1497-1499.
20. Sigarev, E. N., Chernyatevich, A. G., Chubin, K. I. et al. (2011). Desulfurization of hot metal by the injection of disperse magnesium through a submerged rotating tuyere. *Steel Transl*, 41, 487-491. https://doi.org/10.3103/S0967091211060155

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