Microstructural Study of Granulated Ferrosilicon with 75wt% Silicon

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ABSTRACT

Microstructural characterization and PH_3 gas evolution analyses were performed on granulated ferrosilicon containing 75wt% silicon. The results of these analyses were then compared to similar analyses performed on conventionally cast ferrosilicon alloys of similar composition. PH_3 evolution from the granulated alloys was found to be less than 10% of measurements on conventional ferrosilicon alloys. The microstructure of the granules differed from that of conventional alloys primarily in the size and distribution of the major phases and the impurity phases. Also of interest was the presence of an oxide layer on the surface of the granules and a compositional variation between individual granules in the 1-2 mm size fraction.

INTRODUCTION

Ferrosilicon alloys containing 75wt% silicon (FeSi75) are largely used in the steelmaking industry and cast-iron foundries. In steelmaking, FeSi75 is primarily used in the deoxidation of molten steel. In cast-iron foundries, FeSi75 is used as an inoculant to refine the microstructure of the castings. Conventional ferrosilicon is cast into large slabs and crushed to the desired size range. The crushing, sizing and handling of the ferrosilicon alloy generates an excessive amount of fines, which are of little use to the steelmaking or cast-iron industries. Another problem commonly associated with ferrosilicon alloys is the emission of the toxic gas phosphine (PH_3). Under wet or humid conditions, PH_3 may be generated by ferrosilicon alloys which contain certain impurity elements, specifically aluminum, calcium, and phosphorus.[1] It has been shown that reactive phosphide inclusions which contain primarily these impurity elements are present within the microstructure of conventionally cast FeSi75.[2,3] These phosphide inclusions produce PH_3 when they come into contact with moisture. Moisture penetrates the microstructure of the material via microcracks to reach the reactive phosphide inclusions. Previous work has shown that the reaction of the phosphide inclusions with water may also enhance the material's friability and, in extreme cases, lead to spontaneous crumbling.[3]

Elkem Metals Co. has developed a granulation process for the production of ferrosilicon which eliminates the need for crushing.[4] The granulated ferrosilicon is produced by pouring the molten alloy onto a refractory surface which serves to break the liquid stream into droplets. The droplets then fall into a surrounding water bath and are rapidly quenched. The spheroidal granules (ranging in sizes from 1 mm to 25 mm) are then dried and screened. Since the granulation process eliminates the need to crush the ferrosilicon, this process removes one of the major sources of fine generation.

The purpose of this work was to determine the effect of granulation on the microstructure of FeSi75 alloys and on PH_3 evolution. The detection of impurity phases which may lead to PH_3 evolution and material friability was specifically of interest. The results of these analyses were then compared to studies performed on conventionally produced commercial FeSi75 alloys.[3]

EXPERIMENTAL

Microstructural characterizations and PH_3 gas evolution measurements were performed on three

Table 1: Composition of Granulated Ferrosilicon Analyzed (wt%)

Granule Size	Si	Fe	Al	Ca	Mg	P
1-2mm	66.1	32.6	0.98	0.11	<0.01	0.015
8-10mm	75.9	23.1	0.65	0.10	0.01	0.014
+16mm	75.7	22.8	0.74	0.12	0.01	0.014
Conventional FeSi75[3]	73-78	23-27	0.2-0.6	0.3-0.6	~0.03	~0.02

granulated ferrosilicon size ranges: 1-2 mm, 8-10 mm and +16 mm granules. The granulated ferrosilicon was supplied by Elkem Metals Co. The compositions of these granules were determined by wet chemical analysis and are shown in Table I. All of the granules were obtained from the same heat which had a nominal composition of Fe-75wt% Si. It should be noted that phosphorus losses (in the form of PH_3 gas) during wet chemical analysis can produce anomalously low phosphorus readings. In the granulated ferrosilicon, <10% of the total phosphorus evolved as PH_3 gas, therefore the effect of PH_3 gas evolution on the wet chemical analysis of phosphorus was considered insignificant.

Microstructural characterization of the granulated ferrosilicon was undertaken using scanning electron microscopy (SEM). Major phases present within the material were identified using X-ray diffraction analysis (XRD). Minor phases and microstructural features were characterized using a scanning electron microscope equipped with an energy dispersive spectrometer. Quantitative PH_3 evolution analysis was performed using an experimental setup described previously.[2]

RESULTS AND DISCUSSION

PH_3 Gas Evolution Analysis

It was found that the amount of PH_3 gas evolved from the granulated ferrosilicon was a function of the granule integrity. No PH_3 was detected from as-received granules submersed in water for three days. However, when these same granules were dried and fractured, PH_3 was immediately detected upon contact with water. The amount of PH_3 generated by the crushed, granulated ferrosilicon ranged from 5 to 15 ml PH_3 per kilogram of FeSi75 (calculated for STP from the mass of PH_3 evolved). The amount of PH_3 generated from conventional FeSi75 alloys has been found to range from 40 to 60 ml PH_3 per kilogram of FeSi75.[2,3] Thus, the amount of PH_3 generated by granulated ferrosilicon is less than 25% of that produced by conventional FeSi75 alloys.

The relatively low amount of PH_3 evolved from the granulated ferrosilicon is believed to be attributed to the rapid cooling rate, the fact that the granules were already exposed to water in the quench bath and the lower Ca and P contents as compared to conventional ferrosilicon. The rapid solidification rate of the granules may reduce the time allowed for the phosphide inclusions to form. Also, since the granules were quenched from a liquid state and cooled in a water bath, any phosphides near the surface of the granules would have already reacted with the water.

Microstructural Characterization

The scale of the microstructure in the granulated ferrosilicon was much finer than that found in conventional FeSi75 alloys. The microstructures of the three granule sizes ranges (1-2 mm, 8-10 mm, +16 mm) are shown in Figure 1. The fine scale of the microstructure is attributed to the rapid solidification rate of the granules. The dark gray and light gray phases shown in these photomicrographs were found to be silicon and high-temperature $FeSi_{2.4}$ (ζ), respectively. XRD analysis of the granulated FeSi75 alloys showed that silicon and ζ were the only major phases (>1 volume percent) present within the alloys. It should be noted that the ζ phase is a metastable phase below 937°C according to the Fe-Si phase diagram shown in Figure 2. The low-temperature $FeSi_2$ phase (ζ') was not present because the

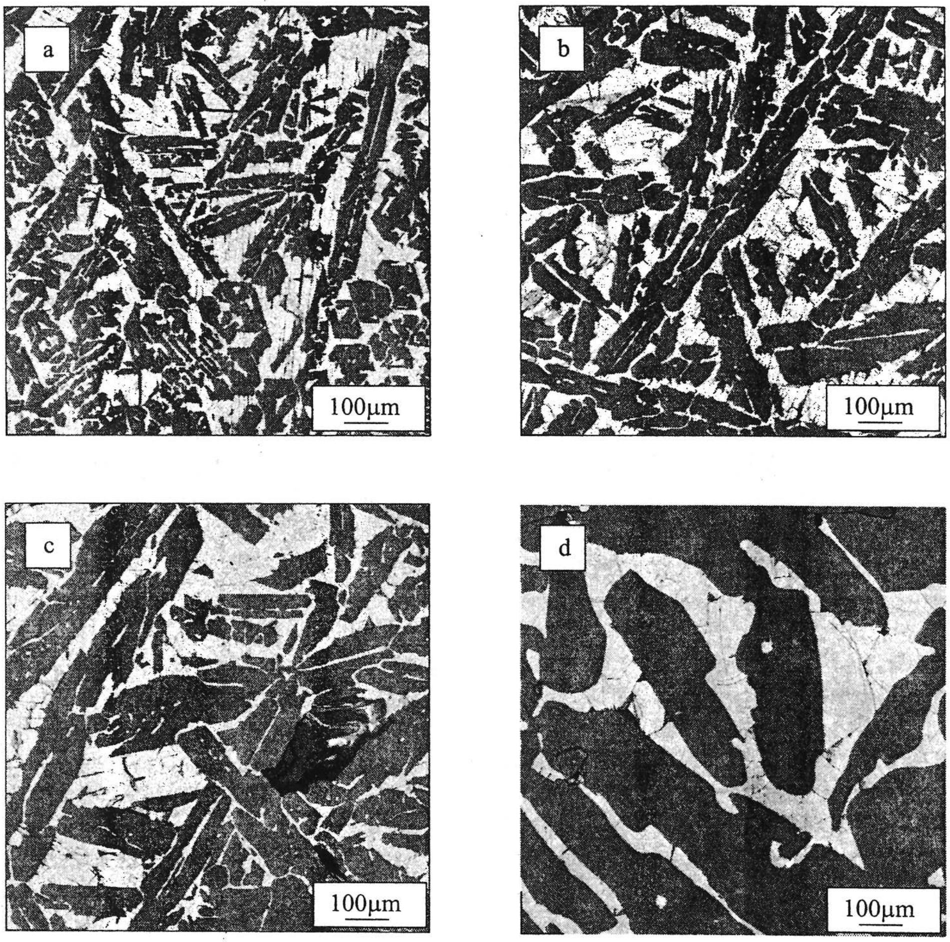

Figure 1 - Back-scattered electron images of typical microstructures in granulated FeSi75 within the size ranges 1-2 mm (a), 8-10 mm (b), +16 mm (c) and conventional ferrosilicon (d).

cooling rate was too rapid to allow the $\zeta \rightarrow \zeta' + Si$ solid-state transformation to occur.[5]

The volume fraction of the silicon phase was similar (approximately 0.65) in all of the size ranges except for the 1-2 mm fraction. The variation in the volume fraction of silicon among 1-2 mm granules can be seen in Figure 3. Using image analysis, it was found that the volume fraction of the silicon phase ranged from 0.18 to 0.66 in the individual 1-2 mm granules. The corresponding compositional range was calculated to be 55 to 77 wt% silicon. This range of compositions was calculated from the volume fraction range and the known densities of the two major phases. The results from wet chemical analysis on the different size fractions showed that the 1-2 mm granules had an average silicon composition of

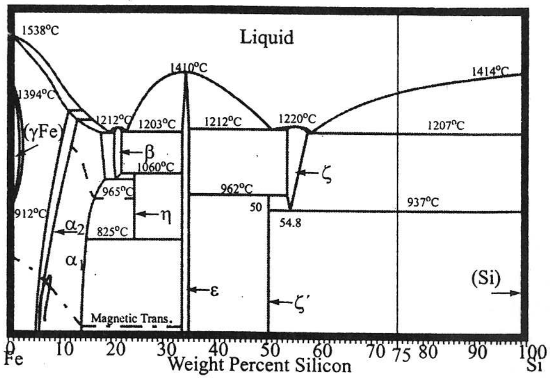

Figure 2 - The equilibrium Fe-Si binary phase diagram.

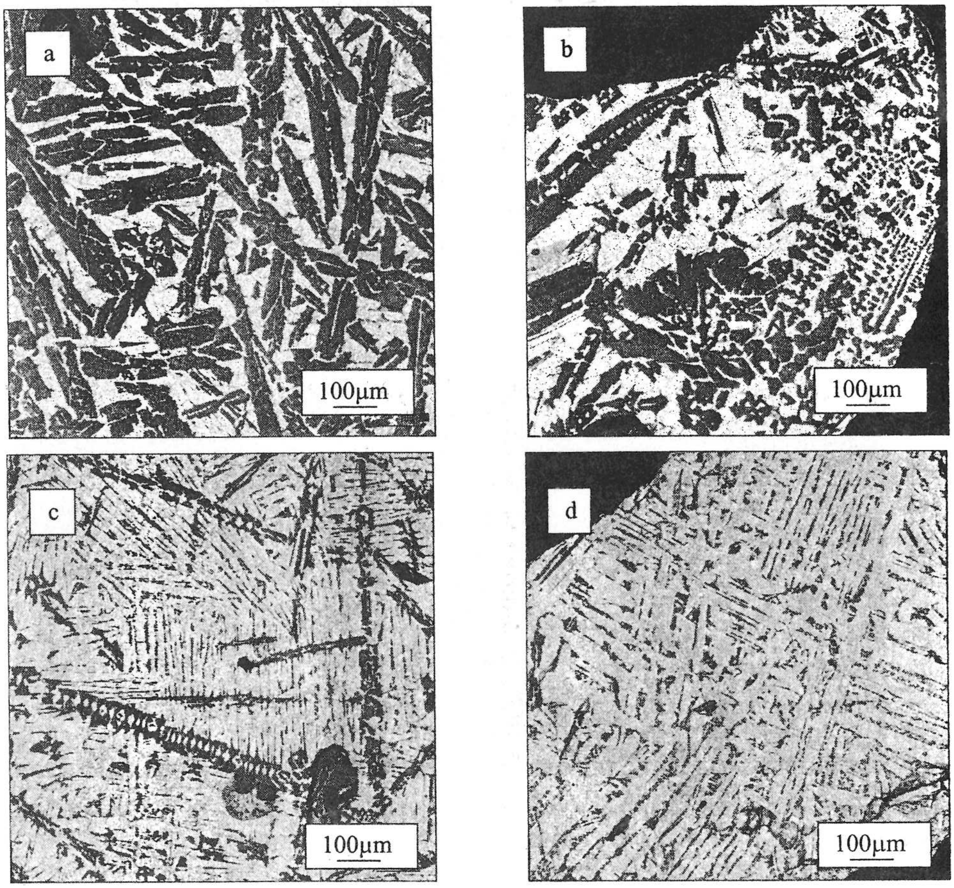

Figure 3 - Back-scattered electron images of 1-2mm granules. The wide variation in microstructures between granules is clearly shown. The total silicon content in each granule determined by image analysis is 71.6wt%, 64.6wt%, 58.3wt% and 54.6wt% for images (a), (b), (c) and (d), respectively.

66.1wt%, which is approximately 10wt% lower than the 8-10 mm and +16 mm granules.

It is believed that the 1-2 mm granules which contained less silicon than the rest of the melt were formed by a different mechanism than the other granules. Most of the granules formed as the spheroidal droplets from the broken stream of molten metal were quenched in the water bath. Granules that formed in this manner had a composition similar to the rest of the melt. It is believed that the granules with low silicon contents were formed by a secondary mechanism, which involved the ejection of silicon-poor liquid from partially solidified granules. From the binary Fe-Si phase diagram in Figure 2, the composition of the liquid ejected from a partially solidified granule could range between the eutectic composition (~58wt% Si) and the nominal composition of the alloy (~75wt% Si). These compositions correspond very well with the composition range of the 1-2mm granules as determined by image analysis. (55 to 77 wt% Si). Also, the liquid ejected from a partially solidified granule should be enriched in impurity elements. Indeed, the results from wet chemical analysis on the 1-2 mm granules showed that these granules did have a higher aluminum content than the other size ranges.

Impurity phases were also identified in the granulated ferrosilicon microstructure. It was determined by EDS analysis that the impurity phases were primarily aluminum silicides with various amounts of iron, calcium and titanium. The aluminum impurity phases were usually found in a layered pattern within the ζ phase, with the layers oriented approximately 90^{o} to the

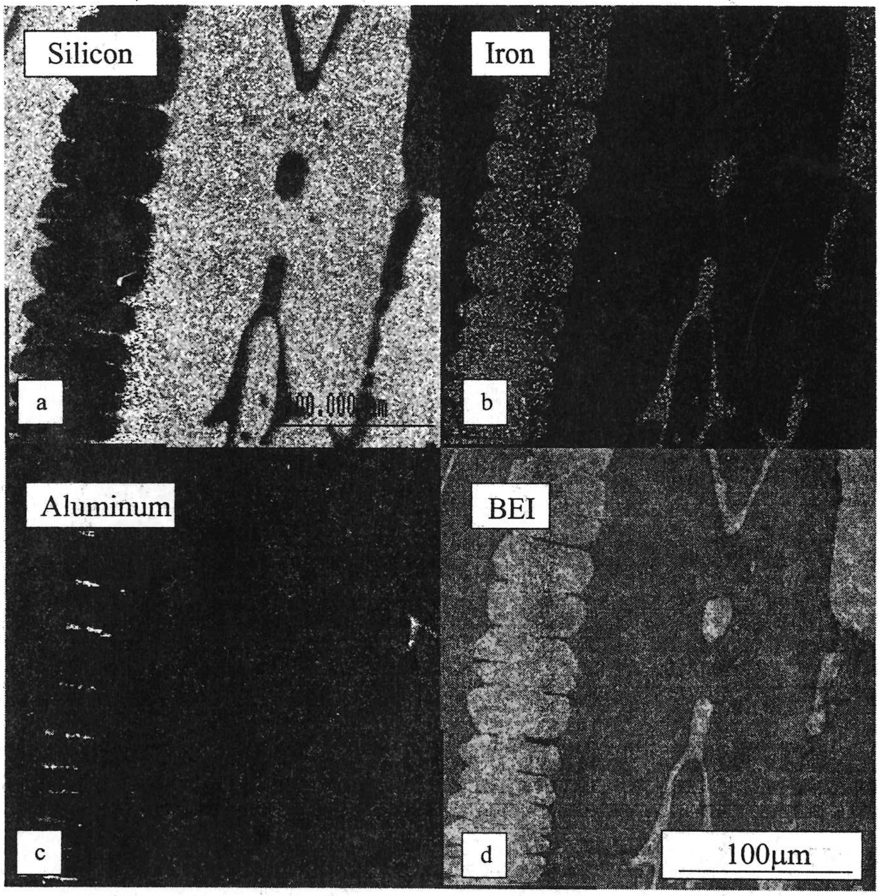

Figure 4 - X-ray elemental maps showing the relative distribution of aluminum impurity phases in the microstructure are shown for: a.) silicon, b.) iron and c.) aluminum. A back-scattered electron image of the region is shown in d.

silicon/ζ interphase boundary. The micrograph and the corresponding X-ray elemental maps of silicon, iron and aluminum in Figure 4 show the spatial distribution of the aluminum impurity phase within the microstructure of the granules. The distribution of impurity phases within conventionally cast FeSi75 alloys differs in that the phases are typically found on the ζ/silicon interphase boundaries. In conventionally cast FeSi75 alloys, the ζ/silicon interphase boundaries are the last-to-freeze regions of the microstructure because of divorced eutectic solidification. In the granulated material, the ζ phase appears to have solidified in a cellular manner, and the impurity phases formed in layers within the troughs between the cells.

Phosphide or phosphorus-rich phases were not found in the granulated ferrosilicon. However, since PH_3 was detected from granulated ferrosilicon, it is hypothesized that these inclusions are present in the microstructure, but that they are either too small or react too quickly with atmospheric moisture during specimen preparation to be observed directly. A smaller phosphide size is would be consistent with the rapid solidification rates of the granules. The cellular solidification of the ζ phase may have contributed to the small size of the phosphides by distributing the impurity elements more finely throughout the microstructure.

Surface Layer

An oxide layer was present on the surface of all of the granules. The composition of the oxide layer was similar on all of the granules and was determined by EDS analysis to be: 25-30at% (32-39wt%) Al, 5-15at%

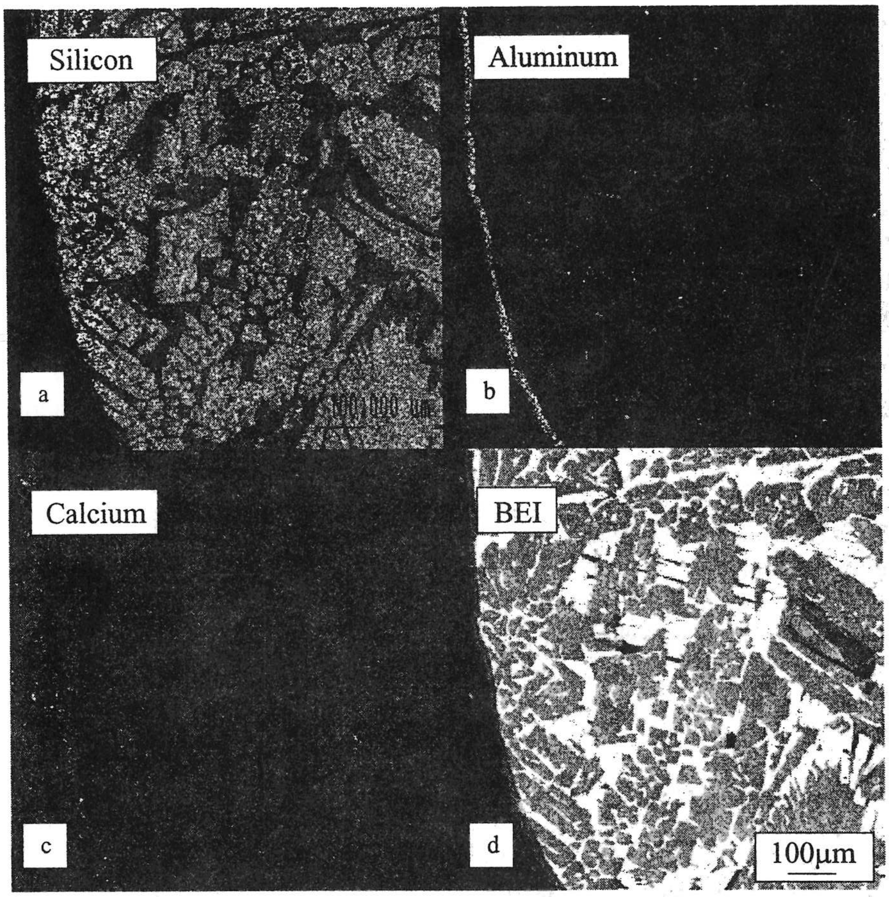

Figure 5 - X-ray elemental maps showing the distribution of elements in the oxide layer. A backscattered electron image of the region is shown in d.

(7-20wt%) Si, 1-5at% (2-10wt%) Ca, ~1at% (~1wt%) Mg, balance O. The thickness of the layer was ~10μm on most of the granules. This layer can be seen in the photomicrograph in Figure 5 and the distribution of elements in the layer is shown in the corresponding X-ray elemental maps. The relatively high amounts of aluminum, calcium and magnesium in the oxide layer is believed to be attributed to the fact that the oxides of these elements are more stable than the oxides of silicon and iron. Also, recent work by Nelson has shown that aluminum may be surface active in molten FeSi75 and therefore is present in higher concentrations at the surface of the granules.[6]

CONCLUSIONS

Microstructural characterization and PH_3 gas analyses of granulated ferrosilicon containing 75wt% silicon has led to the following findings:

- The amount of PH_3 evolved from granulated FeSi75 alloys is approximately 10 times lower than that measured from conventional FeSi75 alloys.

- Phosphide inclusions were not observed in the microstructure. It is suggested that their size is very small (<1μm) compared to the 10-50 μm inclusions found in conventional FeSi75 alloys.

- The smallest size fraction granules analyzed (1-2 mm) were found to have a wide compositional range between individual granules. It was also found that the average silicon content of this size fraction was approximately 10wt% less than the other size fractions.

- A 10μm thick oxide layer was present on the surface of most of the granules. The elements present in the oxide layer were primarily of aluminum and silicon along with a small amount of calcium and magnesium.

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REFERENCES

1- S. M. Copeman, S. R. Bennett and H. W. Hake: "Manufacture and Transport of Ferrosilicon," Metallurgical and Chemical Engineering, 8(3), 1910, pp. 133-138.

2- D.H. Gelwicks, L.A. Badanjek, C.L. Dodson, H.P. Jun, D.T. Rowe and G.D. Rowe, "Ferrosilicon Toxicity Review," Proceedings from the 53rd Electric Arc Furnace Conference, Orlando Florida, 1995.

3- Q.C. Horn, C.L. Nassaralla and R.W. Heckel, "Reactive Phosphide Inclusions in Commercial Ferrosilicon," Proceedings from the 80th Steelmaking/56th Ironmaking Conference, Chicago Illinois, April 1997, In Press.

4- Y.E. Lee, O.S. Klevan and R.I.L. Guthrie, "A Model Study to Examine the Reactions During Reduction Period of AOD Process," 11th PTD Conf. Proc., 1992, pp. 131-158.

5- H. Tveit, "Storkning av 75% Ferrosilisium," Diss., NTH, Norway, 1988.

6- L.S. Nelson, private communication with author, University of Wisconsin at Madison, 3 October, 1997.