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FERROSILICON RESEARCH IN ICELAND

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ABSTRACT

A research cooperation between the University of Iceland and Icelandic Alloys Ltd. within the area of silicon rich ferrosilicon is described. Studies of phase dynamics of zeta phases are analysed and a TTT-diagram for the eutectoid decomposition is presented. The paper turns to the discussion of layer casting for obtaining high quality materials. A computer model has been designed to calculate the various casting parameters and optimise material strength. Finally a discussion is made of a new potential method for slag detection in the finished product.

INTRODUCTION

For the past decade there has been considerable research and development cooperation between the University of Iceland and Icelandic Alloys Ltd. at Grundartangi. The University has expanded its research facilities within metals physics and materials science; and the Icelandic Alloys plant has continuously worked on many aspects of research into ferrosilicon. With the advent of a chair in metals physics at the university, sponsored by Icelandic Alloys, a new era of active research into the ferrosilicon system started in Iceland in 1989 involving research ranging from fundamental metals physics to development of new materials and processes.

In this paper this work will be reviewed starting from studies of the time-transformation-temperature behaviour of $FeSi_2$. Then the paper turns to a description of the relationship between thermal history and strength of ferrosilicon. A study of the effect of layer casting on materials strength is reviewed as well as a method for testing some quality aspects of the product.

The development of a carbon-ferrosilicon based refractories will be described in a separate paper as well as the description of a fruitful cooperation with NTH Trondheim on production processes.

PHASE STABILITIES OF IRON DISILICIDE

The phase diagram [1,2] of silicon rich Fe-Si is shown in figure 1. The major part of the diagram is composed of iron disilicide which occurs in two forms. The stoichiometric $FeSi_2$. usually called the beta-phase, is semiconducting and stable below the eutectoid temperature of 967°C. The beta phase has an orthorhombic structure with 48 atoms in the unit cell and lattice parameters a = 9.863Å; b = 7.79Å; c = 7.883Å [3,4].

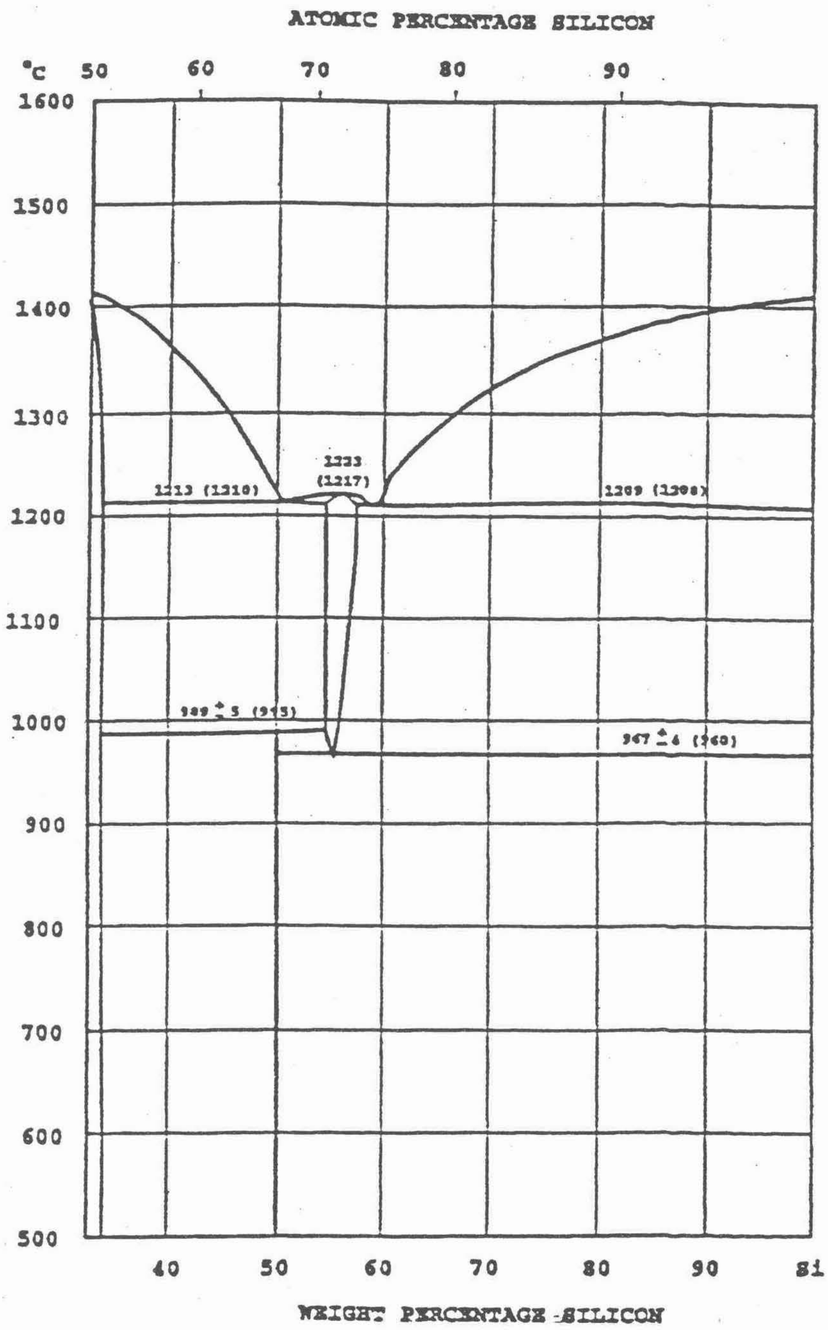

Fig. 1. The phase diagram of the silicon rich part of the Fe-Si system in the vicinity of the zeta phases. Figures in parenthesis are values of calculations by Lee et al. [2].

The so called alpha phase has a tetragonal structure with unit cell dimensions a = 2.69Å and c = 5.13Å. The alpha phase is slightly off-stoichiometric, contains an excess of Si and a considerable content of vacancies in the Fe sublattice. Its electronic structure leads to metallic behaviour.

Bearing in mind the distinct differences in the Fe sublattice of the two phases of iron disilicide it was tempting to make use of the sensitive Mössbauer technique to study the phase dynamics of this compound. It had previously [5] been seen that Mössbauer spectra from samples obtained from different production processes of 75% (Si) Fe-Si showed very different behaviour depending on the rate of solidification of the alloy.

In this way it was possible to examine thermal history of products by examining the proportions of alpha to beta in the Mössbauer spectra. The beta phase is characterised by a well defined double doublet (see figure 2) whereas the alpha phase is characterised by two doublets of somewhat broader line-width. It was observed in the studies of the phase dynamics of commercial products that most of the 75%(Si) Fe-Si contains super-cooled alpha phase.

Samples studied with Mössbauer spectroscopy were prepared in an RF furnace and their thermal history determined by quenching in water following annealing at different temperatures.

In this way a TTT-diagram for high purity samples of nominal alpha composition (55% wt Si) was obtained and is shown in figure 3. Maximum time for a finished reaction was found to occur at about 720°C where the corresponding annealing time is just over ten hours. The eutectoid decomposition as revealed by Scanning Electron Microscopy can be seen in figure 4.

The form and behaviour of the TTT-diagram corresponds well with expected behaviour. The local maximum rate originates in the competing effects of the free energy differences of the two phases on the one hand; and the nucleation rate and velocity of the reaction front on the other. It was concluded from these studies that slow cooling of ferrosilicon would enable the eutectoid decomposition to take place over a larger volume fraction with the resulting crack formation. Therefore rapid cooling would seem favourable during production.

Another major effect of the different cooling rates on 75% Fe-Si is of course related to the grain size effects. As the cooling is slower, Si grains gain more time to expand and grain sizes become larger thus reducing the bonding between the Si grains and the underlying alpha/beta matrix [6]. Similar behaviour has been found by Tveit [7] in his detailed work on the relationship between strength and solidification of commercial ferrosilicon.

At Icelandic Alloys the use of water-spray cooling of carousel surface during casting has considerably improved the efficiency of the casting process and the quality of the material.

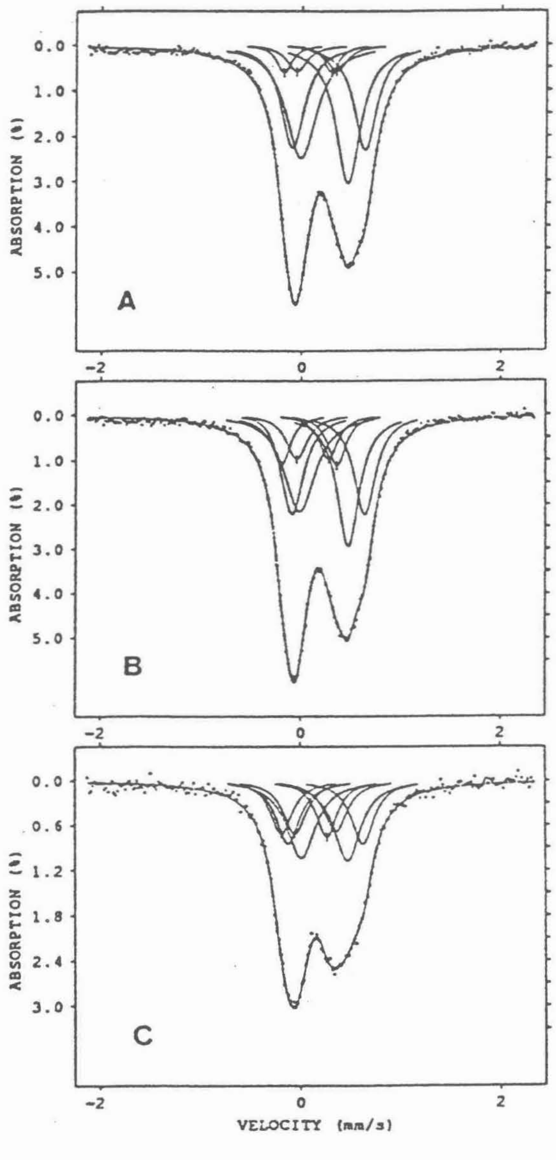

Fig. 2. Mössbauer spectra of commercial 75% ferrosilicon. Sample in Fig. 2A is water quenched. Sample in Fig. 2B was annealed at 900°C for 4 hours and Fig. 2C shows a sample which was annealed at 900°C for 100 hours. Note how the double doublet assigned to the beta phase (shown in the uppermost part of all figures) grows as the eutectoid decomposition takes place.

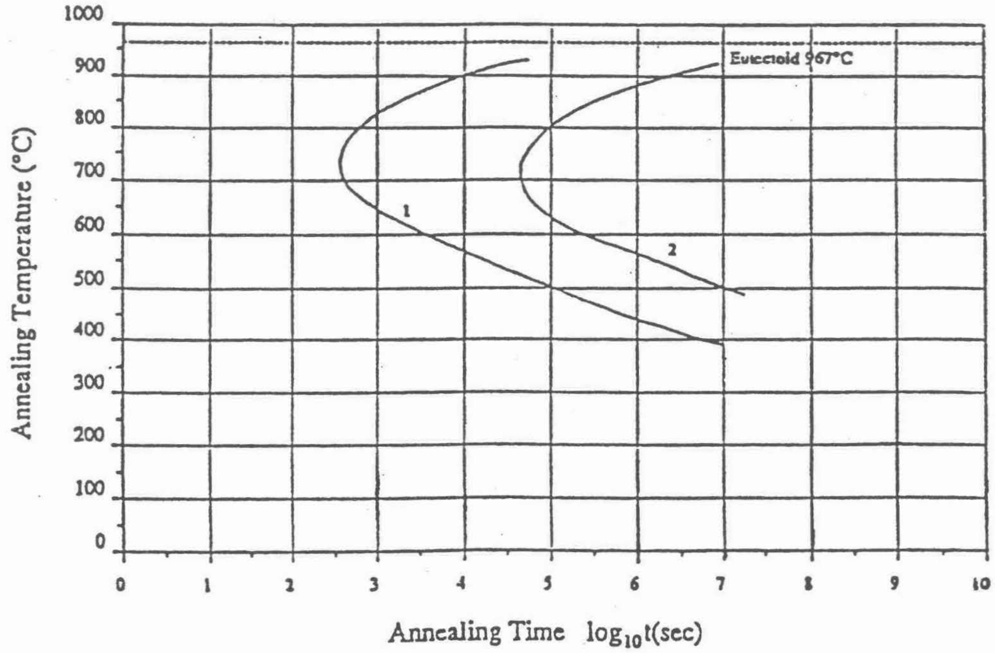

Fig. 3 The Time-temperature-transformation diagram for a sample of nominal zeta-alpha composition (55% wt.). The curve marked (1) shows the beginning of the eutectoid decomposition and the curve marked (2) a finished process.

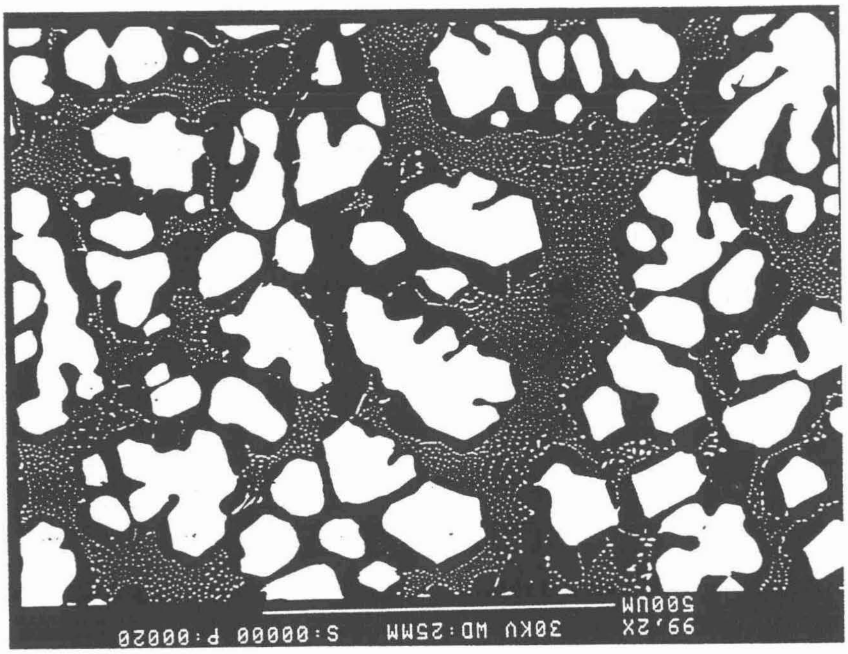

Fig. 4. Scanning Electron Micrograph showing the eutectoid decomposition of a nominal zeta-alpha sample of high purity following annealing. The white spots indicate backscattered electrons from Silicon.

LAYERCASTING AND MATERIALS STRENGTH

Having gained insight into the influence of thermal history on materials strength it was tempting to try to model the effects of layercasting on the quality of ferrosilicon [8]. A 54 m^2 casting bed was constructed and equipped with air blowers blowing vertically down onto the surface of the bed to add the cooling. A 20 cm layer of grained ferrosilicon was put onto the bottom of the bed to insulate it from the concrete floor. A crane was used to pour the contents of the ladle onto the middle of the bed and was kept moving to ensure even distribution of layer thickness. Temperatures could be monitored by using thermocouple thermometry and optical heat sensors. Furthermore temperatures of layer profiles were measured when the bed was broken up after solidification.

A computer programme was used to calculate the heat flow in the bed as a function of time. The result of the calculation of temperatures can be shown in figure 5. The figure shows the evolution of average temperature as a function of time for 18 successive layers of ferrosilicon of about 4 cm thickness each. Comparison with measurements was good apart from some uncertainties around the bottom of each layer due to difficulties in estimating heat flow through and into the bottom layer. Figure 6 shows the results of measurements of temperature profile of an 18 layer bed 29 hours after casting. The temperature distribution after casting is important for determining when the bed can be broken up for transport and crushing.

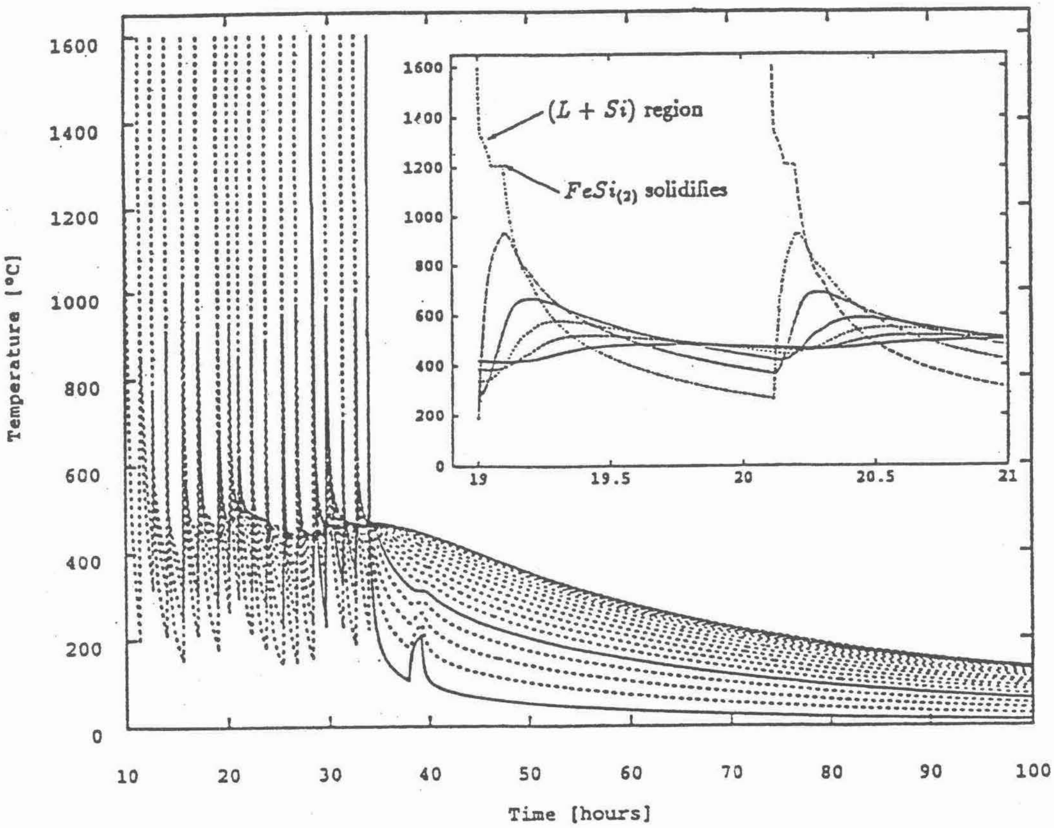

Fig. 5. Average layer temperature for the centre of all layers for 18 successive layers at 0.5 m from the center of the air cooling jet. Inserted figure is an expanded view of the process for an interval of two hours indicating the (L + Si) region and the solidification of irondisilicide.

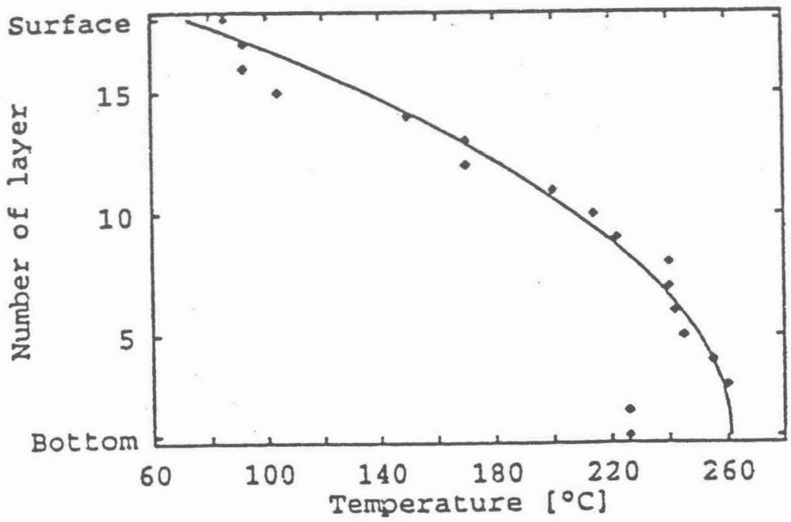

Fig. 6 Comparison of calculated (solid line) and measured (dots) temperature profile of an 18 layer bed, 29 hours after casting.

The crucial time spent in the (L + Si) region between 1207°C and 1350°C was calculated as a function of layer thickness. The time is of course of importance for Si grain size distribution and the resulting material strength through the layer.

Figure 7 shows the results for thicknesses from 2 cm to 8 cm in one cm increments. Notice the maximum solidification time at around 30% of the distance from bottom to top of each layer. Increasing layer thickness from 4 to 6 cm nearly doubles the maximum solidification time in the crucial region.

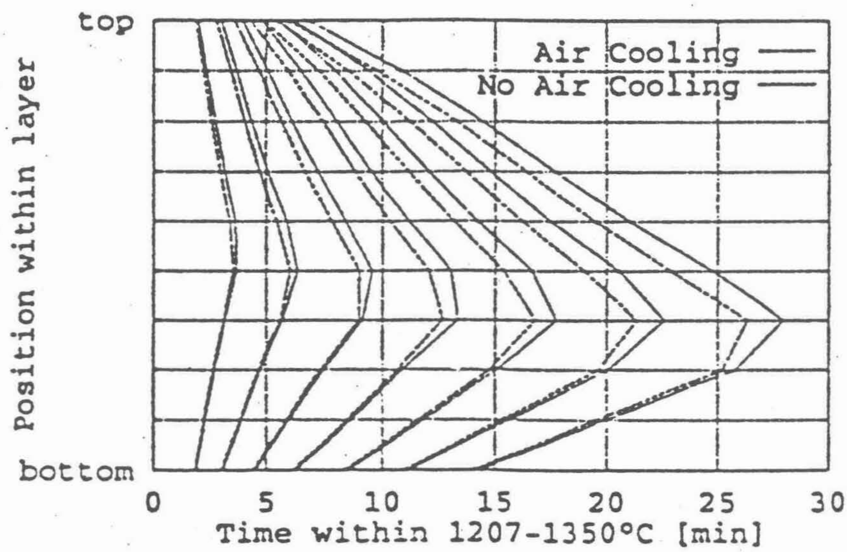

Fig. 7 Solidification times in the (L + Si) region 1350°C to 1207°C for layers of different thickness from 2 cm (far left) to 8 cm (far right) in increments of 1 cm. The simulation assumes for each thickness two different cooling conditions with (left) and without (right) air cooling.

This increased solidification time was found to be clearly reflected in the formation of ferrosilicon fines as measured by a standard tumble test method and shown in figure 8.

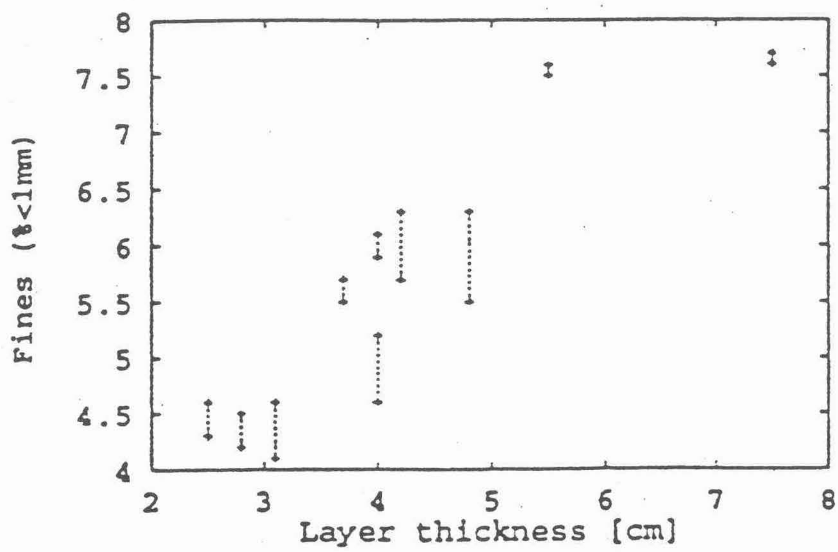

Fig. 8 Percentage of ferrosilicon fines (sub millimetre size) from tumble test plotted against thickness of layer for the experiments with layer casting.

By using the model and the measurements it was possible to optimise the bed size, layer thickness and duration of solidification to a degree that can improve the quality of the ferrosilicon as compared with traditionally carousel cast materials. Evolution of fumes during casting proved, however, to be a problem that calls for good ventilation during casting.

If the cost of carousel wagons is considered it is easy to show the advantages of the layer casting method.

DETECTING SLAG IN PRODUCED METAL

In the production of ferrosilicon it is difficult to totally avoid the occurrence of slag in the product. The main constituents of 75% ferrosilicon are the $FeSi_2$ phase, Si and SiC slags. A high frequency phase-locked susceptibility method was developed and has proven powerful in detecting slag impurities. Electric conductivities of these materials range from 2000 mho/cm for $FeSi_2$ [9] to about 10^{-3} to 10^{-6} mho/cm for Si [10] (depending on impurities) and 10^{-5} mho/cm for SiC [11]. On the basis of the wide ranging values above magnetic susceptibility measurements were performed on various samples of ferrosilicon with known impurity composition and structure.

In an experimental set-up (see figure 9) a driving coil was used to obtain magnetic field with desired frequency and a detector coil to measure the field intensity as influenced by the presence of ferrosilicon in the size range up to about 15 cm diameter. The samples were put between these coils to resemble a possible geometry on a conveyor belt. The amplitude and phase of the detected signal was analysed as the frequency was varied continuously from about 20 to 100 kHz which is a frequency range containing the resonant frequency of the circuit. Samples of different nature were used to test the method.

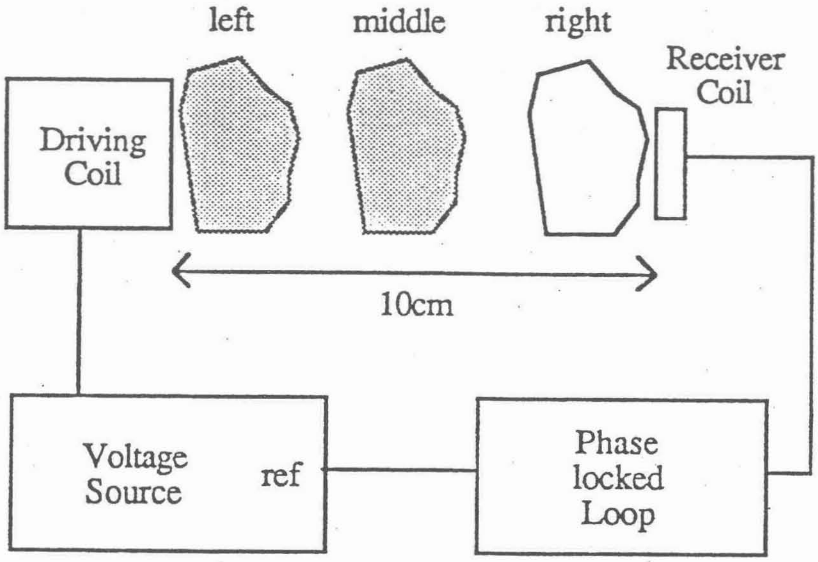

Fig. 9. The experimental set up for the slag test showing the driving coil and the receiver coil spanning a gap of 10 cm where different samples are tested. The distance was chosen to as to resemble a possible geometry on a conveyor belt.

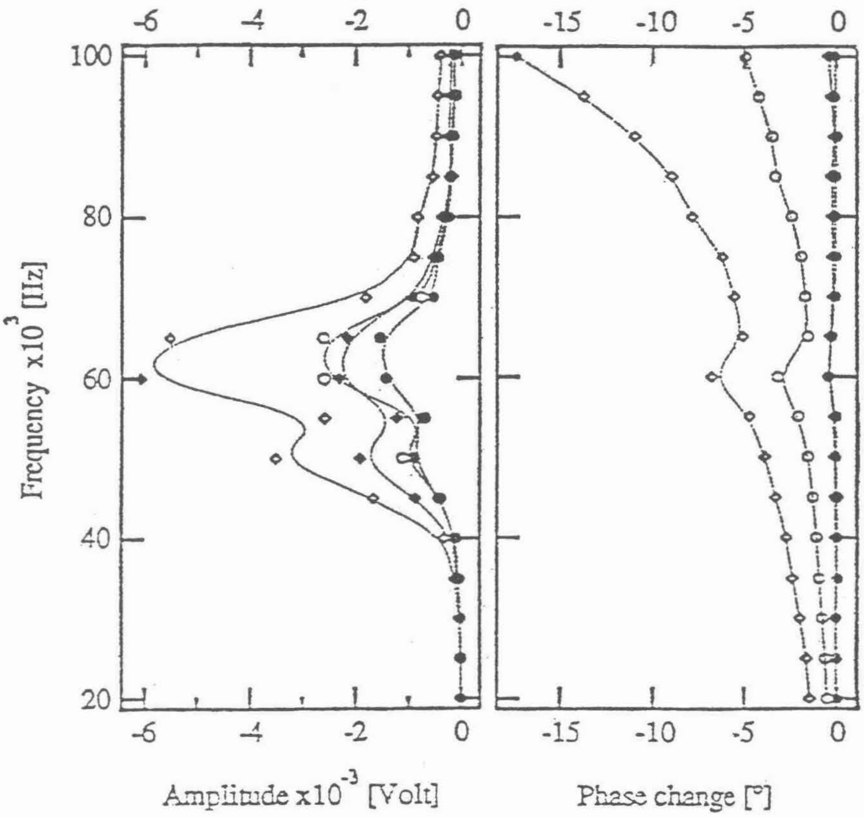

Fig. 10. Variations of amplitude and phase of the measurement circuit as a function of frequency for four different samples of ferrosilicon. The open circles denote ferrosilicon samples of differing purity. The dark circles denote slag-rich samples with limited amount of ferrosilicon.

Figure 10 shows the changes in amplitude and phase for a frequency scan from 20 to 100 kHz in four different samples. The slag rich samples are denoted by dark dots in the figure whereas the ferrosilicon samples are shown by open circles. Slag rich samples distinguished themselves by a simultaneous occurrence of low amplitude and small phase shift at the resonant frequency of the circuit. Further work is needed to improve sensitivity of the method but its potentials for slag detection are promising.

REFERENCES

1. Sigfusson T.I. and Helgason Ô., Hyperfine Interactions, 54 (1990), 861-868.

2. Lee B., Lee S.K. and Lee D.N., Calpad 11, No 2 (1987), 253-270.

3. Hansen M. and Anderko K., Constitution of Binary Alloys, McGraw-Hill, New York (1965).

4. Shunk F., Constitution of Binary Alloys, Second Supplement, Mc Graw-Hill, New York (1969).

5. Helgason Ö and Sigfusson T.I., Hyp. Int. 45 (1989), 415-418.

6. Sigfusson T.I. and Johannesson B., Science Inst. Report RH-04-88 (1988).

7. Tveit H., Thesis, NTH Trondheim (1988).

8. Sigfusson T.I., Matthiasson J., Ingason H.T., Sigurdsson J.V. and Halfdanarson J., Proc. Electric Furnace Conference, Iron and Steel Society (1994), 187-192.

9. Birkholz U. and Schelm J., Phys. Stat. Sol. 34, K177 (1969).

10. Wecht E.H.P., Feuerfest siliciumcarbid, Applied Mineralogy, Vol. 11. 13 (Springer 1977).

11. Sigfusson T.I. and Matthíasson J. "A high frequency phase-locked susceptibility method for detecting impurities in ferrosilicon", Science Institute report for Icelandic Alloys (1991).