Phase Stability in Silicon Rich Ferrosilicon

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Abstract

The phase stability of silicon rich ferrosilicon has been investigated with both high and low temperature Mössbauer spectroscopy. With the aid of room temperature Mössbauer spectroscopy a ttt-diagram was made for the eutectoid phase transition between the α and β beta phases in commercial 75%FeSi.

High temperature Mössbauer spectroscopy has been used to follow the α - β transformation by a time sequence of Mössbauer spectra at a fixed temperature around 800 K. The effect of aluminium impurities has been studied.

Studies with Scanning Electron Microscopy indicate that the β phase is not formed in a normal eutectoid transformation but by first forming a metastable phase in diffusion less transformation. The metastable phase has the same chemical composition as the α phase but shows the characteristics of β in Mössbauer spectroscopy.

Introduction

Ferrosilicon has been produced and used as a deoxidant for steel and an addition to cast iron for over a hundred years, but still realtively little is known about its physical properties. It was not until after 1950 that it was realised that iron disilicide or the so-called ζ phase occurs in two forms, termed α and β as shown on the phase diagram in figure 1. The eutectoid phase transformation between the high temperature α phase and the low temperature β phase has been of interest because of the believed effect on disintegration of commercial ferrosilicon.

The α phase is formed on solidification and is a non-stoichiometric metallic phase. The structure is tetragonal, each unit cell has two Si sites and one Fe site but the Fe site is not always occupied [2, 3]. The chemical composition is Fe_xSi_2 where x is in the range 0,77 - 0,87. The phase is optically anisotropic. The α phase is stable only at temperatures above 937°C [4]. Below that temperature the phase decomposes into Si and the low temperature β phase by the reaction

$$\alpha \longrightarrow \beta + \mathrm{Si}. \qquad (1)$$

The β phase is different from the high temperature α phase. The phase is stoichiometric which chemical formula $FeSi_2$, that is with 66,67at% Si or 50,14wt% Si. The structure is orthorhombic with 48 atoms per unit cell. In the presence of the FeSi phase β can be formed at higher temperature, or 982°C [4], by the peritectic

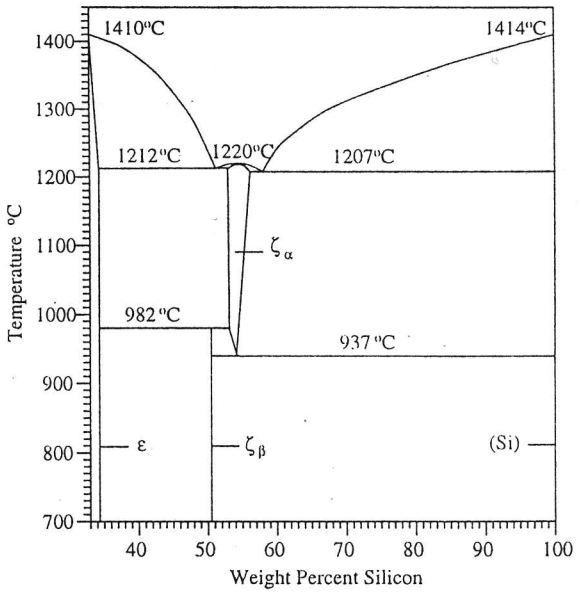

Figure 1: The Fe-Si phase diagram redrawn after Massalski: Binary Alloy Phase Diagrams [1].

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reaction

$$FeSi + \alpha \longrightarrow \beta. \quad (2)$$

The exact mechanism of the eutectoid reaction is not fully understood and Boomgaard [5] has suggested that the reaction take place in two steps. The first step is transformation of α into β supersaturated with Si followed by Si precipitation to form eutectoid particles.

$$\alpha \longrightarrow \beta_{(sat)} \quad (3)$$

$$\beta_{(sat)} \longrightarrow \beta + Si \quad (4)$$

Tveit [6] has by observing cooling rates experimentally verified that there are two reactions connected to the transformation.

Sigfusson and Helgason [7] have published a time temperature transformation (ttt)- diagram for pure ferrosilicon of the α composition. They found that the final transformation goes fastest at about 720°C. Sigfusson et al. also found that samples with 75 % Si showed much faster initial eutectoid decomposition but the time for the final reaction was similar to pure α phase. They agree with Boomgaard that the eutectoid transformation seems to take place in two steps.

In this work Mössbauer spectroscopy was used to study the rate of the phase transformation from α to β. A ttt-diagram was constructed for commercial refined 75% ferrosilicon and the transformation rates were compared with unrefined material. The effect of aluminium impurity on the rate of the transformation has been investigated by comparing transformation of a binary Fe-Si sample to a sample doped with 1% aluminium. At last some Scanning Electron Microscope investigations were done in order to study further the mechanism of the transformation from α to β.

Experimental

Sample preparation

Two types of samples were used in this work; commercial samples and laboratory samples made from pure materials. There were two commercial samples of 75% ferrosilicon provided by Icelandic Alloys Ltd., one refined and the other unrefined. The chemical composition of the commercial samples is given in table 1. The ferrosilicon was cast in 7-12 cm thick layers in the factory and sprayed with water between the layers. From previous measurements made on the factory floor, the cooling rate from solidification down to 900°C was estimated between 100 and 200°C/min [8].

The laboratory samples were binary Fe-Si samples, made from +99.8% iron and 99.9999% silicon. The materials were melted together in an alumina crucible in an induction furnace under argon atmosphere. Small amount of aluminium was added to one of the samples. The composition of the samples is given in table 2.

Table 1: Composition of the commercial samples.

Element	Commercial Samples	
	Refined (%)	Unrefined (%)
Fe	23.4	23.4
Al	0.41	1.11
Ca	0.031	0.13
C	-	0.04
Si	balance	balance

Table 2: Composition of pure samples.

Sample	%Al	%Si	Fe/Si ratio
#1		75.03	
#2		54.93	
#3	1.05	54.43	55.00/45.00

The Mössbauer technique

Useful reference books on Mössbauer spectroscopy are available [9, 10, 11] and the experimental procedure in this work has been described in detail [12]. Only a brief description will be given here.

In Mössbauer spectroscopy the sample is subject to γ-radiation, in this case radiation from ^{57}Fe. An absorption spectrum is recorded as a function of the velocity of the source. The energy of the γ-ray that the sample experiences will vary with the velocity of the source because of the Doppler effect. In this way it is possible to record changes in absorption of the sample as a function of very small changes in the energy of the radiation. The ^{57}Fe nuclei are responsible for the absorption and of natural iron about 2.2% is the ^{57}Fe isotope. The absorption spectrum depends on the geometrical environmen of the iron nucleus and each phase has its characteristic spectrum. A schematic experimental set-up is shown in figure 2. In material like ferrosilicon where practically all the iron rests either in the α or the β phases this is used to tell how large fraction of the iron atoms rest in each phase and thereby to tell the fraction of each phase. Sigfusson and Helgason have described this in previous papers [7, 13].

Measurements with high temperature spectrometer. In the high temperature spectrometer the sample was kept in a furnace while measured. The furnace is made of aluminium and has a two dimensional elliptical inner shape. Figure 3 depicts the furnace

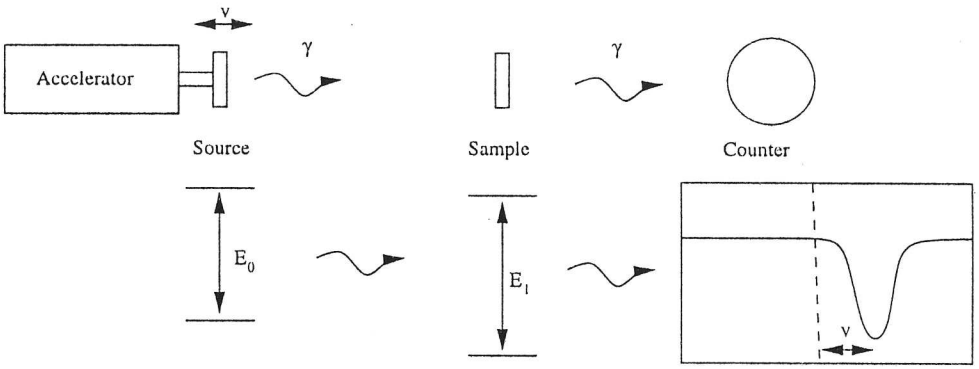
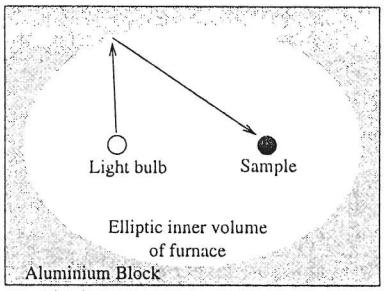


Figure 2: Mössbauer spectrum obtained by Doppler shift in emitted energy from the ^{57}Fe source. E_0 is the energy of the radiation from the source but E_1 is the energy that the sample experiences.

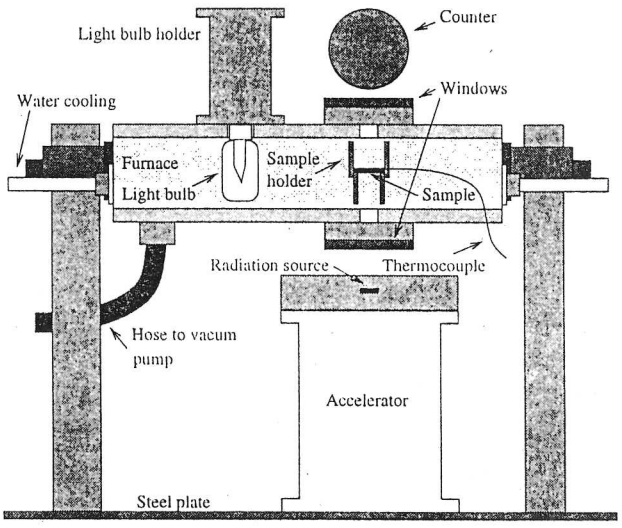
schematically. The sample holder is placed in one focal point and a halogen light bulb in the other. The inner surface of the furnace reflects the light from the light bulb to the quartz sample holder, which is warmed up. A K-type thermocouple is led into the sample holder and is in direct contact with the powdered sample, which is held between two BeO plates. With a power regulator the temperature on the samples was kept constant with a variation of less than 1°C and the pressure was kept at 0.002–0.008 torr while measuring at high temperatures. The aluminium block was water cooled to increase the lifetime of the light bulb. Further information on the furnace can be obtained from Helgason et al. [14].

By the high temperature Mössbauer spectrometer it is possible to follow the phase transition between α and β "in situ", that is, to continuously measure the fraction of each phase while the transition occurs.

The room temperature spectrometer. The room temperature spectrometer is a separate unit from the high temperature spectrometer and does not have the possibility of annealing the sample while measuring. For measurements at room temperature the sample was put in a small, flat box. Boron nitride was added to fill the box so the sample would not slide to one corner. The amount of 75% Fe–Si sample used was 40–60 mg/cm^2, which gave 8–12% absorption.



(a) View from above of furnace



(b) Overview of the system

Figure 3: The high temperature Mössbauer spectrometer.

Results and Discussion

Transformation rates of commercial 75% FeSi

The rates of transformation from α to β were measured for both refined and unrefined samples with the room temperature Mössbauer spectrometer. Refined commercial samples were annealed at different temperatures and for a various time periods. The samples were then taken out of the furnace and crushed in chrome steel crusher.

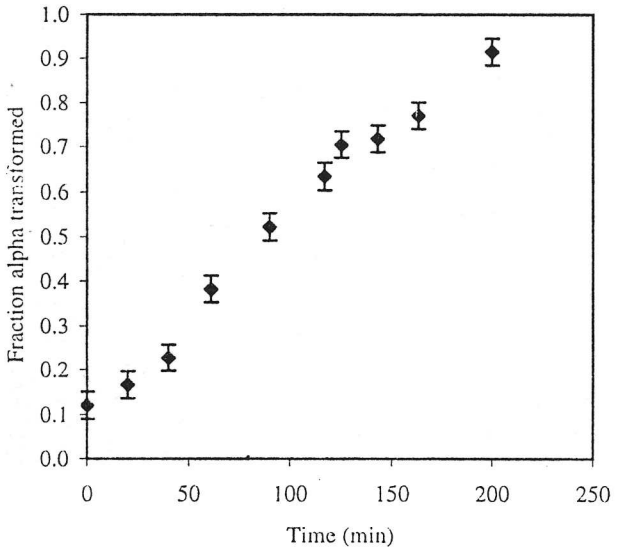


Figure 4: The figure shows the fraction of the α phase that has transformed as a function of annealing time at 700°C. The samples are taken from refined commercial 75% ferrosilicon, initially with 12% of the α phase transformed into β.

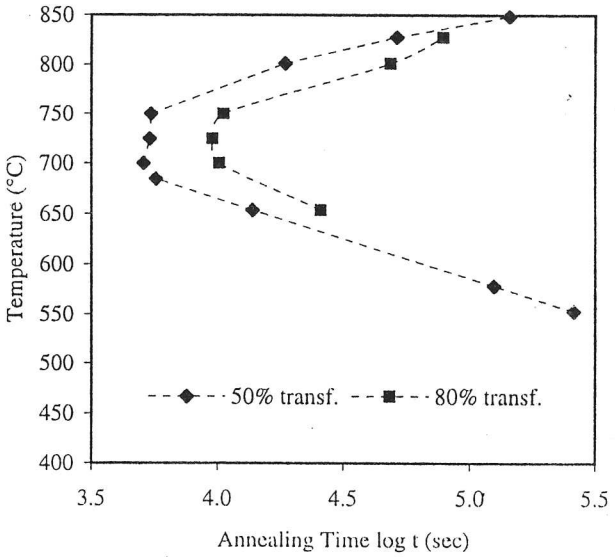


Figure 5: ttt-diagram for refined 75% ferrosilicon where 12% of the α phase had initially transformed.

From the fit of the Mössbauer spectra an estimate of the α/β ratio was obtained.

Initially 12% of the α phase had transformed as a result of slow cooling in the ferrosilicon plant. The estimated accuracy in phase composition is $\pm$ 3% and the accuracy in annealing temperature is estimated to be $\pm$ 5°C.

A typical series is shown in figure 4. The figure shows the fraction of the α phase that has transformed into β as a function of annealing time at 700°C. In figure 5 the results are shown in a ttt-diagram. Two lines are shown in the diagram, the line for 80% of the α phase transformed and the line for 50% of the α phase transformed. The figure shows that the rate of transformation is fastest at 700-750°C and decreases fast outside that interval. According to the phase diagram the temperature at which α and β are in equilibrium is 937°C. When the temperature is close to the equilibrium temperature the driving force for the transformation is small and the transition goes therefore at a slow rate. At temperature well below 937°C the undercooling is larger and the transition goes faster. But when the undercooling becomes to large, diffusion of atoms becomes the limiting factor and the transition again slows down.

To investigate the effect of refining on the rate of transition between α and β, measurements were made on the rate of transformation for unrefined 75% ferrosilicon. Only one annealing temperature was used, or 720°C. Measurements were performed in the same manner as for the refined samples as described before. The results are shown in figure 6. As seen in the figure the transformation goes much faster in refined than in unrefined ferrosilicon. This is in agreement to the general opinion that particles and solute impurity atoms slow down transformation rates.

'In situ' rate measurements

'In situ' measurements were made in the high temperature spectrometer, the samples were kept at a constant temperature and spectra were collected automatically every three hours. To obtain sufficient quality it was necessary to add spectra, usually two or three together. For comparison, measurements were made in order to investigate the effect of aluminium impurities on the rate of the $\alpha \rightarrow \beta$ transformation. The annealing temperature was 535°C. The composition of the samples is shown in table 2. Samples #2 and #3 have approximately the same Si/Fe ratio , 55/45 which corresponds to the silicon rich limit of the α phase. Figure 7 shows the fraction of the α phase that has transformed as a function of annealing time. Almost no difference is seen between the rate of transformation of samples #1 and #2 which is not surprising as the only difference between the two samples is the silicon content. However it is surprising that the transformation goes faster in sample #3 which contains about 1% aluminium. The difference in rate is not large, but detectable. This is of special interest in view of figure 6. The figure shows that in commercial 75%FeSi the transformation goes faster in refined material than in unrefined.

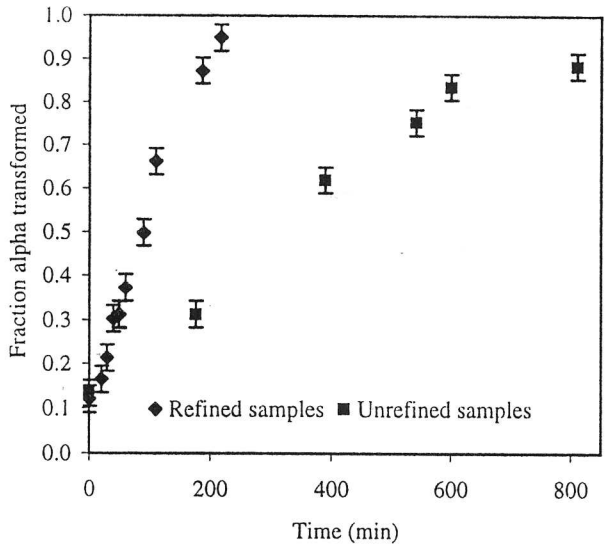


Figure 6: Transition of the α phase as a function of annealing time for refined and unrefined commercial samples. The annealing temperature was 720°C.

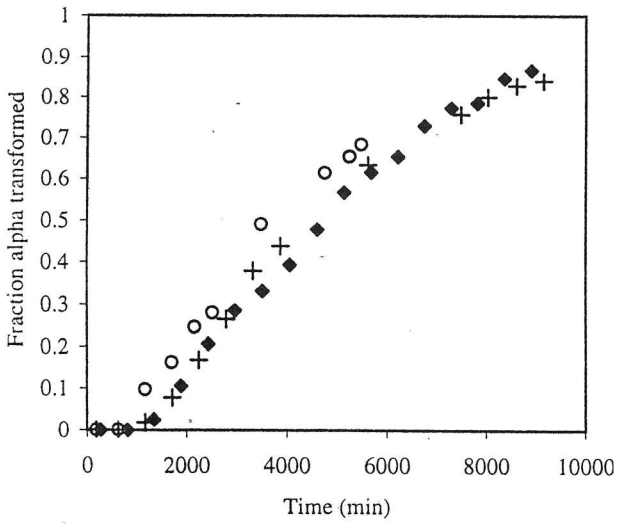


Figure 7: Fraction of transformed α phase as a function of annealing time. The annealing temperature is 535°C. ♦ #1; + #2; ∘ #3.

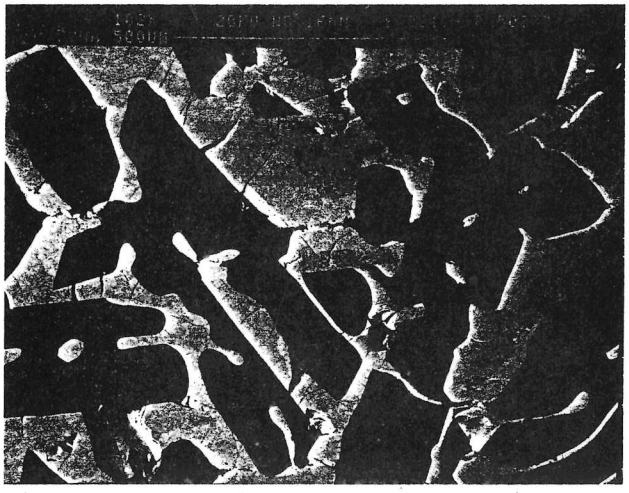


Figure 8: SEM picture of sample C22. The Si phase appears black on the picture. The enlargement is ×102.

X-ray analysis of the α and β phases

Some preliminary studies have been done on the chemical content of the α and β phases on a microscopic scale. Sample from the refined commercial 75% ferrosilicon was investigated in Scanning Electron Microscope and X-ray spectra were collected from different positions in the sample. ZAF correction of intensities of the X-ray spectra was used to determine the fraction of iron and silicon in each of the α and β phases.

The sample had been annealed for 22 hours at 578°C and according to Mössbauer measurements 36% of the α phase had transformed into β. A SEM picture taken with backscattered electrons is shown in figure 8. The Si phase appears black on the picture and the brighter areas are the α and β phases. The β phase appears slightly brighter than the α phase on the figure. X-ray spectra were collected form nine spots from the β phase (bright area) and sixteen spots from the α phase. The results were as follows:

	Fe (%)	Si (%)
α (dark area)	47.6	52.2
β (bright area)	47.8	52.2

The variation in the data was not large, the standard deviation in the silicon content in both areas and in the iron content in the darker area was 0.2% and 0.4% for the iron content of the bright area.

This is an interesting result. There cannot be any doubt that two separate phases were investigated, but both with the same iron–silicon content. Mössbauer measurements of the sample show α:β ratio that is 64:36 and investigation in optical microscope shows that the brighter and darker areas represent different phases. The result can be explained by the theory put forward

by Boomgaard and mentioned earlier [5], that the α phase transforms into β in two steps, first into a β' supersaturated with Si and then later into β plus some Si.

Another possible explanation is that the silicon precipitates are smaller than the SEM resolution. In this case it is not possible separate the Si precipitates from the β phase. The x-ray analysis would give the average composition of the β phase and the Si precipitates. Further conclusions will have to await a more systematic investigation.

Conclusions

1. Transformation rates for refined 75% ferrosilicon have been measured. The rate of transformation is highest at 700–750°C but decreases fast outside that interval.

2. Comparison of refined and unrefined 75% ferrosilicon shows that impurities in general slow down the eutectoid $\alpha \rightarrow \beta$ transformation.

3. By comparison of pure Fe55%Si and a similar sample doped with 1% aluminium it has been shown that aluminium slows down the $\alpha \rightarrow \beta$ transition.

Acknowledgements

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