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RESEARCH PAPER

The Effect of Graphite on the Formation of the Iron-Silicide Compound

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Abstract: *In this article, the effect of graphite on iron-silicon interactions was investigated. It was found that, as graphite enters the iron structure, it permits further development of iron-silicon reactions. It was found that in the stoichiometric ratio of 1:0.5 of iron and silicon, with the addition of graphite into the system, some amount of carbon may dissolve into the iron structure, leading to the production of more iron silicide compound. Silicon also reacted with carbon to form SiC. With more carbon entering into the system, the growth of SiC grains along with the formation of other iron silicide phases, namely FeSi and* Fe_3Si *was observed in the microstructure. Finally diffused carbon into the iron reaches a definite amount that can form* Fe_3C*. In the stoichiometric ratio of 1:1 of iron and silicon, the formation of FeSi and SiC phases was detected. In the stoichiometric ratio of 1:2 of iron and silicon 1:1, a larger amount of silicon is available and, the* $FeSi_2$ *phase was formed in addition to FeSi.*

Keywords: *Graphite, Iron, Silicon, Mechanism, Powder, Reactions.*

1. INTRODUCTION

The iron-silicon and carbon system is of interest in steelmaking, casting, electromagnetic wave absorption, microelectronic devices, and building materials [1-5]. Therefore, some research has been conducted on the thermodynamics of the ternary system of Fe, Si, and C [1]. Fe-Si system is also used as shape memory alloys containing other materials in civil engineering structures [6]. A great deal of previous research has focused on the molten state of the Fe-Si system. Ohnuma et al. [7] have investigated the iron-silicon binary system. In the research has been carried out by Chipman et al. [8] the activity of silicon in molten Fe-Si and Fe-Si-C has been explored. In the research reported by Krishtal et al. [9], based on the different carbon content and silicon, the best mechanical and casting properties have been gained.

It is also stated that the presence of silicon in cast iron, leads to an increase in properties such as corrosion resistance even in 30% sulfuric acid, and wear and thermal resistance [10]. The properties of high silicon cast iron depend on the microstructure and compounds in the system. For example, the best thermal properties of cast iron were obtained in samples containing more than 3% of silicon. High silicon cast iron has about 12% to 18% silicon, which has shown excellent corrosion resistance properties in the range of 14.20% to 14.75% silicon [10]. Other materials can also be prepared from the combination of these three elements. As a case in point, Lee et al. [11] have prepared a composite for rechargeable lithium batteries using these three elements. Wu et al. [12] have considered the changes in microstructure and transformation kinetics and especially C enrichment during isothermal ferrite transformation at 800, 750, 700°C for Fe-(1.5, 3.0) Si-4%C alloys. In their research, the factors affecting the kinetic have been determined and discussed. Pamato et al. [13], have demonstrated that the change in carbon and silicon percentages has notable effects on the density of iron alloys.

Outlining the past-present history of the study, it was determined that no research had performed on the powder system of these three elements to determine the possible compound that can form in the ternary powder system of Fe-Si, and C in different molar ratios of elemental powders.

Therefore, the aim of the present study is twofold. The initial objective of the project was to predict the potential reactions and products in the Fe-Si-C system in different molar ratios of iron, carbon, and silicon, thermodynamically. In the following, the predicted results were compared with the practical outcomes. Finally, a mechanism for the reaction progress in the solid state was proposed. The second aim of the current study was to determine the appropriate molar ratios of Fe-Si, and C powders, and experimental conditions to

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produce predetermined compounds of the aforementioned ternary system. It was found that graphite can pave the way for the production of iron silicide compounds due to the possibility of carbon diffusion in the iron structure and breaking it.

2. EXPERIMENTAL PROCEDURES

2.1. Thermodynamic Analyses

HSC Chemistry 5.11 software was utilized for thermodynamic analysis of the Fe-Si-C system. To do so, the equilibrium compounds that can be formed in the iron-silicon system were investigated. During the process, it was assumed that in the beginning, the ratios of 0.5:1, 1:1, and 1:2 of iron and silicon exist in the system. Gradually, carbon would be included in up to 4 k moles (in 21 steps). Finally, equilibrium phases were predicted by means of the HSC software, "Equilibrium composition" item.

In this part of the software, after determining the raw materials and their amount, the phase that has a variable value should be mentioned. In the following, the amount of its changes in each step is required. Finally, the investigated temperature must be applied. Then the software calculates the possible equilibrium phases. This result is provided to the user in the form of an image.

2.2. Experimental Method

For the practical investigation of the reactions of the Fe-Si-C system, the proportions of iron (Merch< 10 μ, 99%), silicon (Pourian chemical< 5 μ, 99%), and graphite (ChemPur, +325 mesh, 99.95%) were mixed based on Table 1. Moreover, from the mixture, samples of 2 grams were prepared in the form of cylinders with a diameter of 1 cm under the pressure of 300 Psi. Afterwards, the samples were subjected to heat treatment at the temperature of 950°C. Argon atmosphere was used to prevent the oxidation of the specimens.

To eliminate any O_2 present in the argon gas, the argon gas was passed through heated pure Cu at a temperature of 550°C. Ascarite and Drierite have also been used to eliminate the CO_2 and H_2O presented in the argon gas as impurities, respectively.

The type and the composition of formed phases were determined by XRD analysis (Bruker, D8 advance). A FESEM microscope (KYKY, EM8000) equipped with EDS was used to figure out the microstructure and elemental percentage of the phases.

Table 1. The molar ratios of raw materials in the current research.

Fe Molar ratio	Si Molar ratio	Graphite Molar ratio
1	0.5	0
		1
		2
1	1	0
		1
		2
1	2	0
		1
		2

3. RESULTS AND DISCUSSION

3.1. Thermodynamic Analyses

In the initial stage, according to the “Experimental” section, the possible equilibrium phases that can be formed in the Fe-Si-C system were calculated by applying HSC software. As shown in Figure 1, for the initial step at the temperature of 950°C, the ratio of 1:0.5 of iron and silicon was investigated, in which carbon was added in 21 steps (Figure 1a). The vertical axis shows the amount of production phases and the horizontal axis shows the amount of carbon that is added to the raw materials in kmol as can be seen in this figure, in the absence of carbon, FeSi, Fe_3Si, and Fe_5Si_3 phases should be formed. However, with the addition of graphite, the SiC phase is gradually produced in a large amount, and some amounts of Fe_3C can be formed.

By increasing the Si content (Figure 1b), the molar ratio of 1:1 of Fe and Si, it was observed that FeSi is the dominant phase if there is no graphite in the system. By the addition of graphite, one step at a time SiC is formed and its content in each step increases. The process proceeds to the extent that even SiC amount exceeds FeSi amount.

Other types of iron silicides can be seen in small amounts along with a little Fe_3C as is shown at the bottom of the graph. By changing the ratio of iron and silicon to 1:2, similar to the ratio of 1:1 of iron and silicon, FeSi and SiC are generated. Of course, the presence of small amounts of $FeSi_2$ in lower percentages of graphite is not far from expected.

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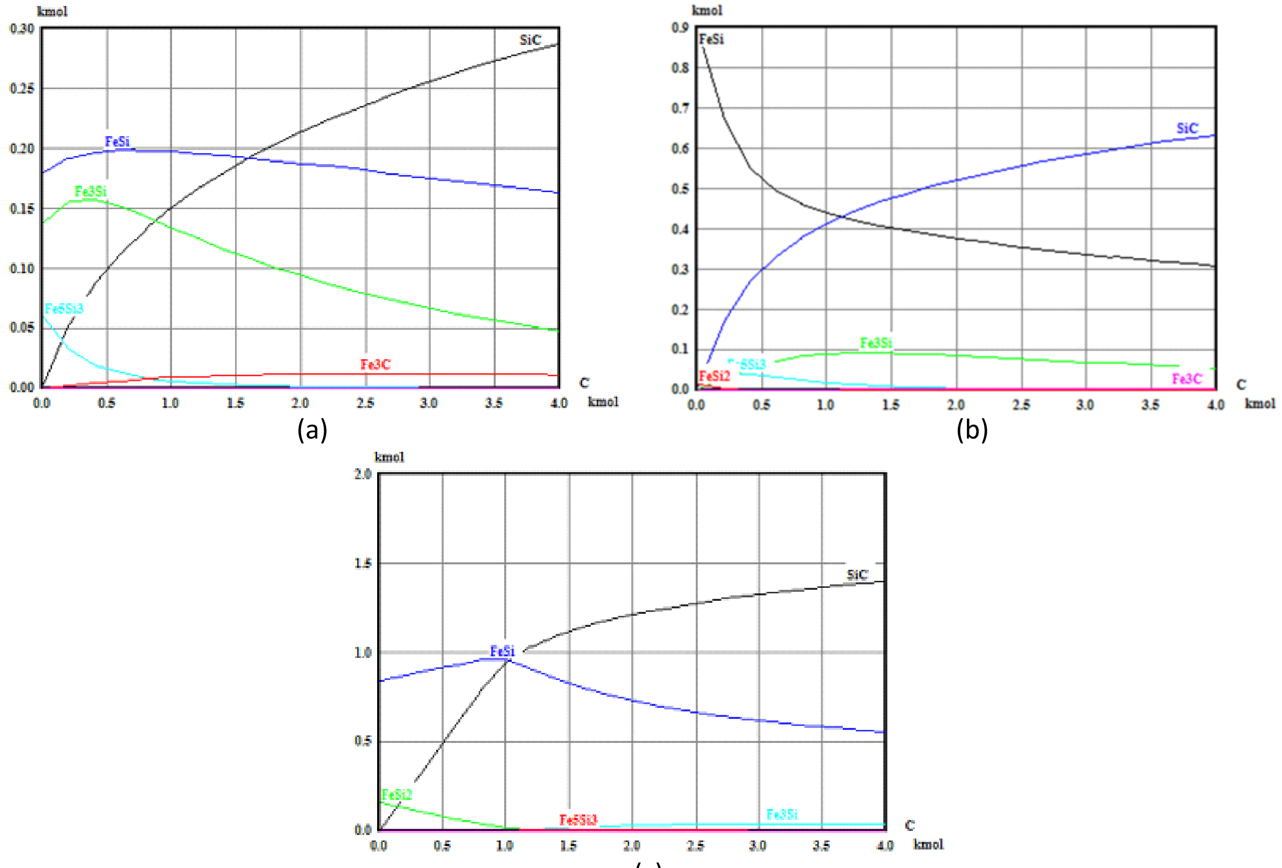

(a) (b)

(c)

Fig. 1. Equilibrium compounds of the Fe, Si, and C system, assuming that the molar ratios of a) 1: 0.5, b) 1: 1, and c) 1:2 of iron and silicon are present in the system and carbon is added up to 4 k moles (in 21 steps) at a temperature of 950°C.

3.2. Experimental Results Analyses

After the thermodynamic analysis, the laboratory samples were prepared based on the conditions explained in the "Experimental" section. In Figure 2, the scanning electron microscope image of the sample containing a molar ratio of 1:1 of iron and silicon in which there is no carbon is illustrated. As can be seen, by the diffusion of Si through the surface of Fe particles, iron silicides were formed.

Standard Gibbs free energy of formation for iron-silicon-carbon compounds, discussed in the present study, is shown in figure 3. The reactions are as following:

$3Fe+C=Fe_3C$ (1)
$Si+C=SiC$ (2)
$Fe+Si=FeSi$ (3)
$3Fe+Si=Fe_3Si$ (4)
$5Fe+3Si=Fe_5Si_3$ (5)
$Fe+2Si=FeSi_2$ (6)

With the addition of graphite to the Fe-Si system, it was expected that carbon would have a greater tendency to react with silicon compared to iron (Figure 3). According to Figure 3, the standard Gibbs free energy of formation for SiC is more negative than Fe_3C.

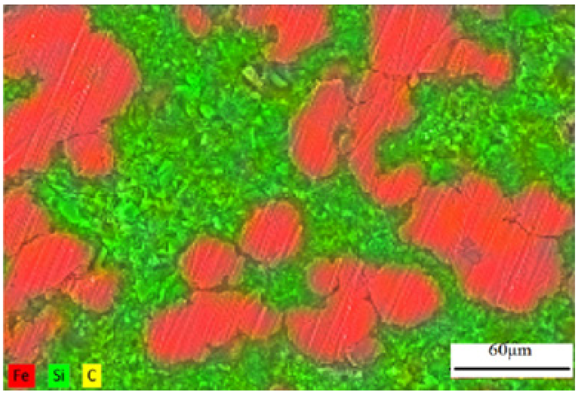

Fig. 2. MAP analysis of a sample containing a 1:1 molar ratio of iron and silicon in which no carbon is present.

The predictions which were made earlier became

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true. At an early stage, when the amount of graphite was low, (Figures 4a and b), carbon only showed a tendency to react with silicon. With the increase in the amount of graphite, this element was also observed in iron-rich sections, which can be the result of the solution and reaction of carbon and iron. On the other hand, as long as iron only reacted with silicon, the form of iron particles remained unchanged (Figures 4a and b).

As soon as carbon enters the iron structure, the structure of iron particles is crushed (Figures 4 c and d).

The reason for this probably lies in the difference in the atomic radius of these three elements. The atomic radius of iron, silicon, and carbon are 1.72, 1.49 and 0.91 angstroms, respectively. The closeness of the atomic radius of iron and silicon leads to the substitution of a solid solution.

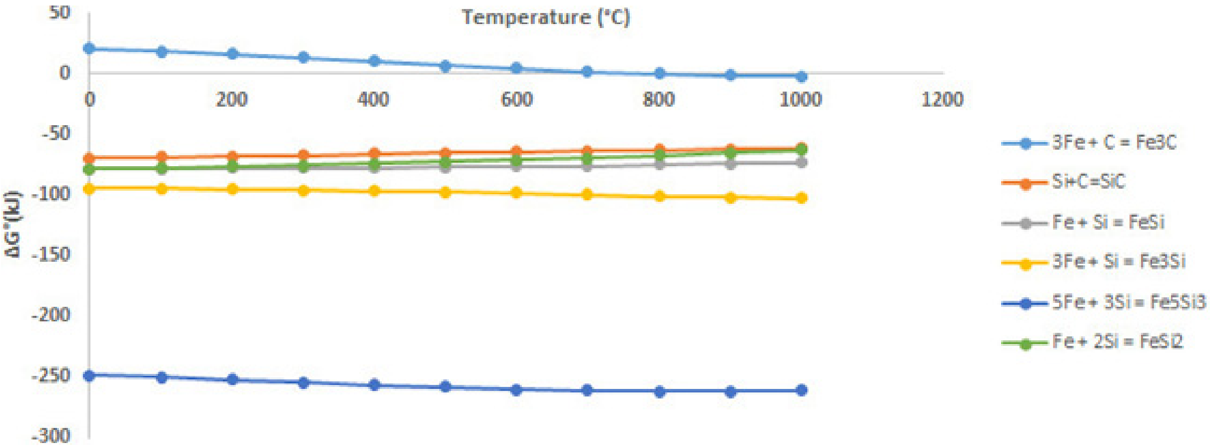
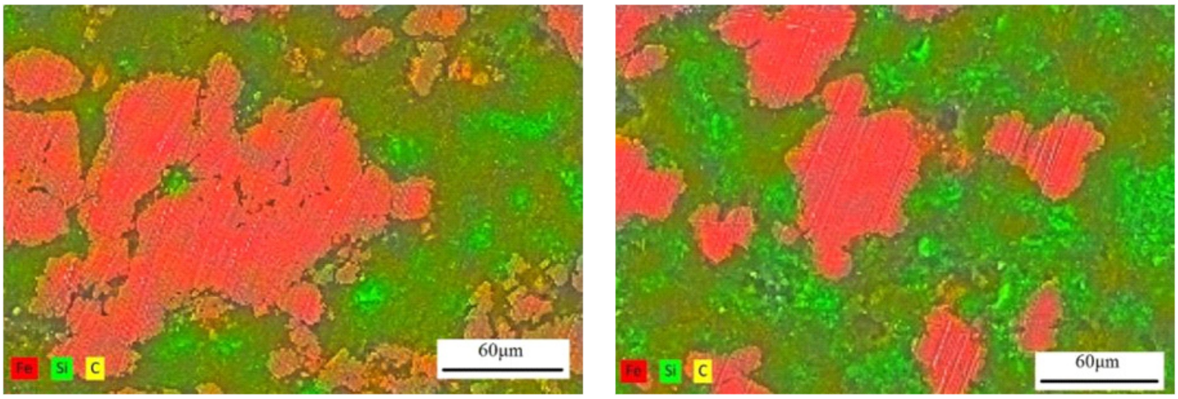
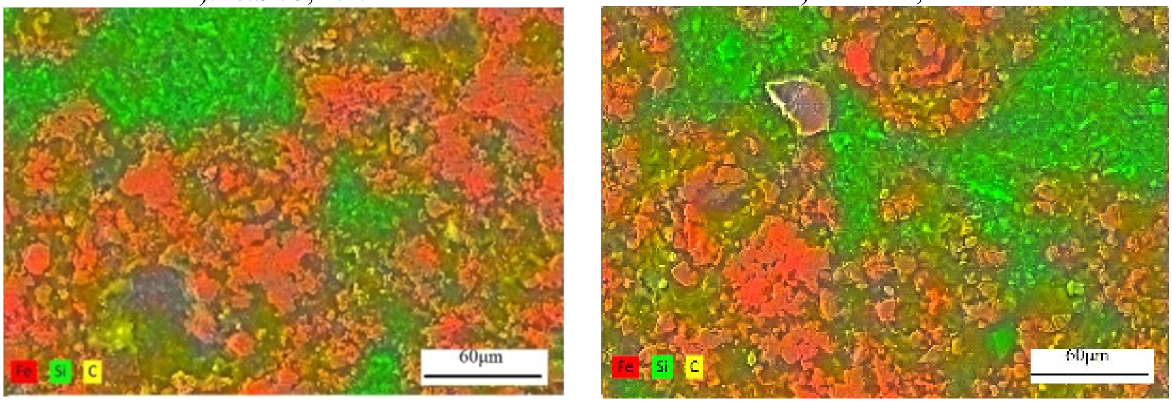


Fig. 3. Standard Gibbs free energy of formation for iron-silicon-carbon compounds in the temperature range of 0 to 1000°C.



a):Fe:Si:C, 1:1:1 b): Fe:Si:C, 1:2:1



c) Fe:Si:C, 1:0.5:2 d) Fe:Si:C, 1:1:2

Fig. 4. MAP analysis the samples containing different molar ratios of iron, silicon, and graphite.

However, due to the low atomic radius of carbon, this element can diffuse in the structure of silicon and iron to form an interstitial solid solution. As a result, it creates a lot of distortion and leads to the breaking of the basic structure of iron or silicon.

According to the carbon-silicon binary diagram, these two elements do not dissolve in each other. They can only react together [14]. Therefore, when silicon and carbon are placed close to each other, a reaction occurs between them, and the SiC phase is formed. This generated SiC layer prevents further diffusion of carbon. To determine whether the diffusion agent through the SiC layer is silicon or carbon, Figure 5 was explored. As can be seen in this diagram, the diffusion of carbon through the formed layer of SiC is easier than the diffusion of Si, so it can be assumed that carbon diffuses into the SiC layer and causes its growth. In contrast with what was previously discussed, Dijen et al. [15] have demonstrated that silicon passes through SiC and reacts with carbon. Of course, the production of Sic by other methods has also been reported [16, 17]. As SiC grows more and the diffusion process becomes more difficult, carbon tends to react with iron to form Fe_3C or other iron carbide compounds. The diffusion of carbon into the iron structure as an interstitial solution, due to creating many distortions, causes the iron silicides to form easier.

Araya et al. [18] have reported that SiC powders decompose in the presence of iron. It also emphasized that the size of SiC particles affects the decomposition process more than the ratio of Fe/SiC sizes. Accordingly, in the current research, it was conceived that by the formation of SiC and the increase in its size, the carbon near the iron particles tends to diffuse more into iron than react with Si. Consequently, carbon diffuses into the structure of iron and causes it to disrupt.

Shuaibo et al. [19] have shown that Fe-containing additives reduce the activation energy for the reactions of Si and C. It also has proven that the formation of FeSi, of course in the molten state, provides a suitable substrate for the transport of C and Si elements.

If the microstructure of Figure 2, in which only the reaction between iron and silicon is shown, is compared with the microstructures containing carbon, it will be identified that the presence of carbon not only helped the reaction between iron and silicon but also increased the thickness of the created layers of iron silicides in the iron particles.

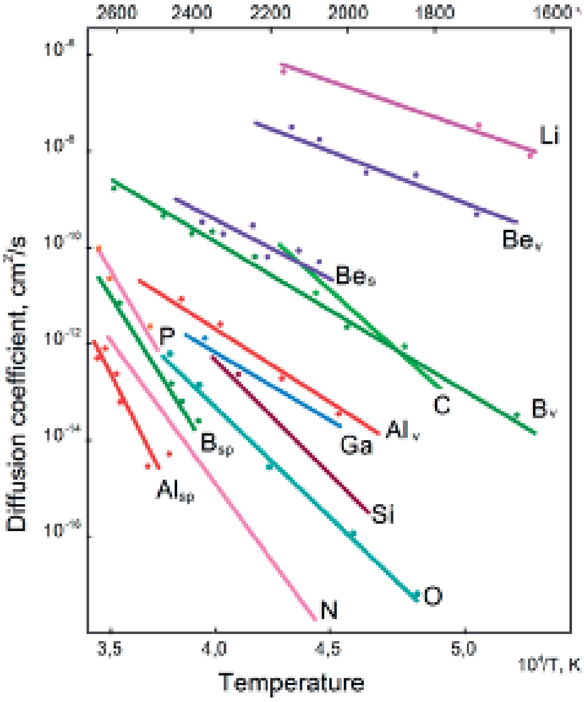


Fig. 5. Comparison of diffusion coefficients of Si and C into SiC in the solid form [20].

Based on the surveys carried out in the current study, a mechanism for the reactions of iron, silicon, and carbon powder system is proposed. The schematic of which is given in Figure 7. As can be seen, in the stoichiometric ratio of 1:0.5 of iron and silicon, if carbon is also present in the system, simultaneously with the reaction of iron and silicon to form Fe_3Si_5, some amount of carbon can dissolve in iron and make it ready to diffuse more Si or C.

Silicon also reacts with carbon and produces SiC. Passing time, the amount of carbon diffused through the formed SiC increases and the growth of SiC proceeds while the other iron silicide phases, namely FeSi and Fe_3Si can form as well. At the same, the content of diffused carbon in the iron reached an amount that can form Fe_3C.

In the stoichiometric ratio of 1:1 of iron and silicon, the formation of FeSi and SiC phases took place; meanwhile, Fe_3C could be produced by dissolving enough quantity of carbon in iron.

In the stoichiometric ratio of 1:2 of iron and silicon, the only difference made compared to the stoichiometric ratio of 1:1 is that due to the availability of a larger amount of silicon, the $FeSi_2$ phase is also shaped.

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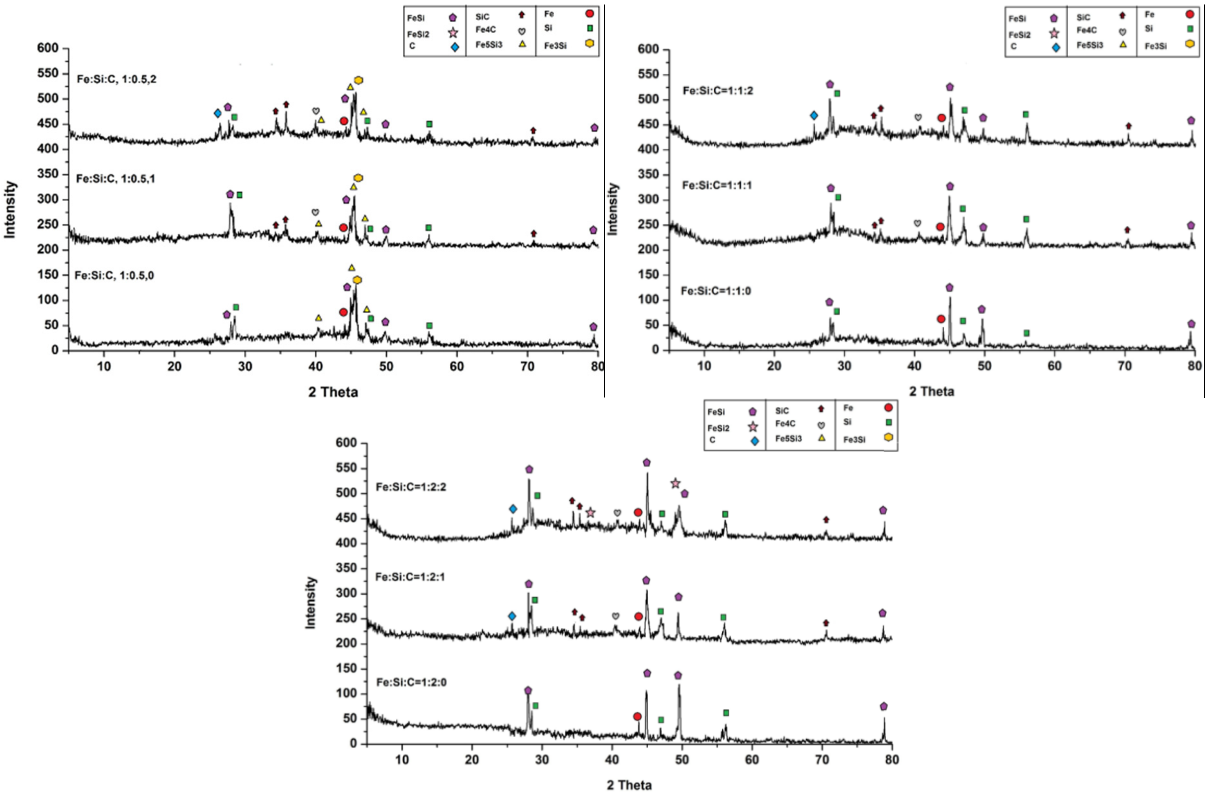

Fig. 6. XRD results for the samples containing different molar ratios of iron, silicon, and graphite.

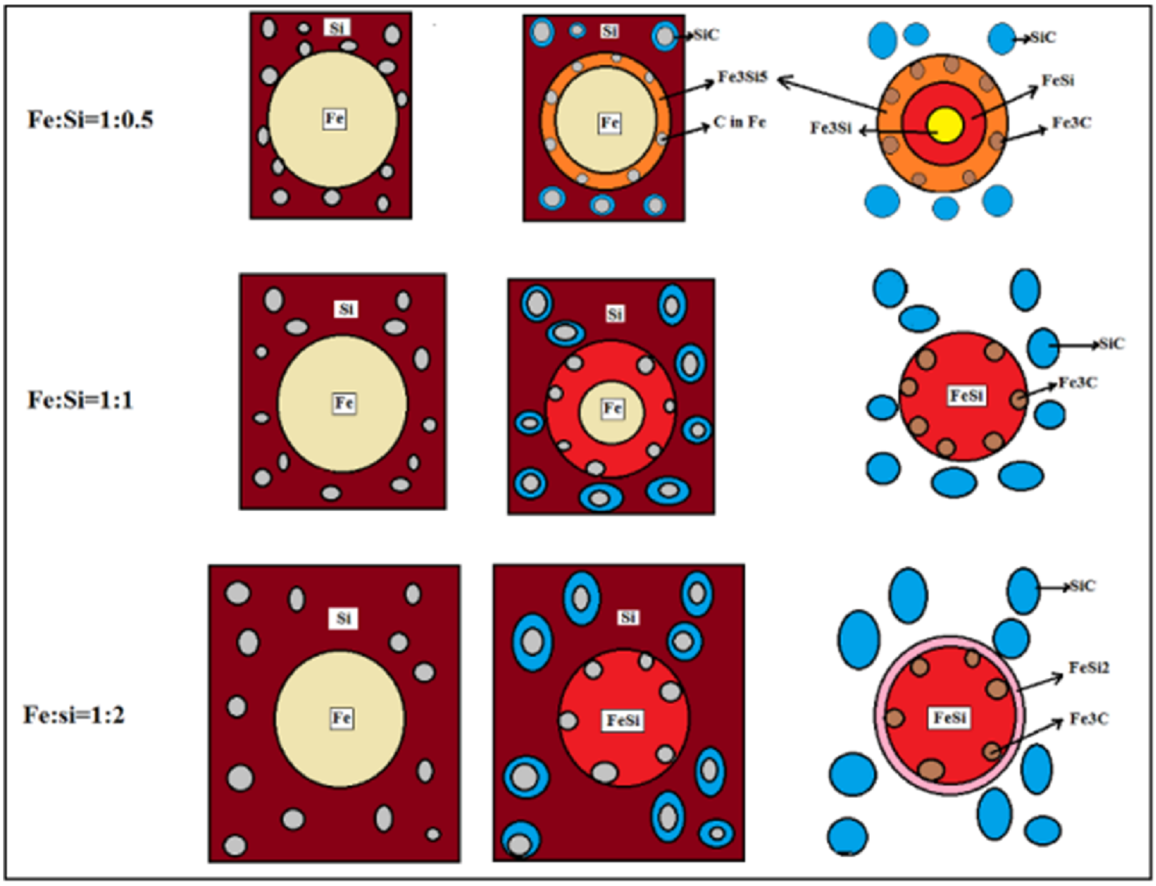

Fig. 7. The proposed mechanism for the reaction process in the Fe-Si/C powder system.

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4. CONCLUSIONS

In this study, by the addition of different amounts of graphite to the iron-silicon powder system, the compounds that can be produced and the mechanism of the reactions were investigated. It was found that due to the possibility of graphite dissolving in iron and making changes in its structure, the formation of Fe-Si compounds is facilitated. Although in small amounts of graphite, it is possible to form SiC and in larger amounts, it is also possible to create Fe_3C.

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