

# Investigation of silicon carbide dissolution behavior in molten cast iron under specific consideration of the formation of reaction layers

Silicon carbide (SiC) is one of the most commonly used substances in cast iron foundries to adjust the carbon and silicon content and in addition to inoculate cast iron melts in order to generate proper graphite structures. Nonetheless, the dissolution behavior of SiC has not yet been clearly defined to explain the effects of this substance in cast iron industries comprehensively. In this set of experiments, the dissolution of SiC in molten cast iron has been studied in detail by introducing SiC particles into molten cast iron under defined conditions. According to the experimental results the dissolution of SiC takes place in several stages that consequently result in different reaction layers around the SiC particles.

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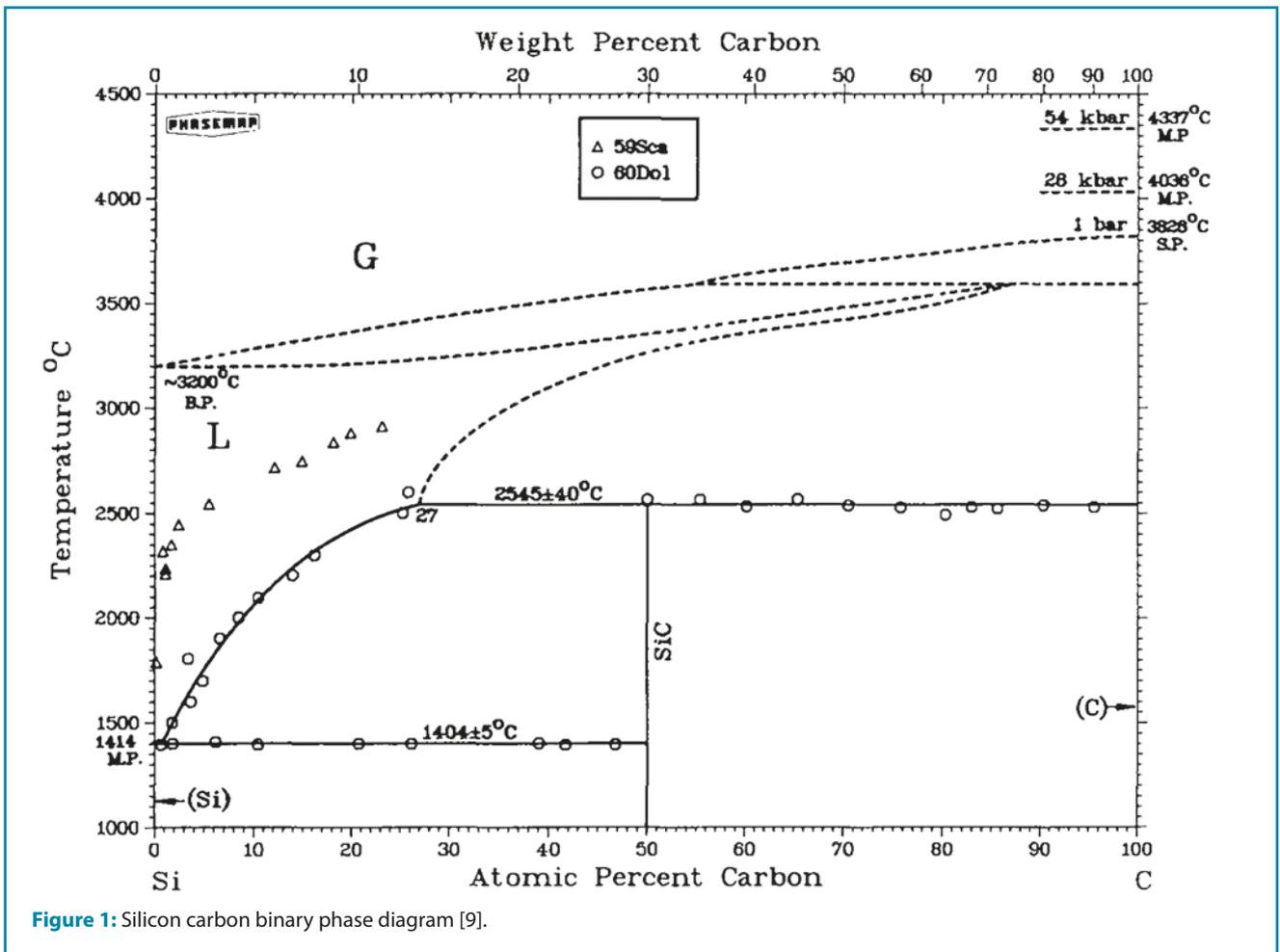
## 1 Introduction

Silicon carbide (SiC) is a chemical compound of silicon and carbon (30 wt-%) that is commonly used in several industrial processes (electronics, refractories, ...) and also in cast iron foundries. SiC is used in cement-bonded briquettes as an alloying element to control the carbon equivalent of molten iron during melting processes in cupolas. In induction furnaces, SiC is generally used as a granular material in different grain sizes. Several publications recently reported that the addition of a specific amount of SiC can also beneficially reduce the necessity of using pig iron as an input material during the production of cast iron [1, 2, 3]. This substitutional mechanism generates an added value of reducing the charging costs. An increasing addition of SiC into the molten iron changes the solidification behavior, reduces liquidus temperatures and increases stable eutectic temperatures as well as decreases values of undercooling [4, 5]. Furthermore, different studies conclusively state an increasing content of A-type graphite for grey cast iron with an increasing number of eutectic cell count and a more uniform spheroidal graphite in ductile cast iron [4, 5, 6]. Moreover, the ferritic structure is promoted and the formation of iron carbides is significantly minimized in the production of ferritic ductile iron [7, 8]. Due to its dissolution behavior in molten iron, SiC does have a so-called pre-inoculation effect that corresponds to a following considerable reduction of inoculant consumption [4].

## 2 State of the Art

The silicon-carbon binary phase diagram (**figure 1**) indicates that SiC will not be melted in liquid cast iron because its melting point is higher than normal operating temperatures of molten cast irons. Instead, the dissolution mechanism occurs during the process of alloying or inoculating the cast iron. Even though SiC is a well-established additive substance in improving the productivity of the iron casting industry, the dissolution behavior of SiC unfortunately has not yet been clearly defined. A comprehensive study in terms of explaining the dissolution mechanism of SiC in cast iron was conducted by Benecke et al. in 1987 [10]. According to these results carbon and silicon dissolve simultaneously in a 1:1 ratio with the effect of local high carbon and silicon contents close to the dissolving solid/liquid interface. Following their theory, very small but numerous hypereutectic regions are created in which graphite clusters will arise. In contact with the molten iron, the graphite cluster should act as a diffusion layer between the SiC particles and the liquid metal. The graphite cluster is expected to be the origin of the graphite nucleation at a certain period due to its stability. However, their study still could not show or clearly define how such clusters can be formed during the dissolution, as well as there were not enough qualitative proofs provided to support the main claim of graphite cluster formation.

The effects of locally high silicon and carbon contents during the dissolution of FeSi particles in cast iron melts were theoretically explained and experimentally proven by Wang and

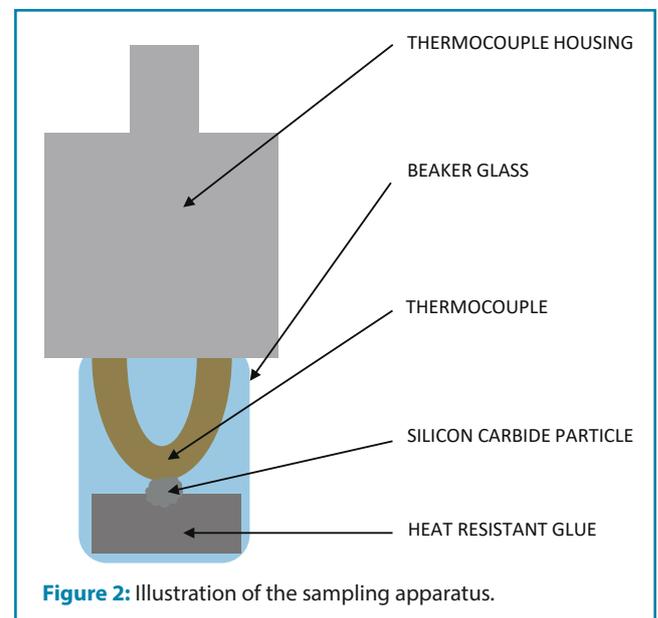


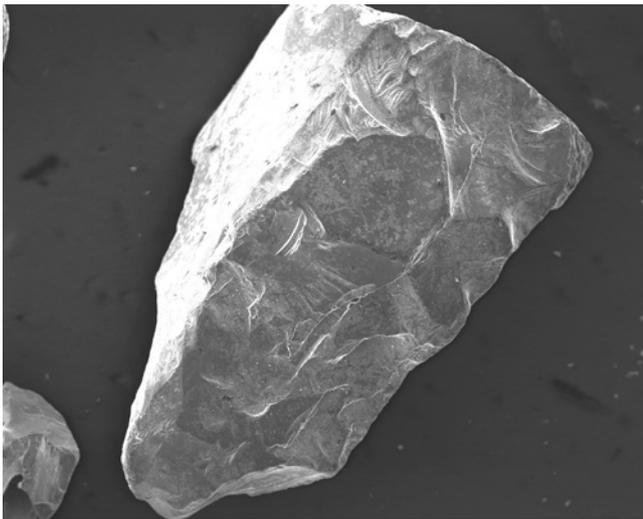
Fredriksson in 1981 [11]. They indicate that in locally inhomogeneous distributions, the dissolved silicon increases the carbon activity to such an extent that carbon supersaturation exists. As a result of this supersaturation, the authors were able to identify SiC particles in the immediate vicinity of the original FeSi particles after very short reaction times. It is reported that the SiC particles are then decomposed to form graphite in the further course. The formation of SiC particles during the dissolution of FeSi particles in molten cast iron was also observed by Müller and Siefer [12, 13] in cooperation with Deike [14] in the dissolution zone in areas with high silicon content (~ 70 wt-%). Further away from the interface, in areas with lower silicon contents (~ 15 wt-%) in the molten cast iron, no SiC could be detected in the surrounding iron-rich areas. This could be in line with the observation of Wang and Fredriksson that SiC particles redissolve [11]. However, it must be considered that these SiC particles may already have been contained in the original FeSi particles. Due to the FeSi production process and the prevailing gas atmospheres, it can be assumed that SiC particles are already formed during the production process of FeSi so that they were already included in the FeSi particles [14].

The purpose of this set of experiments is to provide a better understanding of the dissolution mechanism of SiC in the molten iron by reassessing the previous studies as well as offering a set of conclusive analyses so the results can be the basis for enhanced use of SiC in the cast iron industries.

### 3 Materials and Methods

In order to investigate the dissolution of SiC in detail, the beaker glasses were immersed into molten cast iron at defined tem-





**Figure 3:** Silicon carbide particle (1-2 mm).

**Table 1: Chemical composition of ductile iron in wt-%**

C	Si	Mn	P	S	Fe
3.14	2.20	0.14	0.33	0.01	rest

**Table 2: Chemical composition of silicon carbide in wt-%**

C	Si	Other
33.8	64.5	rest

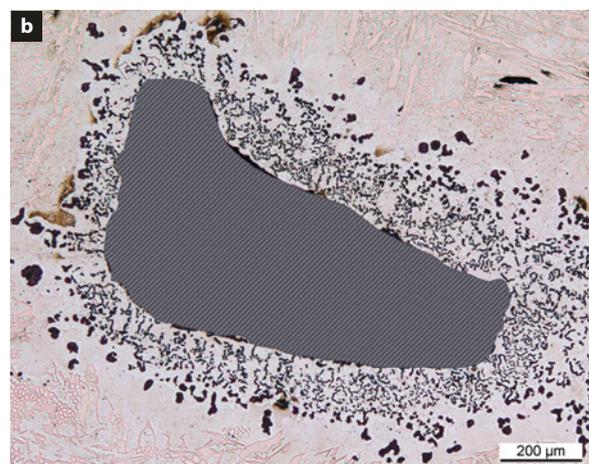
peratures for a certain period. The construction of the sampling apparatus used in these experiments is illustrated in **figure 2**. Metallurgical SiC (**figure 3**) and returns of ductile cast iron were used in the tests. The chemical compositions of SiC and the ductile iron are given in **table 1** and **table 2**, respectively.

The dissolution of SiC was conducted by melting the returns of ductile iron in an induction furnace. After reaching the final temperature of 1300 - 1500 °C, the sampling apparatus was immersed in the molten cast iron. During this process, the molten cast iron flows through a prepared gap into the beaker glass and starts to interact with the SiC particle. After a certain period of liquid-solid interaction (30 sec), the sampling apparatus was pulled out of the melt and the seized cast iron solidified under normal atmospheric condition. The sample was prepared for the metallographic examination and analyzed under a light microscope and scanning electron microscope (SEM).

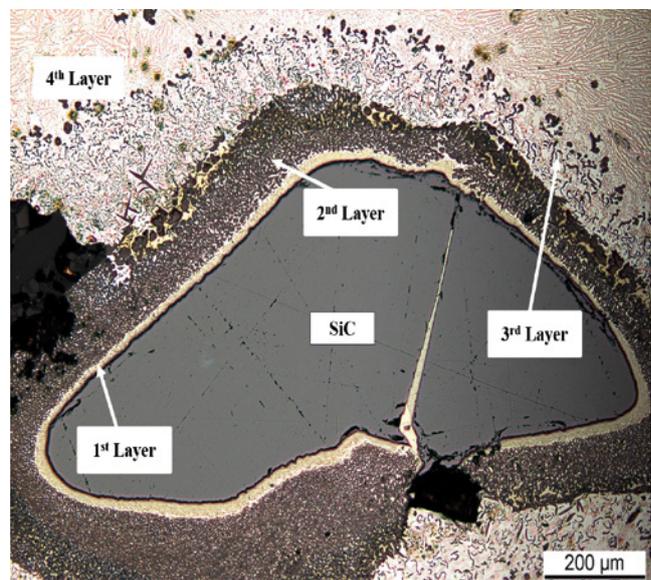
#### 4 Results and Discussion

The results of SiC dissolution in molten cast iron show that in an early phase of interaction between liquid cast iron and the SiC particle, several reaction layers have been formed, but interestingly, without a significant change or distortion on the original geometry of the SiC particle (**figure 4**).

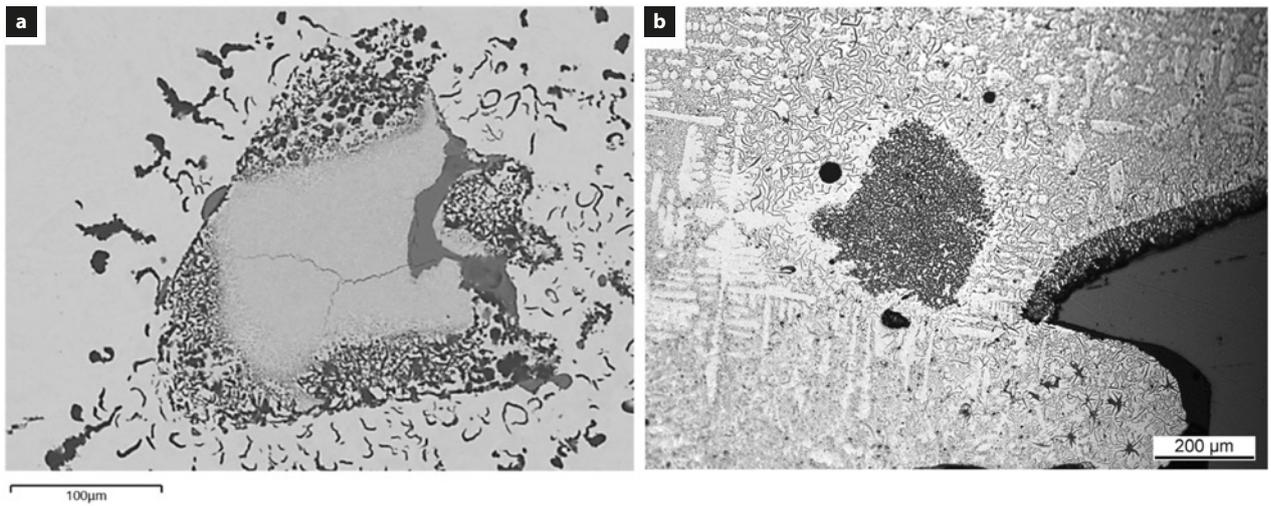
The geometric stability of the SiC particle indicates that at least in the early phase of the dissolution process, the process is strongly diffusion-controlled which results in a clearly uniform reaction layer thickness of the 1st layer. The largely uniform thickness of the 2nd reaction layer also indicates a diffusion-controlled process in which graphite grows in a liquid metal phase (**figure 5**). The structure of the 3rd layer allows to assume



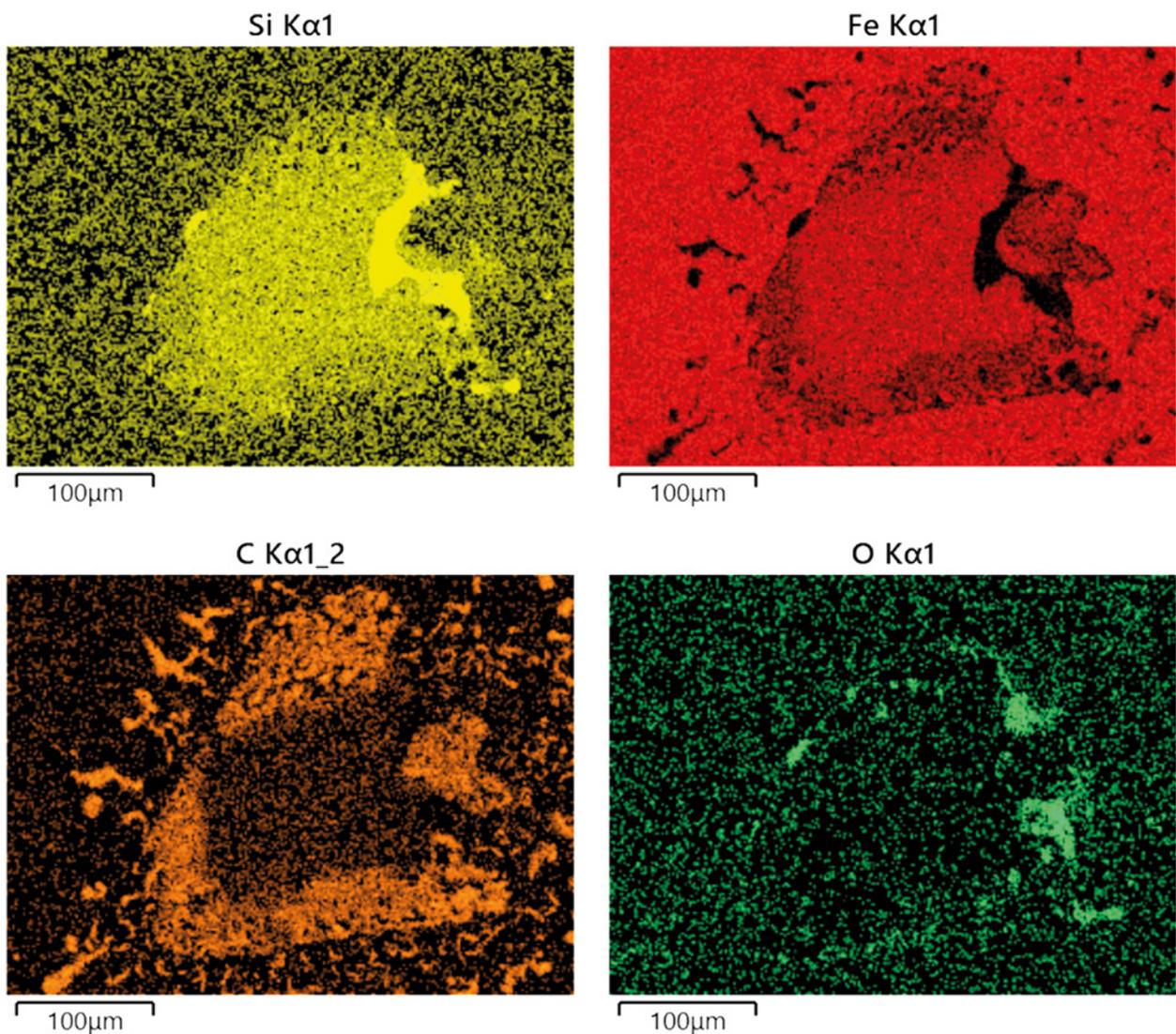
**Figure 4:** SiC particle: a) surrounded by different reaction layers due to the introduction of molten iron; b) original geometry before dissolution trial.



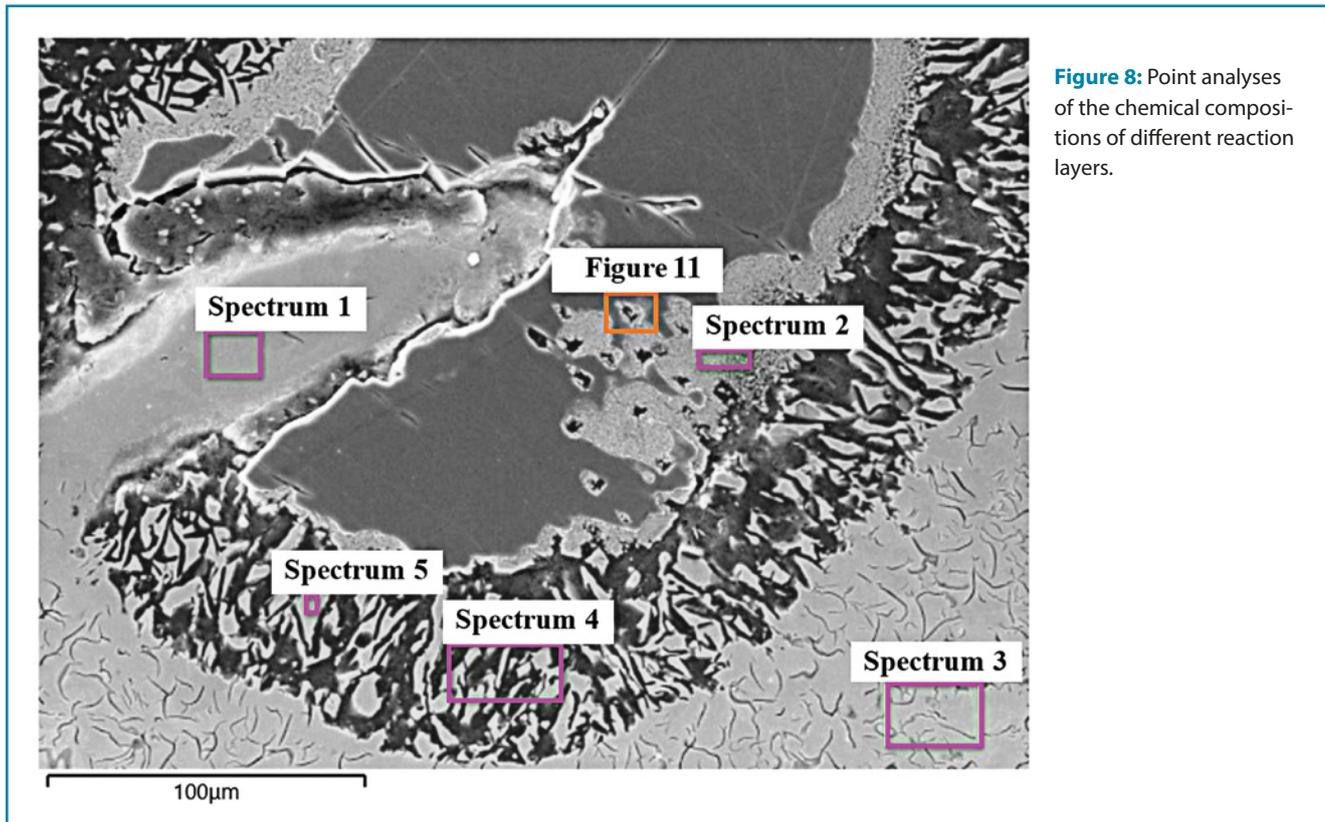
**Figure 5:** Four different layers, typically captured around the SiC particles.



**Figure 6:** Complete decomposition: a) 1<sup>st</sup>-Layer-Type Core, b) 2<sup>nd</sup>-Layer-Type Core.



**Figure 7:** Element mapping of a former SiC particle in figure 6a.



**Figure 8:** Point analyses of the chemical compositions of different reaction layers.

that diffusion also plays a role, although effects of melt flows can also be seen. The original matrix structure is shown in the 4th layer. Certain geometric stability was also observed, even though the former SiC particle was completely decomposed during its interaction with the molten iron (figure 6). The dissolution process of SiC sequentially continues and is finished by the complete dissolution of the former SiC-particle into the whole matrix of cast iron. The core of the particle in figure 6a which still appears as SiC, only consists of the same structure as the 1<sup>st</sup> layer. An element mapping of this particle is shown in figure 7. The carbon distribution clearly shows the graphite formation in the surrounding of the particle. The iron distribution and the considerably high iron concentration inside the particle show that iron diffuses into the former SiC grain, which was not expected to this extent at the beginning. This shows that iron diffused into and not silicon out of the SiC particle and at the same time explains why the growth of the 1<sup>st</sup> layer is determined by iron diffusion. Figure 7 also shows that silicon can be detected together with oxygen in some places. Under the light microscope, it looks like a certain slag is formed in these areas.

In addition to the metallographic analyses with the light microscope, further analyses concerning the chemical compositions of the reaction layers were made with a SEM (figure 8). Based on the chemical analyses (table 3) the main characteristics of the different layers are:

- The 1<sup>st</sup> layer (spectrum 2) consists mainly of an iron-carbon (~ 12 wt-%) - silicon (~ 13 wt-%) melt with small graphite particles (< 100 nm - 2.5 µm), which are responsible for the high total carbon content (~ 28.3 wt-%) in this layer.
- The 2<sup>nd</sup> layer (spectrum 4) is characterized by larger graphite structures (10 – 50 µm in length) with an iron-car-

	Fe	C	Si	O
Spectrum 1	87.6	6.9	3.5	-
Spectrum 2	60.1	28.3	8.6	-
Spectrum 3	76.7	19.2	2.6	-
Spectrum 4	61.5	34.4	1.2	2.1
Spectrum 5	83.7	7.5	6.7	-

bon (~ 7.5 wt-%) - silicon (~ 6.7 wt-%) melt (spectrum 5) in the gaps between the graphite network, that is responsible for the high total carbon content (~ 34.4 wt-%) in this layer.

- The 3<sup>rd</sup> layer (spectrum 3) consists of a nearly regular cast iron melt. It must be assumed that this area is affected due to the dissolution process of the SiC particle. The high total carbon content (~ 34.4 wt-%) in this layer is due to the lamellar graphite. This composition was also measured.

According to the 3 layers presented in figure 4 and 5, it can be assumed that when iron diffuses into SiC silicon will be dissolved and consequently a liquid iron-silicon-carbon melt is formed. This is the mechanism how SiC is decomposed into its components silicon and carbon and absorbed by the melt that occurs. In addition, it can be seen from the binary iron-silicon (figure 9) and ternary iron-silicon-carbon phase diagram (figure 10) that silicon has a much higher solubility in iron compared to carbon. It is known from practical work in cast iron foundries that it is easier to increase the silicon con-

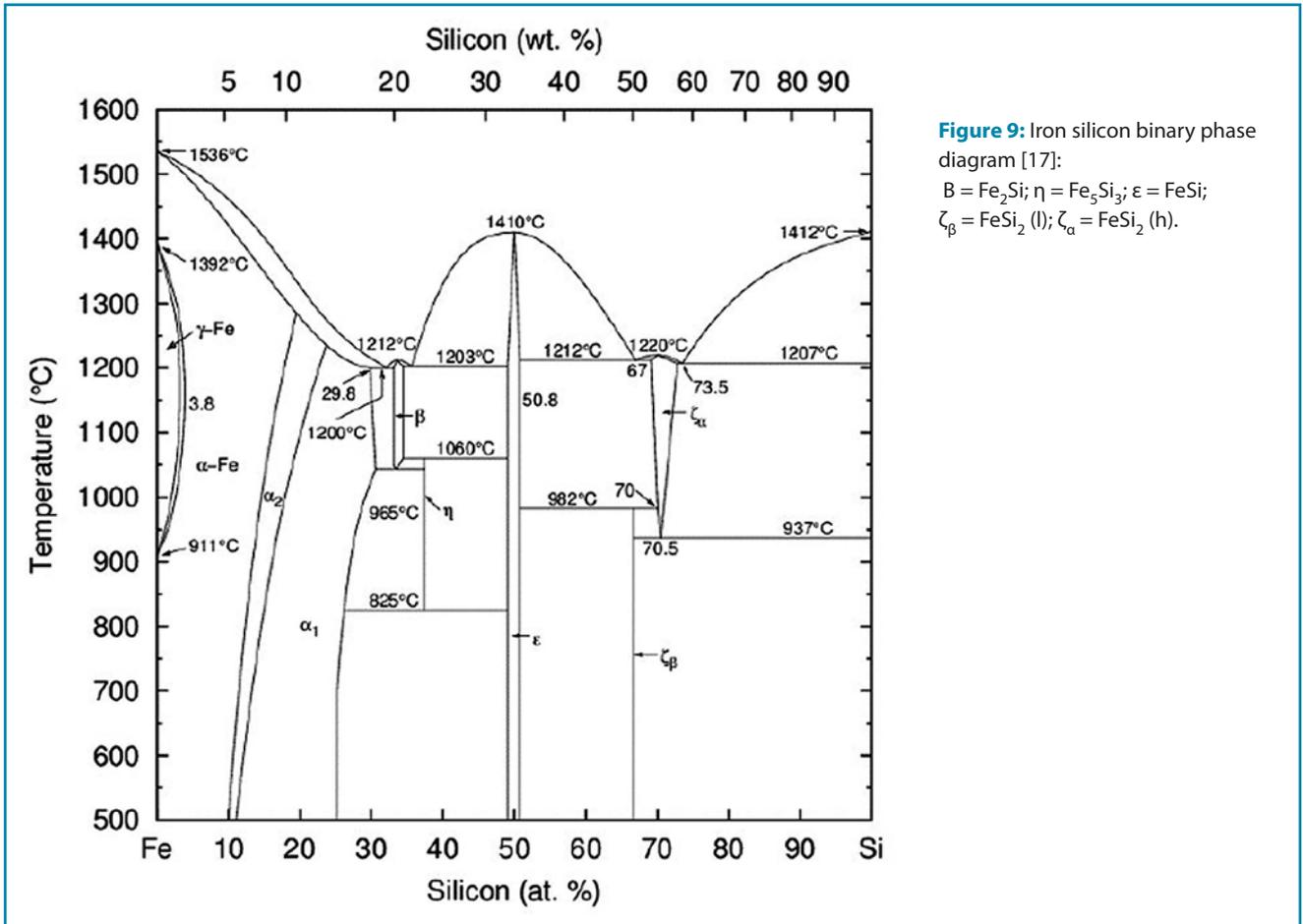


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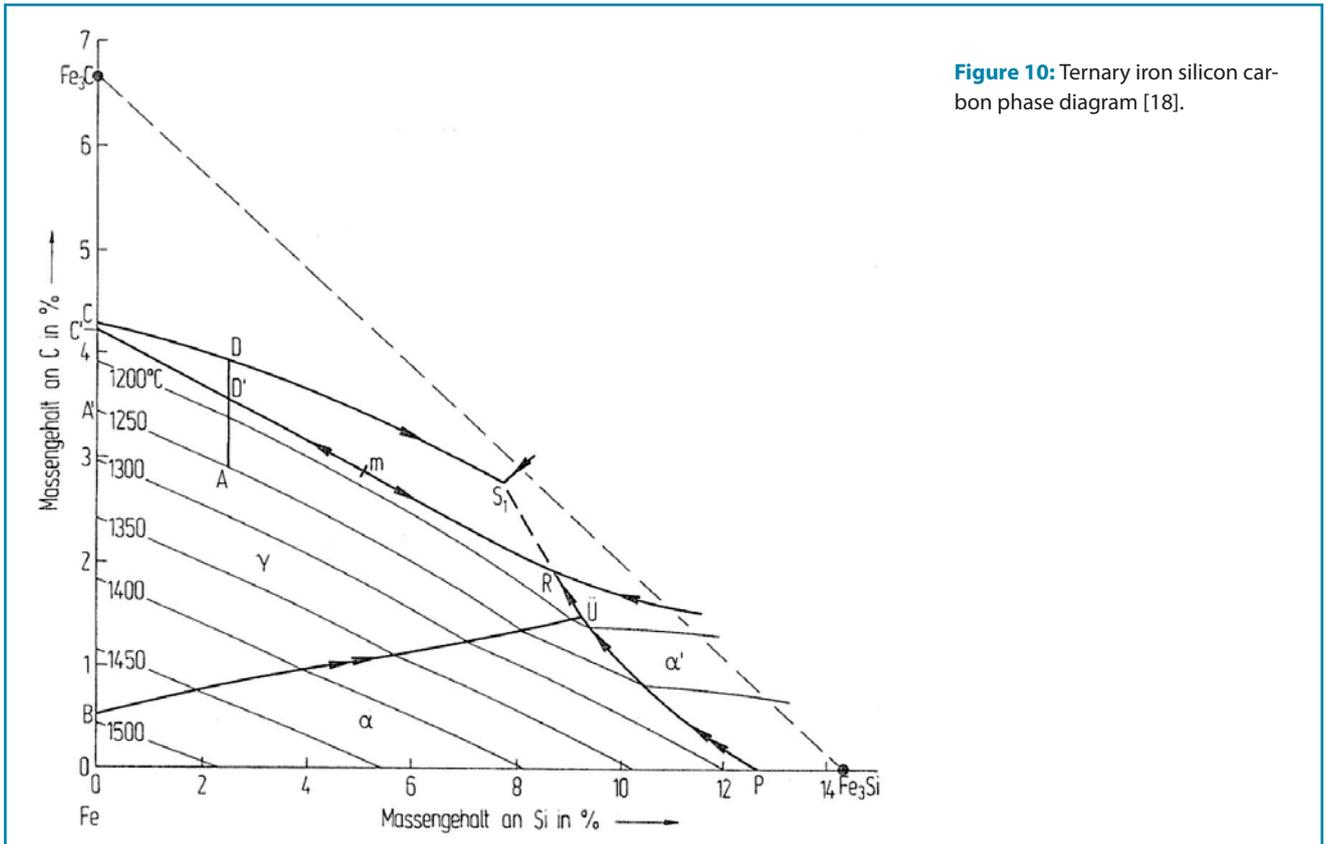
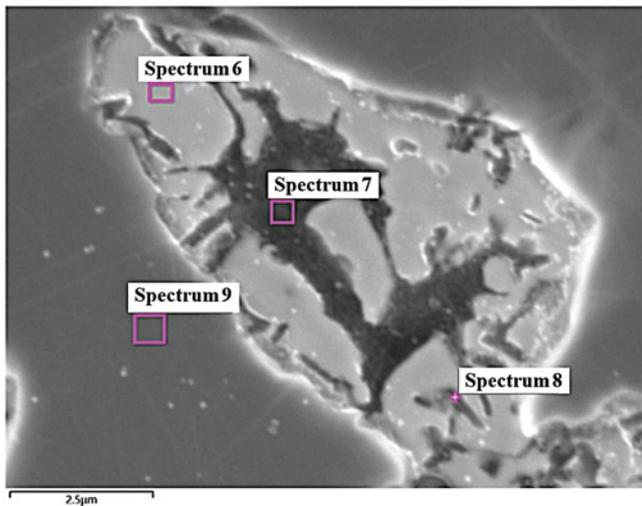
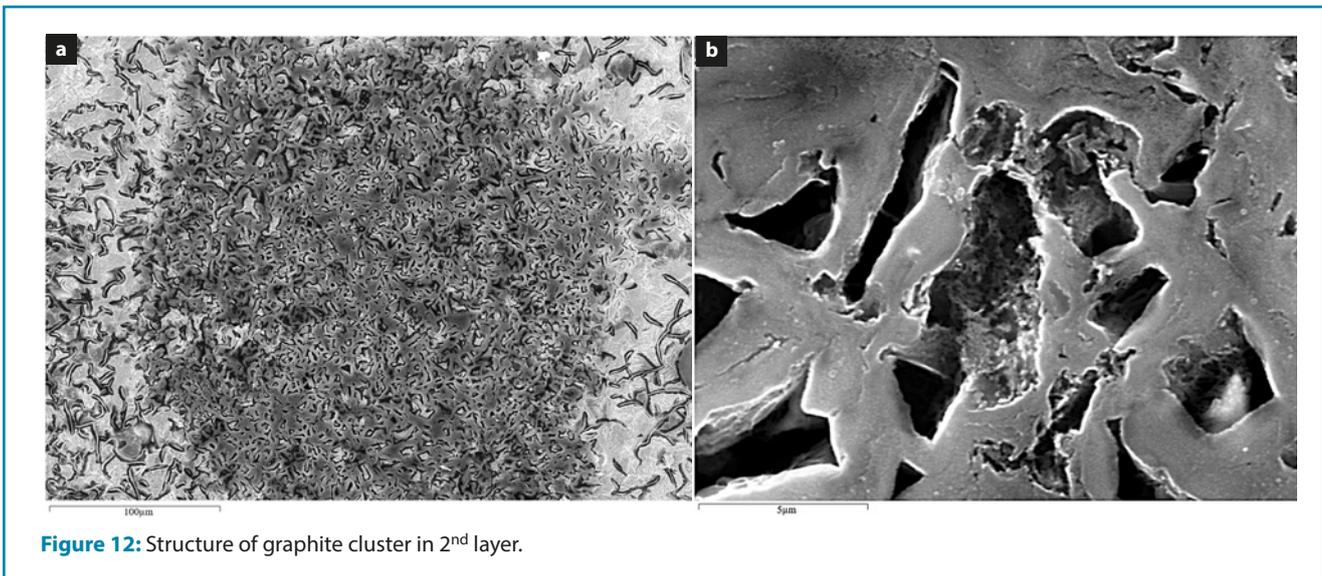


DIAGRAM: SCHUERMANN ET AL



**Figure 11:** Point analyses for the chemical composition of the FeSi Matrix at 1<sup>st</sup> layer.

Table 4: Chemical composition of the selected area in wt-% (figure 11)				
	Fe	C	Si	O
Spectrum 6	73.5	11.7	13.0	-
Spectrum 7	9.1	84.8	3.5	2.7
Spectrum 8	44.8	46.2	7.3	-
Spectrum 9	-	34.3	65.7	-



**Figure 12:** Structure of graphite cluster in 2<sup>nd</sup> layer.

tent in a melt than the carbon content. At almost every possible amount of dissolved silicon in these experiments, their melting points were below the operating temperatures considered in the trials.

Due to the significantly lower solubility of carbon in liquid iron at higher silicon contents (figure 10), locally supersaturated iron-silicon-carbon melts are formed and carbon must be rejected out from the liquid melt [15, 16]. This means that the carbon is forced to crystallize as graphite and in this way the 1st layer is formed (figure 5). A detailed record of graphite nucleation in the FeSi matrix is shown in figure 11. As listed in table 4, the matrix of this 1st layer contains an iron-carbon (~ 12 wt-%)-silicon (~ 13 wt-%) alloy (spectrum 6) and very small graphite particles (< 100 nm -2.5 µm) in an irregular arrangement (spectrum 7).

An increase in dissolved silicon leads to a higher production of melt containing iron, silicon, and carbon, as well as to higher amounts of rejected carbon and crystallized graphite. When the graphite crystallizes in the 2<sup>nd</sup> layer, it forms a certain network, which creates a carbon concentration gradient. Due to the higher amount of liquid the carbon diffusion conditions im-

prove and the crystallization rate increases. For getting a better understanding of the 2<sup>nd</sup> layer (graphite cluster) structure, deep etching was carried out and the sample was afterwards examined with the SEM. The graphite cluster is actually a connected network of graphite with a sponge-like structure (figure 12). This type of structure supports the first statement that the dissolution of silicon and carbon by the molten iron took place at different degrees, thus providing a nucleation site for the forthcoming crystallization of graphite. That the original geometry of the SiC particles remained almost intact even after dissolution is reasoned by:

- the diffusion of iron into the SiC particle,
- the formation of an iron melt high in silicon and carbon inside the former particle,
- the rejection of carbon out of the supersaturated melt,
- the crystallization of graphite in a network-like structure in the area of the former SiC particle.

As shown in figures 5 and 6, the 3<sup>rd</sup> layer has commonly different graphite structures which are in the range of A, B, and C lamellar graphite. On some occasions, nodular graphite could be detected at the interface between the 3<sup>rd</sup> and 4<sup>th</sup> layers.

## 5 Conclusions

Following the results presented in this paper and according to the current state of knowledge, the dissolution of silicon carbide (SiC) in cast iron melts starts with the diffusion of iron into SiC, followed by the dissolution of silicon in iron and the formation of an iron-silicon-carbon melt. Due to the significantly lower solubility of carbon in liquid iron at higher silicon contents locally supersaturated iron-silicon-carbon melts are formed and carbon must necessarily leave the liquid melt, so carbon is forced to crystallize as graphite. It was found that graphite crystallizes in a sponge-like network structure and that is the reason why after complete dissolution of the SiC particle the final network structure is similar to the structure of the original SiC particle. It can be supposed that these structures are destroyed and distributed due to the following melt flow in melt treatment and during the casting process of cast iron, so smaller particles of this former network can act as nuclei for graphite formation during the solidification process. The time delay, called the pre-inoculation effect, observed in iron foundries when SiC is used, can be explained with the necessary time-dependent diffusion of iron into SiC to dissolve SiC.



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