Theoretical foundations of ferrosilicium disintegration

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Abstract. The crystallization processes and solid-phase transformations in alloys FS-75, FS-65, FS-45 and the influence of impurities (aluminum) on the possibility of disintegration of ferroalloys were considered on the basis of state diagrams analysis of Fe–Si and Fe–Si–Al systems. It was shown that the mechanisms of crystallization of melts of different compositions differ quite significantly, both in the chemistry of the process, and in the number and composition of the crystallization products. Process of ferroalloys disintegration depends on many factors: the alloy composition, the degree of superheat, the cooling rate, completeness of solid phase reactions, etc.

1. Introduction

The phenomenon of ferrosilicon disintegration reduces the output of standard quality products of ferrosilicon grades; is accompanied by the release of toxic and flammable in certain conditions and explosive gases [1]. The main causes of this phenomenon are considered to be the occurrence of thermal stresses during polymorphic transformations of leboite, accompanied by a significant increase in volume (ΔV≈17%), the influence of impurities (Al, Ca, As, P, S) on formation in the crystallization process of multicomponent low-melting eutectics, which are located on the grain boundaries of silicon and iron silicides and forming with the target components of the alloy (Fe, Si, C) the complex chemical compounds (carbides, phosphides, arsenides, sulfides), interacting with the atmospheric moisture and forming hydrates (Ca(OH)₂, Al(OH)₃) and gaseous compounds (PH₃, AsH₃, H₂S, C₂H₂) [2, 3].

2. Research and results

A more detailed analysis of crystallization processes and solid phase transformations can be done on the basis of the modern state diagrams (Fe-Si, Fe-Si-Al, and others.) [2, 4-6]. A fragment of the state diagram Fe-Si in the range of concentrations 33–100 wt% Si is given in Figure 1.
Within the range of silicon concentrations 33.3-50.1% by weight monosilicide of iron FeSi is crystallized during cooling, within the range of silicon concentrations 61-100% by weight during the primary crystallization the silicon crystals are formed, in the intermediate range of Si concentrations 50.1-61% by weight leboite is formed from the liquid phase during cooling – ξ phase FeSi$_{2.33}$, congruently melting at 1493 K. Leboite density is 5.06 g/cm$^3$. In solid form, it forms solutions with silicon and monosilicides, the zone of which converge to zero values at 1210 K. With silicon and monosilicides leboite forms eutectics – $e_1$ (1480 K, 61% wt. Si) and $e_2$ (1485 K, 50% wt. Si). Leboite composition corresponding to the congruent melting point (1493 K, 55% wt. Si), is identified as FeSi$_{2.33}$, however, taken into account solutions non-stoichiometry, it is presented as phase FeSi$_2$, critical in the iron content Fe$_x$Si$_{2.33}$ ($x=0.77-0.87$). Leboite participates in two eutectic reactions:

$$L_{e_1} \rightleftharpoons Si + \xi (1480 K),$$

$$L_{e_2} \rightleftharpoons FeSi + \xi (1485 K).$$

When $xFe = 0.77-0.82$ from the supersaturated with silicon solution of leboite during cooling from 1480 to 1210 K the silicon crystals are formed:

$$\xi_{xFe=0.77} \rightarrow Si + \xi_{xFe=0.82}$$

At 1210 K leboite breaks according to peritectoid reaction forming stoichiometric disilicide FeSi$_2$ and silicon:
This transformation proceeds with the increase in volume (to 17%) and is a major cause for alloys disintegration with silicon content 65% wt. and more. Since in these alloys leboite is formed during crystallization of eutectic $e_1$ in the form of a fine-disperse eutectic mixture ($\xi + Si$), and the grain growth practically does not occur during cooling, furthermore, a partial disintegration of leboite takes place with formation of a new phase (silicon). Even at this stage the local stresses and microcracks appear in the eutectic structure of a solid mixture. During crystallization of alloy FS-75 the amount of liquid eutectic melt $e_1 \approx 50\%$. The amount of silicon crystals in the eutectic mixture is less than 10%, thus, the amount of leboite during equilibrium crystallization may reach $\approx 40\%$ of the initial melt mass.

During crystallization of alloy FS-65 the amount of silicon crystals, formed within the temperature range 1570-1480K (point 2-2'), is significantly larger ($\approx 25\%$), and eutectic mixture ($\xi + Si$), formed during the melt crystallization of composition $e_1$ (61% Si), – is significantly higher (75%), resulting in a large, compared with FS-75, propensity to disintegrate (leboite amount in the alloy during equilibrium crystallization may reach 65%). It should be noted that during a substantial alloy overheating above the liquidus surface and subsequent rapid cooling (which often takes place during casting of ferrosilicon) the temperature of the beginning of crystallization reduces, and subsequently, due to a more intense crystallization heat release the temperature of the end of the crystallization also decreases; and the eutectics parameters change (dotted lines in Figure 1).

During crystallization of FS-45 alloy as a primary crystallizing phase in the temperature range 1600-1485K (point 3-3') the monosilicide silicon crystals are formed, their quantity at the eutectic temperature $e_2$ (1485 K) is $\approx 33\%$ ($\approx 67\%$ respectively eutectic $e_2$) at the equilibrium (without supercooling) crystallization.

At 1485 K eutectic reaction (2) proceeds, in the result of which from a liquid melt with composition $e_2$ evolve iron monosilicide FeSi and solid solution of leboite composition of point $F_2$ (50.1% Si). The crystallized eutectic mixture (FeSi+leboite $F_2$) contain $\approx 19\%$ of silicon crystals and, $\approx 81\%$ of leboite, i.e. $\approx 54\%$ of leboite phase.

During cooling to 1255K leboite of $F_2'$ composition reacts with monosilicide:

$$FeSi + \xi_{F_2'} \rightarrow xFeSi_2 + (1 - x)FeSi^0.$$  \hspace{1cm} (5)

Leboite completely disappears, and monosilicide remains in abundance (FeSi$^0$). After the reaction the alloy must contain $\approx 30\%$ of residual monosilicide and 70% of disilicide FeSi$_2$.

During cooling of alloys containing 50-54% of Si ($e_2$ -$F_2$), for example, the alloy of composition point 4, at 1255K interaction of monosilicide FeSi with leboite leads to monosilicide disappearance, and leboite of $F_2'$ composition remains in abundance ($\xi^0$):

$$FeSi + \xi_{F_2'} \rightarrow FeSi_2 + \xi_{F_2'}^0.$$  \hspace{1cm} (6)

With further cooling, the amount and composition of the mixture components disilicide-leboite changes slightly, and at 1210K the residual leboite of composition point $N'$ reacts with disilicide forming silicon, and leboite disappears:

$$FeSi_2 + \xi_{N'} \rightarrow Si + FeSi_2.$$  \hspace{1cm} (7)

Reaction (7) proceeds with the increase in volume, but since the quantity of leboite in point 4’ is low, it does not significantly affect the alloy disintegration.

The alloy crystallization is of particular interest, corresponding in its composition to the point of leboite congruent melting point. In this case, in the absence of impurities during slow cooling the
pseudo-single crystalline crystallization can be observed with formation only large single crystals of leboite, which during cooling to 1210 K dissociate into silicon and disilicide and FeSi$_2$ (eutectoid reaction):

$$\xi_{N/} \rightarrow \text{Si} + \text{FeSi}_2.$$  \hspace{1cm} (8)

This reaction, which was previously identified as polymorphic transformation of leboite, proceeds with the increase in volume, but large single crystals of leboite can withstand stresses for a long time without fracture, and a small zone of intergrain boundaries minimize the impurities influence on the process of disintegration. In this case the system is thermodynamically unstable and in the presence of precipitating factors (long-term storage, the presence of impurities, high humidity) such alloys may also disintegrate.

The impurities Al, Ca, P, As, S, C, which income into the ferrosilicon with raw materials (quartzites, sands, cokes, coals, iron turnings, scale, etc.), are of particular importance for the issue of ferrosilicon disintegration. The influence of impurities on crystallization process with leboite is considered on the example of a well-studied system Fe-Si-Al, the state diagram of which is given in Figure 2 [4].

Aluminium is present in ferrosilicon as an impurity in the largest compared with other impurities concentrations (up to 2% or more) [7-9] and its effect on the crystallization process is most significant.

In accordance with the state diagram of the system Fe-Si-Al, in addition to silicon and silicides in the final phases of crystallization ternary chemical compounds might be formed, melting incongruently: Al$_3$Fe$_3$Si$_2$, Al$_{12}$Fe$_6$Si$_5$, Al$_9$Fe$_5$Si$_5$, Al$_{13}$Fe$_5$Si$_5$, Al$_7$Fe$_5$Si. Directly to the crystallization fields of silicon, leboite and monosilicide the crystallization fields of compounds Al$_3$Fe$_3$Si$_2$, Al$_{12}$Fe$_6$Si$_5$ adjoin, which are present in the final crystallization phases.

During crystallization of alloy FS-75, containing $\approx$1.5% of Al, the alloy composition point (p. 1) lies in the crystallization filed of silicon in 1–1’. From the liquid melt the crystals of silicon are formed. Further, along the boundary curve of monovariant equilibrium $e_1$–$u_6$ from the melt simultaneously two crystalline phases are crystallized – silicon and leboite. Crystallization finishes in the point $u_6$ at a temperature 880°C according to peritectic reaction:

$$L + \text{FeSi}_2 \rightarrow \text{Al}_9\text{Fe}_5\text{Si}_3 + \text{Si}.$$  \hspace{1cm} (9)
Figure 2. Fragment of the state diagram of the system Fe-Si-Al.

Leboite transformation into disilicide FeSi$_2$ takes place along the isotherm 937°C, and specifically for the alloys FS-75 and FS-65 in the point 1'' on the boundary curve e$_1$–u$_6$. Therefore, in the section 1'–1'' the eutectic reaction proceeds:

$$L \rightarrow \xi + Si,$$  \hspace{1cm} (10)

and in the section 1''–u$_6$:

$$L \rightarrow FeSi_2 + Si.$$  \hspace{1cm} (11)

Crystallization ends in the invariant point of the four-phase equilibrium u$_6$ at 880°C, and the aluminum content in the liquid mother melt of composition p. u$_6$ increases to 38%, and silicon content, respectively, is reduced to 36%. The amount of liquid, crystallizing in p. u$_6$, is characterized by the segment 1–N$_1$ on the line N$_1$–u$_6$ and is ≈4.5%, the proportion is Si:FeSi$_2$:1:1.

Crystallisation of alloy FS-65 (Al≈1%) – p. 2, proceeds similarly, differing only in the fact that the quantity of silicon crystals, formed on the section of primary crystallization (2–2') will be considerably lower (≈20%), and crystals FeSi$_2$, formed by the reaction (11), – higher (≈78%), which largely determines the increased ferrosilicon disintegration.

Crystallization of alloy FS-45 (Al≈1%) occurs otherwise. The point of alloy composition 3 is in the elementary phase triangle FeSi–ξ–Al$_2$Fe$_3$Si$_2$, thus, the melt completes crystallization in the invariant point of four-phase equilibrium u$_4$ (Al 26%, Si 32%) at a temperature ≈1000°C. Since the composition point of alloy FC-45 lies in the crystallization field of monosilicide FeSi, then in the result of primary crystallization in the section 3–3' the crystals of monosilicide are formed in the quantity of ≈33% of the melt mass. During further cooling the crystallization follows monovariant boundary curve e$_2$–u$_4$ with the appearance in the section 3'– u$_{11}$ of two solid phases – monosilicide FeSi and leboite Fe$_3$Si$_2$. Aluminum concentration in the remaining mother melt rises to 26%, and silicon concentration is
reduced to 32%. In the final invariant point of crystallization $u_4$ (35% Si, 26% Al) peritectic reaction proceeds:

$$L_{u_4} + FeSi \rightarrow FeSi_2 + Al_3Fe_5Si_2.$$  (12)

The amount of the final liquid melt of composition $t. u_4$, crystallizing at 1000°C with the initial aluminum content of 1%, is ≈7%.

During crystallization of alloys containing 55-56% Si, the composition point of which lies in the crystallization field of Leboite, for any aluminum content in the alloy (3-2% or more) the monocryalline leboite crystallization takes place, ending in the point $u_5$ according to peritectic reaction:

$$L_{u_5} + \xi \rightarrow Al_3Fe_2Si_2 + Al_6Fe_5Si_5.$$  (13)

Quantity of the finite crystallized liquid $u_5$ (35% Si, 37% Al) and, respectively, the secondary crystallized phases depends on the aluminum content in the initial melt. If the aluminum content in the alloy is ≈2%, the amount of liquid will be ≈3%.

It should be noted that the eutectoid and peritectoid reaction (5)-(7) in the presence of impurities (Al, Ca, P) proceed in the presence of a liquid phase, and the part of the stresses arising due to the increase of volume are accepted by the liquid, which leads to a significant increase of pressure, and after crystallization – to a stress concentration on the grain boundaries of matrix crystals (FeSi, FeSi$_2$, Si) and abundant desorbing phase (complex compounds with impurities).

The presence of calcium and phosphorus in the structural phases of ferrosilicon complicates the analysis, since the calcium content is by 4-5 times and phosphorus content is by 40-50 times lower than the aluminum content, the compounds proportion with calcium and phosphorus is very low and their quantitative participation in crystallization process is insignificant.

3. Conclusions

Based on the analysis of state diagrams of the systems Fe-Si and Fe-Si-Al, it is shown that the mechanism of the process of ferrosilicon disintegration is complex and depends on the alloy composition, the overheating degree, cooling rate and degree of completion of solid phase eutectoid and peritectoid reactions, relative to the amount of eutectic structures and, respectively, the area of intergrain surfaces in the crystallized mixtures, the presence of impurities, providing phase and chemical transformations in the presence of a liquid phase up to a final crystallization temperature, which is 300-400 K below the crystallization temperature of double eutectics e1 and e2, and leading to a significant increase of the amount of intergrain desorbing phases, their composition and structure.

4. References

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