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CORRELATION BETWEEN THE STRUCTURE AND PROPERTIES OF FERROALLOYS

I. N. Kel' , V. I. Zhuchkov, O. V. Zayakin

Vatolin Institute of Metallurgy of the Ural Branch of the Russian Academy of Sciences (101 Amundsena Str., Yekaterinburg 620016, Russian Federation)

dunnington@mail.ru

Abstract. The paper reviews the studies on relationship between the structure, phase composition, and properties of ferroalloys, as well as their impact on the quality of treated metals. The requirements for ferroalloys include not only chemical composition but also a range of properties: optimal melting temperature, oxidation resistance, density, and time of dissolution in the treated melt. The structure and phase composition of the alloys are also crucial, as they affect friability, element segregation within the ingot, crushability, and formation of fine fractions. The study presents research findings aimed at addressing the issue of spontaneous disintegration of ferrosilicon caused by the eutectoid transformation of leboite and presence of impurities. Methods to prevent ferroalloy disintegration are proposed, including rapid cooling, reducing impurity content, and stabilizing the structure through additives such as boron. The structural features of other alloys, such as silicocalcium, are also examined, where improved crushability is achieved by slowing crystallization and modifying phase composition. Approaches to modeling the phase composition of ferroalloys are discussed, including thermodynamic-diagram methods and polygonal phase diagram analysis. The results of studies on rapid cooling of modifiers demonstrate enhanced efficiency due to the fine-grained structure and uniform distribution of active elements. It was established that the structure of ferroalloys influences the primary crystallization of cast iron, determining graphite morphology and matrix structure. The impact of phase composition and non-metallic inclusions (oxides, sulfides) in ferroalloys on steel properties is also demonstrated. Based on the review, the necessity of considering the structural and phase characteristics of ferroalloys is highlighted, as this can improve metallurgical product quality, reduce material consumption, and minimize adverse effects.

Keywords: structure, phase composition, ferroalloy, inclusions, modifiers, physicochemical properties

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КОРРЕЛЯЦИЯ СТРУКТУРЫ И ХАРАКТЕРИСТИК ФЕРРОСПЛАВОВ

И. Н. Кель , В. И. Жучков, О. В. Заякин

Институт металлургии имени академика Н.А. Ватолина Уральского отделения РАН (Россия, 620016, Екатеринбург, ул. Амундсена, 101)

dunnington@mail.ru

Аннотация. В статье представлен обзор исследований взаимосвязи структуры и фазового состава со свойствами ферросплавов, а также их влияния на качество обрабатываемых металлов. Требования, предъявляемые к ферросплавам, включают в себя не только химический состав, но и ряд свойств: рациональную температуру плавления, устойчивость к окислению, плотность и время растворения в обрабатываемом расплаве. Структура и фазовый состав сплавов также имеют решающее значение, поскольку они влияют на рассыпаемость, ликвацию элементов в объеме слитка, способность к дроблению и образованию мелких фракций. В работе приведены результаты исследований, направленных на решение проблемы самопроизвольного рассыпания ферросилиция, вызванного эвтектидным превращением лебюита и наличием примесей. Предложены методы борьбы с дезинтеграцией ферросплава путем быстрого охлаждения, снижения доли примесей и стабилизации структуры с помощью таких добавок, как бор. В статье рассмотрены структурные особенности других сплавов, например, силикокальция, где улучшение дробимости достигается за счет замедления кристаллизации и изменения фазового состава. Обсуждаются подходы к моделированию фазового состава ферросплавов, включая термодинамически-диаграммный метод и анализ полигональных диаграмм состояния. Результаты исследований по быстрому охлаждению модификаторов демонстрируют повышенную эффективность за счет мелкодисперсной структуры и равномерного распределения активных элементов. Установлено, что структура ферросплавов влияет на первичную кристаллизацию чугуна, определяя морфологию графита и матрицы. Показано влияние фазового состава и типа неметаллических включений (оксиды, сульфиды) ферросплавов на свойства стали. На основе проведенного обзора

подчеркивается необходимость учета структурно-фазовых характеристик ферросплавов, что позволит повысить качество металлургической продукции, снизить расход материалов и минимизировать негативные эффекты.

Ключевые слова: структура, фазовый состав, ферросплав, включения, модификаторы, физико-химические свойства

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A key objective of metallurgy is the development of new types of metal products capable of maintaining their operational characteristics under extreme environmental conditions. Consequently, the development of metals with improved properties and the emergence of advanced smelting technologies have stimulated interest and deeper studies of the physicochemical characteristics of ferroalloys that affect these properties.

This has created a need to produce ferroalloys with a low melting temperature and oxidation susceptibility, optimal density, minimal dissolution time, and minimal cooling of liquid steel upon their addition. The quality of ferroalloys depends not only on their chemical composition, impurity content, and gas saturation, but also on friability, element segregation within the ingot, magnetic properties, crushability, and the tendency to form fine fractions.

Given these requirements, the Institute of Metallurgy of the Ural Branch of the Russian Academy of Sciences (IMET UB RAS) proposed an approach to developing new compositions of complex ferroalloys that more effectively improve the service characteristics of the treated metal, achieve higher assimilation by steel, dissolve more rapidly, and introduce less contamination [1]. The most extensively studied parameters include the melting temperature, density, oxidation resistance of ferroalloys, the thermal effect during interaction with steel, dissolution time in liquid steel, and thermophysical characteristics. At the same time, the relationship between the structure and phase composition of ferroalloys and their properties has been largely overlooked.

Reference books and monographs [2 – 4] provide data on the phase composition of various industrial grades of ferroalloys. For each alloy, these data can vary significantly, as they depend on the casting method and ingot crystallization rate.

The structure and phase composition of a ferroalloy affect not only the alloy's own properties (melting temperature, hardness, strength, etc.) but also the characteristics of the treated metal (cast iron or steel), particularly during modification.

Researchers turned their attention to the structure of ferroalloys after frequent occurrences of spontaneous disintegration of ferrosilicon were reported [1; 5; 6]. Its structural components are intermetallic phases (silicides): Fe_2Si (β -phase), Fe_5Si_3 (η -phase), and FeSi_2 (ξ -phase,

leboite), which has two allotropic modifications – high- and low-temperature. During cooling of the alloy after crystallization, the initial stages of the eutectoid transformation occur in metastable leboite, leading to the formation of Guinier–Preston zones, while the resulting elastic stresses cause cracking of structural components. This process is also associated with the presence of unstable excess phases in the ingot when exposed to a humid atmosphere.

It has been observed that even at standard phosphorus levels (0.03 – 0.04 %), ferrosilicon with 49 – 51 % Si is prone to disintegration. In 75 % ferrosilicon (FeSi75), the excess-phases formation – primarily promoted by calcium, aluminum, and phosphorus – triggers ingot disintegration and the release of phosphine (PH_3) and arsine (AsH_3). Within these excess phases, silicon and iron help stabilize the structure, reducing the ingots' susceptibility to disintegration in the presence of atmospheric moisture. Trace arsenic present in the melt tends to become enriched in Ca–Al–P-bearing phases.

According to [1; 5], ferrosilicon disintegration is associated with several factors: the eutectoid transformation of leboite; silicon segregation accompanied by the formation of silicon-enriched melt; and elevated concentrations of impurity elements (Al, Ca, Ti, As, P, S, C), which tend to form phosphides that readily react with atmospheric moisture.

Electron microscopy of disintegrating ferrosilicon samples revealed aluminum enrichment along crack paths, with pronounced segregation, including as aluminum phosphide (AlP). In FeSi65 ingots, this results in structural regions prone to disintegration. In addition to a significant amount of aluminum phosphide, titanium phosphides and magnesium arsenides were also identified in the disintegrating alloys; these compounds may likewise act as crack initiators.

Structural analysis indicates that FeSi65 disintegration is primarily caused by (i) reduced silicon content ($<65\%$), (ii) elevated aluminum content ($>1\%$), including as phosphides, and (iii) segregation driven by casting and crystallization conditions. These factors favor the formation of structurally unstable leboite and the enrichment of impurity phosphides in localized regions of the ingot, leading to FeSi65 disintegration in the presence of atmospheric moisture.

According to [5], effective mitigation measures include promoting rapid crystallization to suppress silicon and component segregation, lowering the contents of phosphorus, calcium, and aluminum, and stabilizing the ferrosilicon by introducing alloying additions such as boron into the melt.

A case was reported in [7] where a new, efficient alloy (AMS) containing 60 – 65 wt. % Mn, 25 – 30 wt. % Si, and 5 – 8 wt. % Al failed to be adopted in practice due to disintegration. Although its production showed high technical and economic efficiency, and its use as a steel deoxidizer improved steel quality while significantly reducing ferroalloy consumption, the alloy underwent substantial disintegration during storage in air, accompanied by the release of explosive gases containing PH_3 . Structural examination established that the disintegration was driven by the interaction of phosphides and carbides with atmospheric moisture. The authors of [7] further note additional causes of AMS disintegration: the reaction of aluminum carbide with water, forming aluminum hydroxide and metallic aluminum; and polymorphic transformations in the $\text{Mn}_4\text{Si}_2\text{Al}_3$ phase and in the solid solution of silicon with Mn and Al, which initiate micro-crack growth and ultimately lead to alloy failure.

Another unfavorable characteristic of ferroalloys is poor crushability, which accelerates wear of crushing equipment and complicates casting.

The effect of structure and phase composition on the crushability of the calcium–silicon alloy (grade SK15, containing 15 wt. % Ca, 20 wt. % Fe, 1 wt. % Al, 0.2 wt. % C, balance Si) was investigated in [8]. The principal phases are FeSi_2 and CaSi , and their ratio depends directly on the calcium content (10 – 30 wt. %). It was found that impurity elements in silicocalcium form a series of discrete secondary phases as fine precipitates – such as CaAl_2Si_2 , $\text{Ba}(\text{Si},\text{Al})_4$, and Ca_2MgSi_3 . The presence of numerous small, rounded FeSi_2 -type crystals in the SK15 alloy leads to structural refinement, which decreases its crushability. To improve crushability, it was proposed to slow the crystallization rate to obtain a coarse-grained structure and to reduce the iron content. Additions of chromium, manganese, nickel, and copper lead to the formation of the corresponding disilicides and modify the CaSi_2 phases, thereby affecting the properties of silicocalcium and, in particular, improving its fire and explosion safety.

Approaches to modeling the phase composition of ferroalloys have been developed. Akberdin et al. [9] introduced a thermodynamic–diagram approach that constructs ternary and quaternary phase diagrams from the geometric regularities of phase equilibria and, from these diagrams, derives mathematical relations to predict the most probable phase assemblages.

Another approach, proposed by B.F. Belov et al. [10], is the prediction of the phase composition of ferroal-

loys using structural–chemical analysis of the condensed phases of a polygonal phase diagram (PPD). This method is based on geometrically subdividing the concentration triangle using field lines (edge–edge) or radial lines (vertex–edge). The intersection points of these lines represent the reaction products, i.e., the phases of the ternary system.

Systematic research into how the structure and phase composition of ferroalloys affect the properties of treated metals dates to the late 20th century. Brodova et al. [11 – 13] showed that the structure of master alloys – specifically the size and defect density of Al_3Zr intermetallic crystals – governs the efficiency of zirconium alloying and modification of aluminum alloys.

Ryabchikov and colleagues [14 – 16] investigated the production and application of quenched micro-crystalline silicon ferroalloys containing alkaline-earth metals and magnesium, and assessed their effect on cast-iron properties.

In [14], they compared two magnesium-containing modifiers (48 wt. % Si, 5 – 6 wt. % Mg, 2 wt. % Ca, 6 wt. % REM, balance Fe) used for cast-iron treatment: one rapidly cooled between two rotating copper rolls and the other cast into ingots.

The rapidly cooled (chip-type) modifier exhibited a structure markedly different from that of the ingot. Its structural components were 10 – 100 times smaller, and the chemically active elements were distributed more uniformly throughout the volume. When used in cast iron treatment, the rapidly cooled modifier reduced the white layer depth from 7 to 4 mm. Moreover, the modifier consumption decreased by 25 – 30 % while maintaining the same modification efficiency. The rapidly cooled modifiers were also easily crushed, provided a higher yield of usable fractions, and exhibited less tendency to overgrinding compared with the conventional modifier.

A comparative morphological assessment presented in [14] showed that both types of modifiers contained the same primary phases: FeSi_2 , free silicon, magnesium-containing phases (Mg_2Si , CaMgSi_x), and a small amount (<0.1 %) of *X*-ray amorphous SiMgO (according to *X*-ray and electron probe microanalysis). No differences in phase composition between chip-type and ingot-type modifiers were detected by *X*-ray diffraction. Metallographic analysis, however, did not reveal clear boundaries between magnesium-containing phases. Differences in phase fractions were observed: FeSi_2 fraction in ingots was, on average, about 4 % higher than in chips; free silicon was about 7 % higher in ingots; conversely, the magnesium–silicon phase content was higher in chips by an average of 12.7 %. Consequently, the phase containing the elements responsible for the modification effect occupied a larger area fraction in chip-type modifiers than in ingot-type ones. In addition, the modifiers differed in the thick-

ness of FeSi_2 lamellae. In ingots, FeSi_2 lamellae were about five times thicker than those of the Mg_2Si phase, whereas in chip-type modifiers the characteristic lamellar thicknesses were comparable. According to the authors, this promotes a more uniform distribution of modifying elements throughout the cross-section, faster dissolution kinetics, and higher recovery (uptake) during modification with chip-type modifiers.

Further research on the effect of ferroalloy microstructure on the properties of treated metals was conducted by A.G. Panov, D.A. Boldyrev, E.S. Zakirov, and others [17 – 19].

According to [17; 19], the effect of modifier structure on cast iron properties is attributed to primary crystallization processes that alter the morphology and quantity of graphite, as well as the matrix structure of the treated metal.

Structural fragments of FeSi and $\alpha\text{-FeSi}_2$ transferred from the modifier into the cast-iron melt interact with melt components exhibiting short-range order similar to that of cementite. As a result, chemical bonds between Fe, Si, and C atoms are rearranged, forming new carbon-depleted Fe-C-Si structures. Upon subsequent cooling, these structures act as precursors and nucleation sites for ferrite and austenite. Consequently, in cast irons treated with coarse-crystalline modifiers, the primary crystallization of graphite, austenite, and ferrite proceeds more actively, whereas in those treated with fine-crystalline modifiers, these processes are suppressed and cementite and ledeburite crystallize instead.

Magnesium–silicon phases (Mg_2Si) inherited from the modifier participate in the formation of disordered regions within the cast-iron melt. Their size affects both the rate of magnesium removal and the elimination of non-metallic inclusions from the melt. This, in turn, influences the amount and morphology of graphite. Refinement of magnesium-containing phases enhances both spheroidizing and graphitizing effects.

In addition to the structure and phase composition of ferroalloys, their non-metallic inclusions (oxides, sulfides, and others) also influence the quality of the treated metal [20 – 25].

Studies [20 – 22] have shown that ferrosilicon contains a certain amount of SiO_2 , which, during alloying, transfers into the steel and contributes to its contamination.

The authors of [24] investigated non-metallic inclusions in ferrotitanium and their behavior during steel alloying. This ferroalloy contains large, irregular inclusions primarily composed of CaO and SiO_2 , which, upon entering the treated metal, transform into spherical inclusions containing TiO_2 , Al_2O_3 , and CaO .

In [25], the effect of ferroniobium inclusions on the early stages of its dissolution during steel micro-

alloying was examined. The study identified a mechanism for the formation of Al-O and Al-Ti-Nb-O inclusions in steel. According to the authors, Ti-O inclusions transform into heterogeneous inclusions consisting of a Ti-O core surrounded by an outer Nb-Ti-O shell.

CONCLUSIONS

The review underscores the need to account for the structure and phase composition of ferroalloys, as well as the potential to modify both the alloys and the treated metal by transforming the ferroalloy's structural and phase characteristics.

Accordingly, further research should focus on the effects of the cooling rate and time–temperature parameters on the phase-structure evolution in ferroalloys, and broaden the range of alloys investigated.

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Information about the Authors

Il'ya N. Kel', *Cand. Sci. (Eng.), Senior Researcher of the Laboratory of Steel and Ferroalloys, Vatin Institute of Metallurgy of the Ural Branch of the Russian Academy of Sciences*

ORCID: 0000-0001-6411-6932

E-mail: dunnington@mail.ru

Vladimir I. Zhuchkov, *Dr. Sci. (Eng.), Prof., Chief Researcher of the Laboratory of Steel and Ferroalloys, Vatin Institute of Metallurgy of the Ural Branch of the Russian Academy of Sciences*

ORCID: 0000-0002-8621-7467

E-mail: ntm2000@mail.ru

Oleg V. Zayakin, *Corresponding Member of RAS, Dr. Sci. (Eng.), Chief Researcher, Head of the Laboratory of Steel and Ferroalloys, Vatin Institute of Metallurgy of the Ural Branch of the Russian Academy of Sciences*

ORCID: 0009-0009-9831-1993

E-mail: zferro@mail.ru

Сведения об авторах

Илья Николаевич Кель, *к.т.н., старший научный сотрудник лаборатории стали и ферросплавов, Институт металлургии имени академика Н.А. Ватолина Уральского отделения РАН*

ORCID: 0000-0001-6411-6932

E-mail: dunnington@mail.ru

Владимир Иванович Жучков, *д.т.н., профессор, главный научный сотрудник лаборатории стали и ферросплавов, Институт металлургии имени академика Н.А. Ватолина Уральского отделения РАН*

ORCID: 0000-0002-8621-7467

E-mail: ntm2000@mail.ru

Олег Вадимович Заякин, *член-корреспондент РАН, д.т.н., главный научный сотрудник, заведующий лабораторией стали и ферросплавов, Институт металлургии имени академика Н.А. Ватолина Уральского отделения РАН*

ORCID: 0009-0009-9831-1993

E-mail: zferro@mail.ru

Contribution of the Authors

I. N. Kel' – search and generalization of literary data, writing the text.

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