THE SOLID FINE PRECIPITATES BEHAVIOUR IN FESICR SOLUTION DURING LADLE RAFINATION

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Abstract

Possibility of FeSiCr alloys production, with low content of carbon, in industrial conditions depends upon various factors like temperature of the solution, refining time, chemical compositions and others. In order to identify the evolution and behavior of solid inclusions in the solution, laboratory tests for alloys at high temperatures of 1400-1500 °C have been carried out. For identifying the trajectory of inclusions, numerical simulations, in industrial conditions, have been performed for velocity and temperature distribution in a ladle furnace. Microscopy identification of selected inclusions, important from industrial refining viewpoint, has also been performed. The paper summarizes results of theoretical calculations and laboratory tests for ultra low carbon (ULC) FeSiCr alloys.

Keywords: Metallurgy, FeSiCr-alloys, refining in ladle, numerical simulation, temperature, velocity profile

1. INTRODUCTION

The ferroalloys of the highest purity are desirable in the steelmaking processes. Hence, there are the need to manufacture ferroalloys with low carbon, nitrogen, oxygen and phosphorous content. This applies also to the ferrosilicochrome (FeSiCr) alloys. In this article, attention was paid to the analysis of the phenomenon of solid precipitates in the form of carbides in the liquid solution of FeSiCr. In industrial conditions, these alloys are produced in an arc-resistance furnace where the obtained carbon level is relatively high. The possibility of lowering the carbon content in the alloy occurs only in the refining ladle, outside the furnace [1]

The process of carbon removal in the form of carbides from the alloys as a result of refining (flotation) process enables obtaining an alloy with a very low final carbon concentration. The heterophasic analysed system forms a suspension composed of a liquid (solution of ferroalloy) and precipitates (mainly compounds of silicon and chromium, like carbides, nitrides and probably in a small amount oxides). There is little possibility of removing nitrogen from the liquid solution in the form of nitrides. However, precipitation and flotation of carbides is possible [1, 3-7].

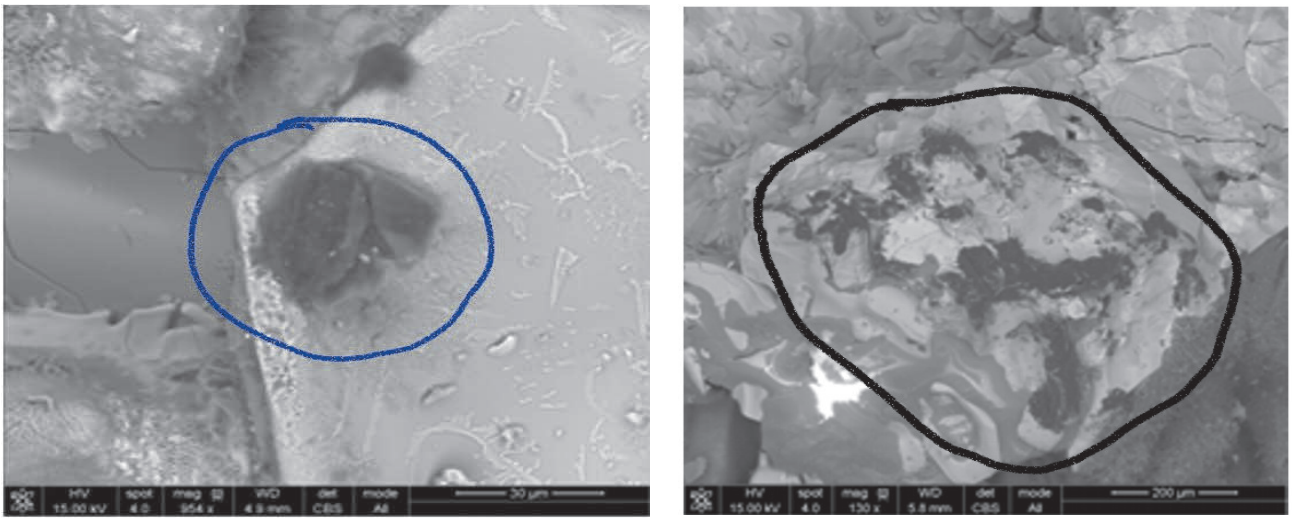
1.1. Phenomena of floating

For spherical particles $\Psi = 1$, and for non-spherical particles $\Psi < 1$. More irregular the shape of the particle lower is the value of Ψ. The value of sphericity, for particles of different shape, is given in literature, e.g. [2]. Flotation is an effective method of separating light particles from liquids in a heterogeneous system. It uses the difference in density between a particle or particle attached to a gas bubble (if gas is used) and liquid in which they are suspended. Due to this, the phenomenon of separation can occur. If agglomerates have a lower density than the medium in which they are suspended, they float up to the surface (floating), if they have a higher density - they settle down (sedimenting) [3, 6].

2. RESEARCH RESULTS

In order to identify the shape and size of solid carbide precipitates, laboratory tests were carried out for the FeSiCr solution saturated with carbon in the temperature range of 1400-1500 °C. In the first stage, the ULC alloys of FeSiCr were melted in an induction furnace in a closed graphite crucible and then the carburisation process were carried out to achieve the assumed carbon concentration. However, tests of the refining time of alloys were carried out in a resistance chamber furnace in the alund type crucibles in a protective atmosphere - argon. An alloy with a following chemical composition was used (wt. %): 46.2 Si; 34.3 Cr; 17.9 Fe; 0.114 C. Such chemical composition is similar to the composition obtained immediately after the tapping from the electric arc-resistance furnace in industrial conditions.

In the second stage, analysis of the shape and size of carbides and nitrides precipitates using the scanning electron microscope EDS (backscattered electrons BSED) was performed. A chemical analysis was also carried out at the point using the micro probe. In **Figure 1** solid carbide inclusions from the solution are presented.



a) b)

Figure 1 Image of solid carbide precipitates: a - a single particle (SiC); b - the agglomerate of solid particles of SiC

Figure 1a shows a single particle (SiC), while in **Figure 1b**, the agglomerate is in the form of clusters of individual solid particles. The solid carbide precipitates from the solution presented in **Figure 1** have the following chemical composition (wt. %): 18.15 C, 0.35 O, 0.42 Na, 0.95 Al, 78.38 Si, 0.05 P, 0.18 S, 0.97 Cr, 0.32 Fe. As can be seen from the chemical analysis presented above, there are two main elements: silicon and carbon. This proves that these precipitates are silicon carbides SiC.

The shape of a single particle as well as the agglomerate (clusters of individual particles) is rather regular, close to spherical. The size of the particles and clusters ranges from 30 μm to 200 μm.

3. CALCULATIONS

Movement of solid particles in a liquid by flotation is described by the same equation as the phenomenon of sedimentation, but with the opposite direction of forces acting on a solid particle. The basic equation used in flotation, as in processes controlled by gravity, is the Stokes law (in the laminar flow range), which is used to determine the movement intensity of bubbles, agglomerates or aggregation. The rate of movement of particle suspended in the liquid is determined by the Stokes equation (1):

$$\vec{V} = \frac{2}{9}\frac{r^2 g(\rho_{solvent} - \rho_{solid})}{\eta} \quad (1)$$

The modified equation (2), taking into account the shape of the flotating (or sedimenting) particle is as follows:

$$\vec{V} = \frac{2}{9} \cdot \frac{r^2 g(\rho_{solvent} - \rho_{solid})}{\eta} \cdot \left(0{,}843 log\left(\frac{\Psi}{0{,}065}\right)\right) \quad (2)$$

where:

Ψ - shape factor (for non-spherical < 1),
$\rho_{solvent}$ - density of liquid (solvent),
ρ_{solid} - density of solid,
η - viscosity of liquid,
r - radius of silid.

Based on equation (2) the rates of motion of solid particles in the liquid were calculated. The following assumptions have been made. The liquid in which the flotation (or sedimentation) occurs is FeSiCr solution with specific density $\rho_{solution}$ = 4.688 g/cm^3. The dynamic viscosity coefficient of the solvents varied in the range $\eta_{solvent}$ = 0.001 – 0.0023 Pa·s.

Based on the results of laboratory tests, it was assumed that precipitated from the FeSiCr solution and flowing particles are silicon, iron and chromium carbides or nitrides.

The calculations of the average time of movement of the precipitated particles were made, assuming the height of the liquid metal is 140 cm. This assumed height is also a distance used in industrial practice to overcome the considered non-metallic inclusions. Taking into account the shapes and sizes of non-metallic inclusions obtained during laboratory tests, shown in **Figures 1a) and 1b)**, the following assumptions were made for calculating the movement of particles in liquid FeSiCr:

particle shape Ψ = 0.85 – 1.0

particle diameter d = 0.004 – 0.04 cm.

In **Tables 1** there was shown the calculated values of critical flotation times (**Table 1**) and sedimentation time (**Table 2**) for solid particles precipitated from the liquid alloy of FeSiCr.

Negative values should be treated as an absolute value of the average sedimentation time; the minus sign "-" indicates only the opposite return during the particle's motion - sedimenting to the bottom of the ladle. It should be noted that the particles that will move towards the bottom (sedimenting) are mainly chromium compounds (**Table 2**) [4, 5]. Whereas flotating elements are primarily silicon compounds (**Table 1**). It is also evident that the times of descent (sediment) have time values greater than the flotation times.

Table 1 The simulation results of solid particle flotation time in liquid alloy of FeSiCr

Viscosity	„SiC"				„SiN"			
	Ψ = 0.85	0.9	0.95	1.0	Ψ = 0.85	0.9	0.95	1.0
Pa·s	Floating time (min)				Floating time (min)			
0.0010	86.49	88.41	90.23	91.89	101.95	104.21	106.36	108.31
0.0015	129.74	132.62	135.35	137.84	152.92	156.32	159.54	162.47
0.0018	155.69	159.15	162.42	165.41	183.50	187.58	191.44	194.97
0.0020	172.98	176.83	180.47	183.79	203.89	208.43	212.72	216.63
0.0023	196.96	201.34	205.48	209.26	232.16	237.32	242.20	246,66

Table 2 The simulation results of solid particle sedimentation time in liquid alloy of FeSiCr

Viscosity	„Cr3C2"				„Cr2N"			
	$\Psi = 0.85$	0.9	0.95	1.0	$\Psi = 0.85$	0.9	0.95	1.0
Pa·s	Settling time (min)				Settling time (min)			
0.0010	-104.97	-107.31	-109.52	-111.53	-60.24	-61.58	-62.85	-64.00
0.0015	-157.46	-160.96	-164.27	-167.30	-90.36	-92.37	-94.27	-96.01
0.0018	-188.95	-193.16	-197.13	-200.76	-108.43	-110.85	-113.13	-115.21
0.0020	-209.95	-214.62	-219.03	-223.06	-120.48	-123.16	-125.70	-128.01
0.0023	-239.05	-244.37	-249.39	-253.98	-137.18	-140.23	-143.12	-145.75

The exemplary results are presented graphically in **Figures 2 a) and b)**

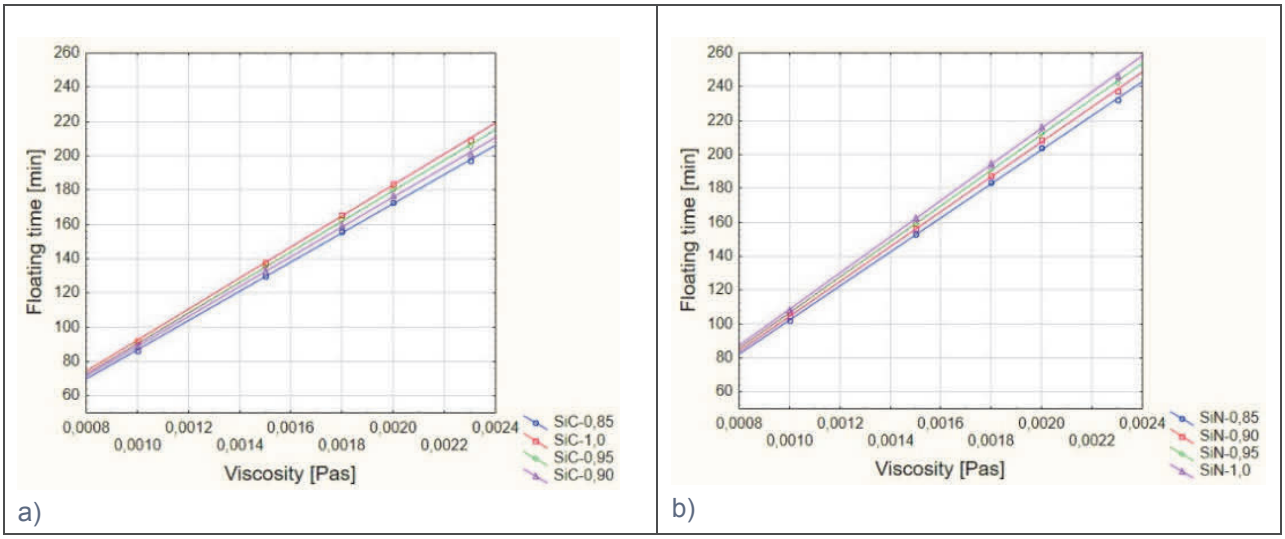


Figure 2 Change in the average time of flotation of solid particles as a function of the change in the dynamic viscosity of the solution: a) - for SiC, b) - for SiN

As can be seen from the lines shown in **Figure 2a)**, the change in the average flotation time of the inclusions depends strongly on the dynamic viscosity of the solution (solvent) from which the solid particles are precipitated. With increasing viscosity (with lowering the temperature of the liquid alloy) the time of floatation for the inclusions to reach to the surface is almost three times longer. As can also be seen, the shape of inclusions is important, but there is no such a significant change in the floatation time (the changes are from a few to several dozen minutes). One can also see the difference in floatation time depends on the type of inclusions i.e. carbide or nitride. Silicon carbide will float faster to the upper surface of liquid alloy.

From the presented test results and simulations, the mean time of floatation of solid solid particles (carbides and silicon nitrides) varies from 86 to 246 min. depending on its shapes, type and liquid (solvent) viscosity. However, the time of sedimentation is significantly different for carbides and nitrides of chromium. For chromium carbides as well as silicon nitrides - it is longer in the case of chromium nitrides and silicon carbides - it is shorter.

4. COMPUTER SIMULATION

An attempt has been made to simulate this industrial process. Usually in the industry, they leave the ladle for some time to settle/remove the inclusion after the refining process. For the same conditions, the calculations of inclusion removal have been described in the previous section. In the calculation section 3, using the simple

Stokes equation the prediction of inclusion/particle flotation/settling time is made considering the industrial ladle condition. However, that does not take into account the liquid alloy velocity which could be there due to natural convection when the ladle is left for half an hour or so to settle down the inclusions/particles. In order to know the liquid alloy velocity in the ladle, computer simulations have been carried under simplfied industrial conditions and described below.

The typical computational domain is shown in **Figure 3**. Ladle has been considered taperd in cylindrical shape with axi-symmetry having liquid (FeSiCr alloy) height 140 cm, lower radius 65 cm and upper radius 70 cm. The liquid alloy temperature at the top and bottom of the ladle has been assigned 1773 K and 1663 K respectively. For simplification, the side wall temperature condition of the ladle has been taken as an average of top and bottm temperatures of the liquid i.e. 1663 K. Standard Navier-Stokes equation for natural convection coupled with temperature equation have been considered along with the continuity equation [7]. Atmospheric pressure has been considered at the top of the liquid. Using the upwind scheme, the governing equations along with the boundary conditions have been solved sequentially using the commercial CFD solver ANSYS Fluent [8]. Stable transient solutions are obtained with relatively small time steps, typically 1×10^{-6} s. In the present model, quad-map 0.001 mm strong grid cluster was used along the central line (axi-symmetry) of ladle and grid size of 0.1 mm was used away from the central line of the ladle. The convergency criterion for continuity, X-direction and Y-direction velocity and energy were 10^{-6}.

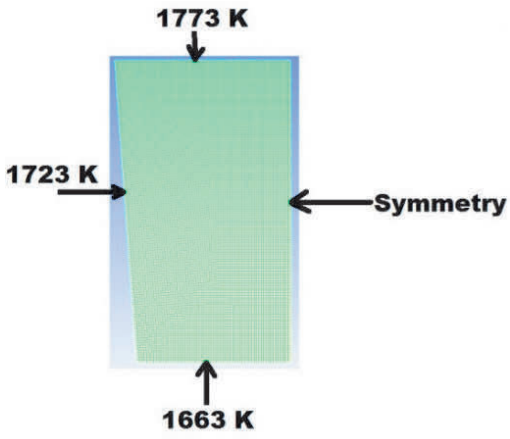


Figure 3 Computational domain with boundary conditions to simulate ladle furnace

Figure 4 shows a typical temperature distribution profile in the ladle for the given conditions. It is clear that a good temperature gradient exists within the ladle which can certainly induce the natural convection (by density difference of liquid alloy with temperature) in liquid alloy and can set the liquid in motion.

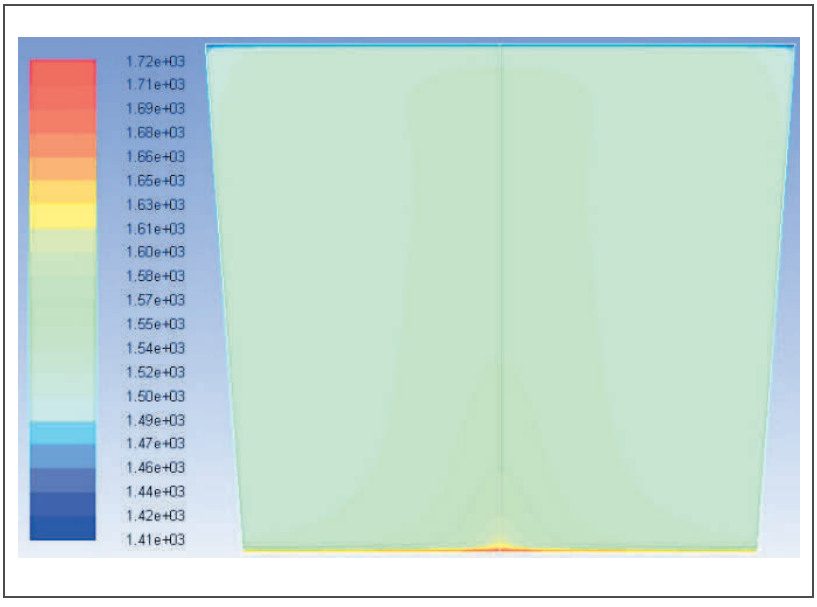


Figure 4 Liquid alloy temperature distribution (K) in the holding ladle.

Figure 5 shows the velocity profiles of the liquid alloy FeSiCr in the ladle. Indeed, one can clearly see that at some locations, the liquid velocity has reached upto 15 cm / s which is quiet substantial. Therefore, Stokes equation will not be able to give the correct time of removal of inclusions/particles in the ladle. In order to get the correct settling time one has to take into account the liquid motion inside the ladle.

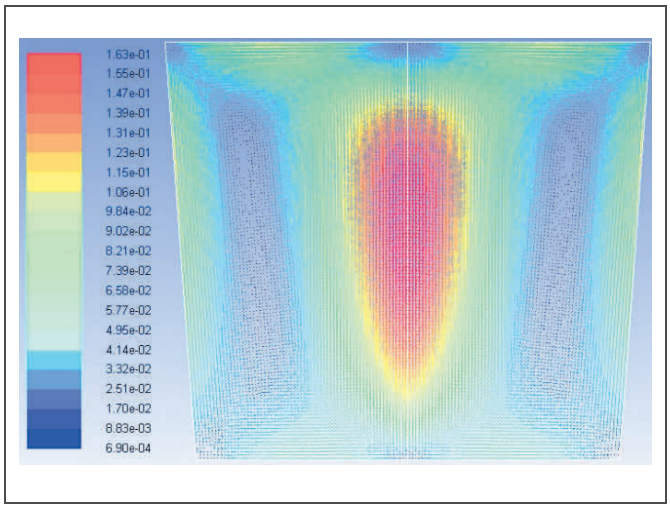


Figure 5 Liquid alloy velocity distribution (m/s) in the holding ladle

Depending upon the location of the inclusions inside the ladle, the liquid motion either can assist its removal in less time than predicted by Stokes equation or may retard its motion/removal and may thus increase the removal time. This point is illustrated in another simulation where particle trajectory has been captured using Lagrangian Particle Tracking Method [8], which solves a transport equation for each inclusion as it travels through the previously-calculated constant liquid alloy flow field. The following properties of the liquid alloy have been considered in this simulation: viscosity = 0.001 Pa s; denstiy of SiC = 3.217 g / cm^3; diameter of SiC inclusion = 0.04 cm and spherecity = 1.

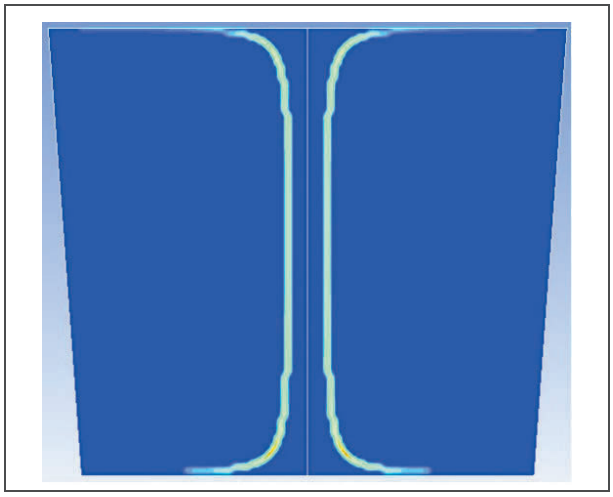


Figure 6 Typical SiC inclusion trajectory in the holding ladle

Results are shown in **Figure 6**. Particle/ inclusion is injected closer to the bottom (in the medium liquid velocity region) and is carried away by liquid towards the top. In this condition, liquid is assisting inclusion to float and brings it up at the top. Total time it takes is about 82s (1.37 min). Time predicted by Stokes equation under the similar condition is about 100 s (1.67 min) which is about 20 percent higher than the simulated results. This is due to ignoring the effect of liquid motion.

5. SUMMARY

As results from the obtained test results and simulations, solid particles or their agglomerates with the smallest diameter can flow to the surface of the solution, exceeding the real time of the technological operation. The largest solid particles, separated or coagulated, need significantly less time to float. Medium size particles have a chance to float to the surface depending on the temperature, chemical compositions and dynamics of the system. The smallest particles are not able to flow up by gravitation from the liquid under the described conditions and will remain in the liquid. Simplified computer simulation results, under the industrial condition, show that when the ladle is in holding position in case refining operation the would be substantial liquid motion inside the ladle due to natural convection effect. This can influence the inclusion floating or settling time substantially and must be taken into account when deciding for the holding time of ladle to minimize amounts of the solids/particles.

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