Effect of Thermal History and Internal Stresses on Disintegration of Ferrosilicon

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Abstract

Disintegration of ferrosilicon has been quantified in tumble tests for material produced by different casting methods. Thickness of casting and cooling method were found to have a strong effect on the abration index. By casting thinner and using water spray cooling the abration index can be decreased by at least 30%. Eshelby model calculations of internal stresses in ferrosilicon caused by volume changes associated with phase transformations and thermal mismatch have been carried out. These mechanisms can cause high tensile stresses in unrelaxed model systems. In commercial materials, relaxation processes like cracking act to reduce the high stresses. The implications of these results are discussed in the context of how the undesirable disintegration and generation of fines in ferrosilicon can be minimised.

1. Introduction

Disintegration of silicon rich ferrosilicon alloys is a problem that has concerned the manufacturers and users of this product throughout the history of the industry. The problem can arise from directly acting on the material by handling or crushing, from processes taking place in the material such as phase transformations and thermal misfit on cooling, or a combination of the two. Both phenomena can cause unwanted generation of fines with the consequences of financial losses for the manufacturer and inconveniences for the user. In addition, the storage and transportation of ferrosilicon has often been accompanied by evolution of poisonous and explosive gases which resulted in numerous accidents in the first half of this century. Early investigations showed that these problems arose with alloys in the range 33-100 weight % Si, but alloys in the range 53-57% Si were most susceptible. The ς - phase or "Lebeauite" (now called α - phase) has a composition of 53.5 - 56.5% Si and experimental work done in the 1950's and 1960's focused on this phase and how it is related to disintegration. Phase transformations occuring in the α phase are accompanied by considerable volume changes [1] and substantial differences are between coefficients of thermal expansion for the phases in ferrosilicon [2]. Both phenomena were identified early on as potential causes of disintegration. Several other factors directly or indirectly influence the undesirable crumbling and generation of fines. In this paper we present experimental and theoretical work on some aspects of the disintegration process. In section 2 we report on experiments carried out to quantify the disintegration of ferrosilicon produced by different casting methods. Calculations of the magnitudes of internal stresses caused by phase transformations and thermal misfit are presented in section 3. We discuss the implications of the results and how they can be used to minimise the undesirable disintegration and generation of fines.

2. Quantification of disintegration of ferrosilicon

It is well known that disintegration of ferrosilicon is to a great extent determined by thermal history. In an effort to characterise the production process at the Icelandic Alloys Ltd. plant at Grundartangi, Iceland, the effect of thermal history on the microstructure of the material has been studied [3, 4]. The temperature of the ferrosilicon was measured during sample and carousel casting and, subsequently, the resulting average size of Si grains in the material measured. Three main classes of cooling rates were identified; on the one hand, rapidly cooled small samples and on the other hand, slowly cooled and water cooled material cast in the carousel. The results for the average grain size as a function of cooling rate are summarised in fig. 1, which shows that a higher cooling rate results in a smaller average grain size. To measure the direct effect of thermal history on disintegration of ferrosilicon, it is best to imitate the handling of the material after solidification. For that purpose, tumble tests are convenient for quantifying the disintegration. The method used here is based on ASTM Standard C131-66, but the dimensions of the barrel were changed slightly for practical reasons. Dry ferrosilicon ingots with a known thermal history were crushed and 10 kg of the material (mass before testing, M_B, see eq. 1) with a size distribution of 25-75 mm selected for the

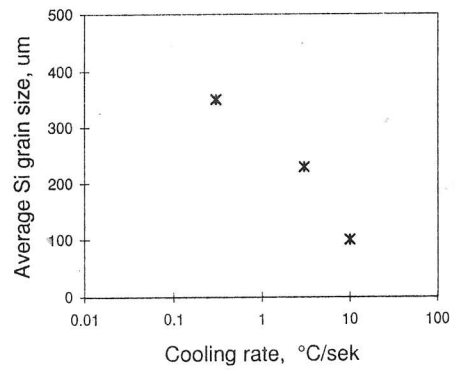

Fig. 1. Average size of Si grains in commercial ferrosilicon with 75 weight % Si, shown as a function of cooling rate. The average Si grain size was determined by the line intersection method.

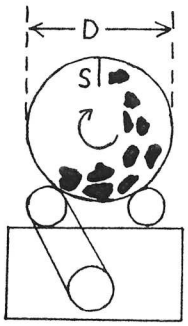

Fig. 2. A schematic diagram of the experimental set-up used in the tumble tests. The barrel diameter (D) and length is 35 cm and 55 cm respectively and the height of the shovel (S) is 5 cm. During the test, the barrel rotated at a rate of 30-33 rpm. This type of tumble test is often called the "Los Angeles" test.

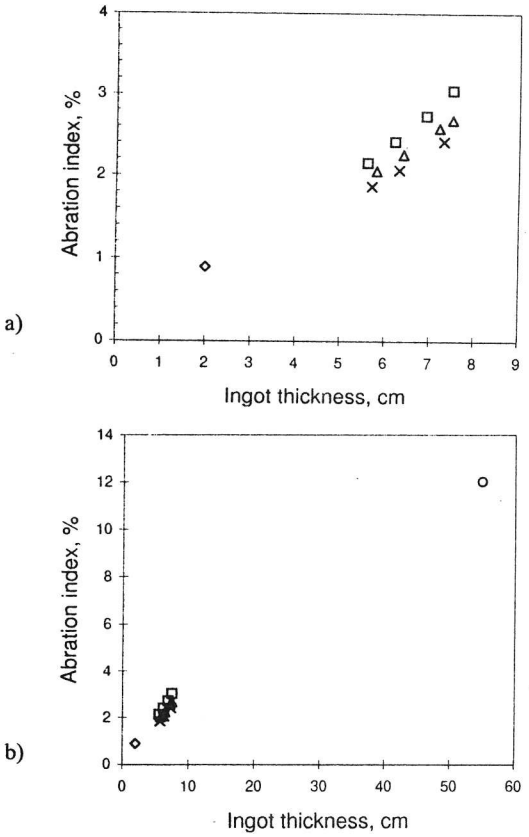

Fig. 3. The abration index measured in tumble tests. a) Results for the thinner castings, showing two classes of materials. The rapidly cooled small samples (thickness 2 cm) have the lowest abration index. Typical factory products have thickness between 5.5 and 7.5 cm and three cooling methods were used. 1) slow cooling (boxes), where the material solidifies and cools down without any additional cooling, 2) water cooling (triangles), where water is added from a hose to the top of the ingots and 3) water spray cooling (x-es), with water being sprayed over the ingot. b) Results for the whole range of ingot thicknesses. Material from a 55 cm thick slowly cooled bed (circle) has by far the largest abration index.

test. The tumble barrel (see fig. 2) rotated at a rate of 30-33 rpm for a total of 1000 turns. Material with dimensions under 8 mm was then separated and weighed, giving a measure of the mass after testing with dimensions larger than 8 mm (M_A). The abration index, A, can then be found

$$A = 100\frac{M_B - M_A}{M_B} = 100\left(1 - \frac{M_A}{M_B}\right) \quad (1)$$

Samples were taken from 20 ingots cast in the carousel, of which 12 had a well characterised thermal history. Emphasis was placed on testing ferrosilicon from typical factory products, i.e. from ingots of thickness 5-8 cm. Rapidly cooled small samples (2 cm thick) and material from slowly cooled large beds (55 cm thick) were also tested. The results of all the tests are shown in fig. 3, which gives the abration index as a function of thickness of casting. The abration index increases with thickness of casting and therefore, with grain size (thicker castings have lower cooling rates and larger average grain sizes, see fig. 1). The results fall into three groups. First, the thinnest casting, which also has the lowest abration index. Second, the material cast in the carousel, showing the effect of casting thickness and cooling method on the abration index. For these two groups the thermal history and average grain size are known (see fig. 1). However, we point out that because the shapes and sizes of the rapidly cooled samples are different from the other material, care must be exercised in comparing the data. Third is the material cast in large beds, which has by far the largest abration index. Of particular interest here is the material cast in the carousel, with thickness 5-8 cm. The bulk of the ferrosilicon produced at the factory at Grundartangi is in this category. Referring to fig. 1, for a given thickness, the ingots which solidify and cool down without water cooling (boxes) have the largest abration index. The water cooled ingots (triangles) have a lower abration index and the ingots cooled by water spray (x-es) have the lowest abration index. The decrease in each step is about 10-15%. It is also interesting to note how strongly the ingot thickness affects the abration index. As an example, a 7 cm thick slowly cooled ingot has an abration index of about 2.75%. Cooling with water spray can decrease the abration index to about 2.30%, but 1 cm thinner casting has the same effect. Compared to the worst case in this group, the abration index can be reduced by about 30% by casting with 5.5 cm thick ingots and using water spray cooling. By casting yet thinner ingots the abration index could be reduced even further.

The results presented here clearly show how the casting and cooling methods affect the microstructure of the material and, thus, the abration index. A higher cooling rate results in a smaller average grain size, giving a stronger material with a lower abration index. In the next section we turn our attention to another phenomenon relating to the microstructure, that is, how internal stresses can build up in the material and the role they play in the disintegration process.

3. Internal stresses in silicon rich ferrosilicon.

Several factors have been observed to influence disintegration in ferrosilicon directly or indirectly and other factors have been suggested as possible culprits in the disintegration process [5, 6, 1, 2, 7]

1. Presence of impurities and gases, e.g. Al, Ca, P, H_2, N_2, CH_4.
2. Humidity.
3. Chemical reactions.
4. Grain size (cooling rate, tapping temperature).
5. Temperature gradients in ingots.
6. Anisotropic thermal expansion of grains.
7. Mismatch in thermal expansion between phases.
8. Volume changes caused by phase transformations.

How the first three factors on this list affect disintegration is beyond the scope of this paper. Grain size has a strong influence of the production of fines in ferrosilicon as experimentally demonstrated in section 2. The total area of grain boundaries in large grained slowly cooled material is much smaller than in fine grained, rapidly cooled material. Pressure because of impurities and gases is therefore higher in coarse grained ferrosilicon, making it more susceptible to disintegration. In coarse grained material the local areas of high stress concentration around inclusions are also larger and it is more likely that the areas of high stress concentration will contain flaws or weaknesses, thus leading to crack formation. The cracks which form will also be larger than in a fine grained material. Temperature gradients in ingots can be considerable, but they are more likely to cause macroscopic cracks in and through the ingots, rather than being a direct cause of disintegration. Anisotropy in coefficients of thermal expansion of the grains can cause stresses in the material but experimental data for such anisotropy is lacking.

Measurements of coefficients of thermal expansion for the various phases (α, β, ε, Si) have been made (see e.g. references in [2]) and data on the volume expansion associated with phase transformations is now also available [1, 2]. Using that data it is possible by model calculations to estimate the magnitude of internal stresses in unrelaxed model systems caused by phase transformations and temperature changes.

3.1. Internal stresses induced by phase transformations.

According to the equilibrium phase diagram, the α phase decomposes into β and Si at 955-970°C, $\alpha \rightarrow \beta + Si$ (e.g. [8, 9]). There are indications that this phase transformation proceeds in two stages [7, 10]

(i) $\alpha \rightarrow \beta(Si)$
(ii) $\beta(Si) \rightarrow \beta + Si$

Dilatometric studies by Holdhus [1] on pure ferrosilicon have shown that the phase transformation is accompanied by relatively large volume changes. Boomgaard [7] suggested that the volume changes take place after the first step, when the β phase, saturated in Si, is formed. Later experimental work [10-13] has shown that a solid state reaction in the α phase takes place on cooling, forming a new phase, β(Si), with different optical properties than the α phase [11], but without the equilibrium structure of Si rods in a β matrix. This supports the two stage model and raises questions about whether the large volume changes and associated high stresses can act as a barrier and obstruct formation of the equilibrium structure of β and Si. The greatest change in length observed by Holdhus [1] in an alloy with 56.6 weight % Si (i.e. α phase) and for that alloy the expansion in length on cooling was found to be 0.6% (corresponding to a volume increase of 1.8 %). Calculations by Espelund [2], based on the known densities of the phases, show the expected linear contraction to be about 1%, which is somewhat larger than the measured contraction. By using a model based on the Eshelby method of internal stress determination it is possible to calculate the mean stress arising from volume changes associated with phase transformations (for overviews of the Eshelby method, see e.g. [14-17]). The model material used in the Eshelby method calculations consists of ellipsoidal inclusions with a given aspect ratio and a certain inclusion volume fraction, embedded in a matrix of a material with a different stiffness. We adopt the Nye notation [18] in which strain is expressed as a 1×6 vector and stiffness as a 6×6 matrix (e.g. [17]). Fig. 4 shows schematically the morphology used here in model calculations of stresses resulting from volume changes associated with phase transformations. The phase transformation proceeds in spherical regions which are randomly distributed throughout the matrix of α phase. The volume fraction of transformed regions is f, which is zero in the beginning and increases as the phase transformation proceeds. The volume change associated with the phase transformation is described by a transformation strain

$$e^{T*} = e_L(1, 1, 1, 0, 0, 0) \quad (2)$$

where e_L is the linear expansion. The mean stress in the matrix can then be expressed as (e.g. [14, 15])

$$< \sigma >_M = A(f)\, e^{T*} \quad (3)$$

with

$$A(f) = f(S - I)\left[(C_M - C_I)(S - f(S - I)) - C_M\right]^{-1} C_M C_I \quad (4)$$

f is the inclusion volume fraction, C_M and C_I are the stiffness matrices for the matrix and inclusion, respectively, S is the Eshelby tensor and I the identity matrix (C_M, C_I, S and I are 6×6 matrices). The Young's modulus for the α, β and Si phases are 130 GPa, 205 GPa and 112 GPa, respectively [2]. The Poisson's ratio for Si is 0.44 [19] and a value of 0.4 was assumed for the α and β phases.

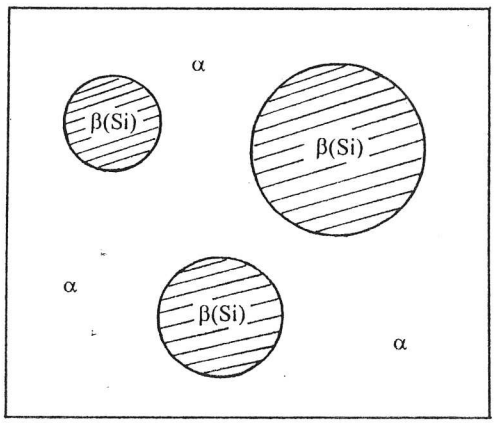

Fig. 4. A schematic diagram of the morphology used in model calculatioins of stresses resulting from volume changes associated with phase transformations in the α phase. Spherical regions, randomly distributed in the α matrix, transform into β(Si), which results in a strain misfit e^{T*}. As the transformation proceeds, the spherical regions of β(Si) grow and their volume fraction increases, but they maintain their spherical shape.

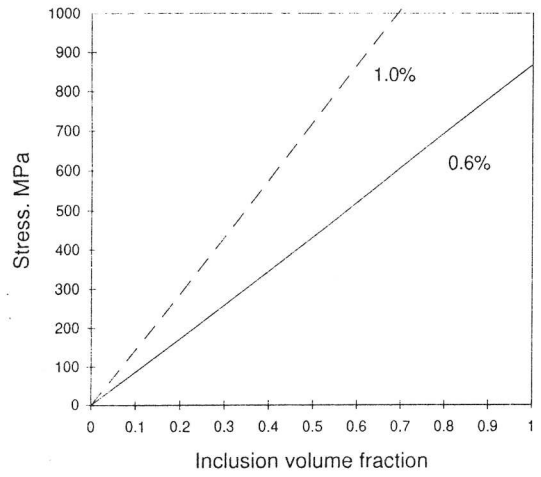

Fig. 5. Calculated tensile mean stress, $\langle\sigma\rangle_M$, in the α matrix, resulting from a linear strain misfit of 0.6% and 1.0%. The transformed regions are spherical (see fig. 4) and their volume fraction increases from zero as the transformation proceeds.

Upon cooling, the phase transformation results in a volume increase of the transformed regions [1]. This causes a compressive stress in the inclusions, which is balanced by a tensile stress ($\langle\sigma\rangle_M$) in the α matrix. Any crack formation would therfore be expected to take place in the α matrix. This conclusion is in agreement with the observation of several researchers that in disintegration of ferrosilicon, cracks form in the α phase [10, 11]. Calculations for the mean matrix stress are shown in fig. 5. The two curves are for a linear expansion of 0.6% and 1.0%, which are the measured and calculated values of linear expansion, respectively. When 30% of the matrix has transformed, the mean tensile matrix stress is expected to be between 275 and 460 MPa and when 40% has transformed, between 360 and 610 MPa. We point out that because the inclusions are assumed to be spherical, the mean tensile matrix stress is hydrostatic. In commercial materials the transformed regions are rarely spherical.

3.2. Internal stress induced by temperature changes.

When the temperature of a composite is changed, a misfit is generated between the shape of the inclusion and the hole in the matrix in which it sits. The resulting strain mismatch between inclusion and matrix can be represented by the transformation strain as (e.g. [14, 15])

$$e^{T*} = (\alpha_M - \alpha_I)\Delta T \qquad (4)$$

ΔT is the temperature change and α_M and α_I are the coefficients of thermal expansion for the matrix and inclusion, respectively, with

$$\alpha_M = \alpha_M(1, 1, 1, 0, 0, 0) \qquad (5)$$

Coefficients of thermal expansion for the different phases in silicon rich ferrosilicon have been measured [20, 2] and the values relevant to this discussion are reproduced here below

$\alpha_{Si} = 2.7 \cdot 10^{-6}/°C$
$\alpha_\alpha = 8.3 \cdot 10^{-6}/°C$
$\alpha_\beta = 7.7 \cdot 10^{-6}/°C$

For the composite system shown in fig. 6, the mean matrix stress induced by the temperature change can be calculated by eqs. 3-6 and the results are shown in fig. 7. For ferrosilicon with 75 weight % Si, the volume percentage of the Si phase lies between 55 and 60%. That alloy solidifies at about 1207°C and cools down by about 1200°C to the ambient temperature. During cooling it is likely that some plastic relaxation of internal stresses can take place in the first few hundred degrees after solidification. However, it is clear that at lower temperatures, say below 500 - 600°C, plastic

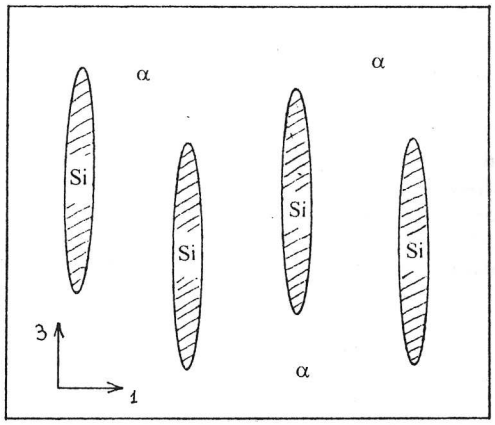

Fig. 6. Randomly distributed ellipsoidal Si inclusions in an α matrix. In the calculations, the inclusions all have the same shape and the same aspect ratio (length/diameter) of 10 and , thus, the same S tensor.

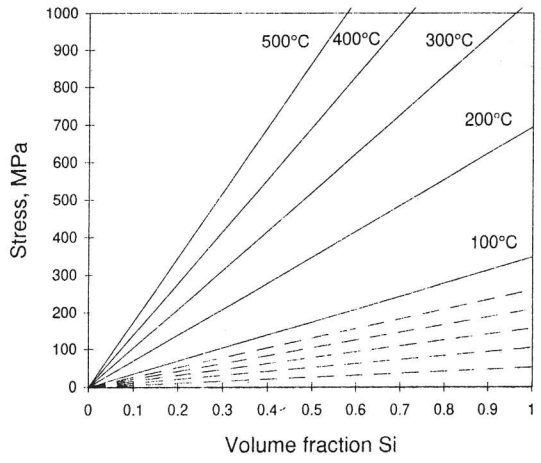

Fig. 7. The tensile mean matrix stress, $\langle\sigma\rangle_M$, in the α matrix resulting from a thermal misfit between the α matrix and the Si inclusions. The whole lines are calculations for the stress component in the 3 direction, $\langle\sigma_3\rangle_M$ (see fig. 6), and the temperature change ΔT is shown for each curve. The broken lines represent the $\langle\sigma_1\rangle_M$ transverse component (which is identical to $\langle\sigma_2\rangle_M$), with inverted sign. The lowest broken curve is for ΔT = 100°C and the highest for ΔT = 500°C.

relaxation is minimal. The calculations show that in unrelaxed model materials, a temperature difference of only 300°C gives rise to a tensile mean stress in the matrix of about 600 MPa. We point out that thermal misfit of the kind discussed here does not contribute to internal stresses in ferrosilicon with 56.6% Si by weight, which consists only of α phase. However, the tendency of ferrosilicon to disintegrate is known to be most pronounced in alloys of that composition, showing the importance of the phase transformation in the disintegration process.

In summary, the calculations have shown that both phase transformations and temperature changes can cause quite considerable tensile stresses in the α matrix of an unrelaxed model system. In commercial materials, the build-up of internal stress is limited by relaxation processes which act to reduce the stress. It is not known what is the nature of the bonding between the α and Si phases and data for the toughness of α is not available. However, several observations of the microstructure of ferrosilicon (e.g. [10, 11]) have shown that at room temperature, cracks appear only in the α phase. In view of the calculated high stresses caused by phase transformations and thermal misfit, it is likely that these mechanisms are the most important causes of internal stresses in this material. Presence of impurities and gases, humidity and chemical reactions are therefore elements which accentuate the problem rather than being primary causes. We point out that nature's design of both the phase transformation and coefficients of thermal expansion results in high *tensile* stresses in the α phase at room temperature. This, and the apparent low toughness of the α phase are probably the main reasons for the propensity of ferrosilicon to disintegrate.

In the light of these results it is clear that the most effective means of reducing disintegration of ferrosilicon is to increase the cooling rate of the material. This can be achieved by thinner castings, using water spray cooling and keeping the temperature of the molten ferrosilicon as low as possible, immediately before casting. Efforts to decrease the level of impurities and gases in the material and measures to decrease the level of air humidity can possibly decrease disintegration but such measures may be difficult in practise and their effect has yet to be quantified.

4. Conclusions

1. Correlation of temperature measurements during casting of silicon rich ferrosilicon and resulting grain sizes have shown how the average grain size decreases with increasing cooling rate during and after solidification.

2. Tumble tests on ferrosilicon have shown how strongly thermal history of the material affects the abration index. Thinner castings and water cooling result in a stronger material and less abration and disintegration.

3. The mean internal stress caused by volume changes associated with phase transformations was calculated for an unrelaxed model material. Upon cooling, the phase transformation results in a volume increase, which causes a compressive stress in the transformed regions. This compressive stress is balanced by a tensile stress in the brittle α matrix. The calculations show that when 40% of α has transformed to β(Si) in an unrelaxed model material, the tensile stress in the α matrix is between 360 and 610 MPa.

4. The mean internal stress caused by temperature changes was calculated. In an unrelaxed model system of a typical ferrosilicon product, with 75% Si by weight, a temperature difference of only 300°C gives rise to a tensile stress in the α matrix of about 600 MPa.

5. The high tensile stresses in the α matrix caused by phase transformations and thermal misfit are reduced by stress relaxation processes such as cracking of the brittle α matrix. The high tensile stresses and the apparent low toughness of the α matrix are probably the main reasons for the propensity of ferrosilicon to disintegrate.

6. The most effective measure to decrease disintegration in ferrosilicon is to increase the cooling rate of the material during and after solidification. Substantial reduction in disintegration can be achieved by thinner castings, water spray cooling and keeping the temperature of the molten ferrosilicon as low as possible, immediately before casting.

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