

DETERMINATION OF SMALL AMOUNTS OF SILICON IN STEEL DRILLINGS USING X-RAY FLUORESCENCE TECHNIQUE

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A set of standards for the determination of silicon in steel drilling samples by X-ray fluorescence has been prepared by melting weighed quantities of silicon and iron. The calibration graph was found to be reliable when employed for three different steel drilling samples of certified silicon contents. Only 0.1 g of sample is required.

The Si $k\alpha$ fluorescence intensities of the standards were found to be about one third of those of silicon-iron powder mixtures. An explanation is attempted for this on the basis of a mathematical treatment following Claisse and Samson [1].

INTRODUCTION

An operation commonly used in metallurgical research is the annealing treatment of alloys in evacuated and sealed silica tubes. As this might lead to a contamination of alloy by reaction with the silica, it is important to check the purity of the annealed specimen by silicon analysis. The samples are often fairly small in this type of work and the material available for analysis may be of the order of 0.1 g.

This study was undertaken to examine the possibilities of using X-ray fluorescence technique for silicon determination in low alloy steel samples in powder form.

METHOD

A first series of specimen, set (1), was prepared from mechanical mixtures of silicon and iron powders, with silicon concentrations from 0.01% to 0.5%. The contents were carefully weighed, mixed thoroughly and pressed to form tablets with semi-smooth surfaces on cellulose backings. The linear relationship between the silicon concentration, C_{Si} , and the Si $k\alpha$ count-rate is shown by graph (1) in Fig. 1. When this graph was used for silicon estimation in three samples of steel drillings with certified silicon contents, (indicated by squares in Fig. 1), much too low values were obtained. Evidently, simple mechanical

mixtures of silicon and iron cannot be used in calibration of solid solutions.

A second series of powder samples, set (2) was prepared from alloys synthesized by arc-melting silicon and iron. The calibration graph (2), obtained by this set, could be used to determine silicon concentrations of the three certified steel samples. The values obtained were 0.12%, 0.18% and 0.28% whereas the certified values were 0.13%, 0.18% and 0.28%, respectively. No effects on line intensities of silicon were discerned from the presence of manganese (1.0%), carbon (0.6%) and sulphur (0.15%).

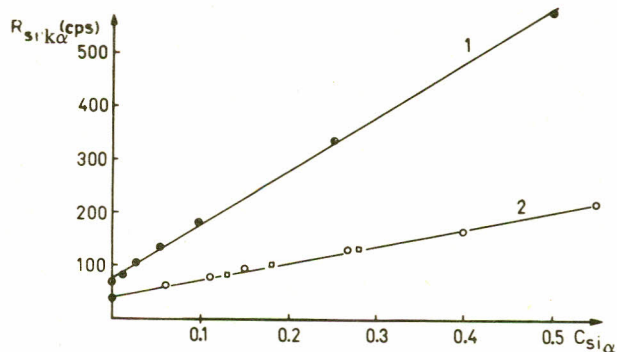


Fig. 1. The Si $k\alpha$ count rates for two sets of specimens: mixtures of iron and silicon powders (1) and iron-silicon alloys (2).

DISCUSSION

The two curves in Fig. 1 correspond to the following equations:

$$I'_{Si} = 80 + 1015 C_{Si} \quad (\text{Set 1})$$

$$I''_{Si} = 40 + 320 C_{Si} \quad (\text{Set 2})$$

The difference in slope may be explained by the following treatments, related to that of Claisse and Samson [1].

For monochromatic primary radiation Eq. 1 relates the net fluorescence intensity of silicon, I_{Si} , to its weight percentage C_{Si} in a homogeneous specimen [2].

$$I_{Si} = P_{Si} I_o \frac{\mu_{Si}(\lambda) C_{Si}}{\mu(\lambda) + \mu(\lambda_{Si})} \quad (1)$$

P_{Si} is a constant for the spectrometer and the fluorescent element Si; I_o the intensity of the primary radiation; $\mu(\lambda)$ and μ_{Si} , the matrix and silicon mass absorption coefficients; λ and λ_{Si} the wavelengths of the primary and the Si α radiations.

Assume that the grain size of the two elements in the specimens of set (1) is equal and larger than the critical thickness of pure Si. The random distribution (a) will then be equivalent to (b), which may be replaced by (c), Fig. 2.

The observed Si α intensity for set (1) will thus correspond to that of a pure silicon specimen, multiplied by the silicon area fraction. In a pure Si specimen Eq. 1 is reduced to:

$$I_{Si} = P_{Si} I_o(\lambda) \cdot 100$$

as the matrix absorption of fluorescence radiation in this case is very small. The area fraction of Si is equal to the volume concentration of Si, so that

$$I_{Si} = [P_{Si} I_o (\rho_{Fe} / \rho_{Si}) C_{Si}] / [1 + C_{Si} (\rho_{Fe} - \rho_{Si}) / 100 \rho_{Si}]$$

$$I'_{Si} = P_{Si} I_o C_{Si} \frac{\rho_{Fe}}{\rho_{Si}} = P_{Si} I_o \cdot 3.2 C_{Si}$$

For the samples in set (2) we represent the primary radiation by the Si α absorption edge, $\lambda = 6.45 \text{ \AA}$. For low C_{Si} the matrix may be regarded as pure iron so that Eq. 1 gives:

$$I''_{Si} = P_{Si} I_o \frac{3000 C_{Si}}{1620 + 2072}$$

$$= P_{Si} I_o \cdot 0.8 C_{Si}$$

where $\mu_{Si}(\lambda) = 3000$, $\mu(\lambda) = \mu_{Fe}(\lambda) = 1620$ and $\mu(\lambda_{Si}) = \mu_{Fe}(\lambda_{Si}) = 2072 \text{ cm}^2/\text{g}$.

Thus we obtain the ratio

$$\frac{I'_{Si}}{I''_{Si}} = \frac{3.2}{0.8} = 4$$

to be compared with the experimental value of 3.

For a polychromatic primary beam of intensity $I_o(\lambda)$ equation (1) can be written as

$$I_{Si} = P_{Si} C_{Si} \int_{\lambda_{min}}^{6.8} \frac{I_o(\lambda) \mu_{Si}(\lambda)}{\mu(\lambda) + \mu(\lambda_{Si})} d\lambda$$

6.8 being the Si α absorption edge

$$\text{Thus } I_{Si} = P_{Si} C_{Si} \frac{P_{Fe}}{P_{Si}} \int_{\lambda_{min}}^{6.8} \frac{I_o(\lambda) \mu_{Si}(\lambda)}{\mu_{Si}(\lambda) + \mu_{Si}(\lambda_{Si})} d\lambda \quad (2)$$

$$\text{And } I''_{Si} = P_{Si} C_{Si} \int_{\lambda_{min}}^{6.8} \frac{I_o(\lambda) \mu_{Si}(\lambda)}{\mu_{Fe}(\lambda) + \mu_{Fe}(\lambda_{Si})} d\lambda \quad (3)$$

In the evaluation of the integrals in (2) and (3), the primary spectrum of the gold target was obtained [3] by measuring the radiation scattered by a cellulose sample from 4.0 to 7.0 \AA . A graph describing μ_{Si} against λ for the same range was plotted from the Tables [2]. The functions to be integrated were then plotted and the areas determined graphically as 503 cm^2 and 377 cm^2 , respectively.

$$\text{Thus } \frac{I'_{Si}}{I''_{Si}} = 3.2 \frac{503}{377} = 4.3 \text{ A correct quantitative calculation}$$

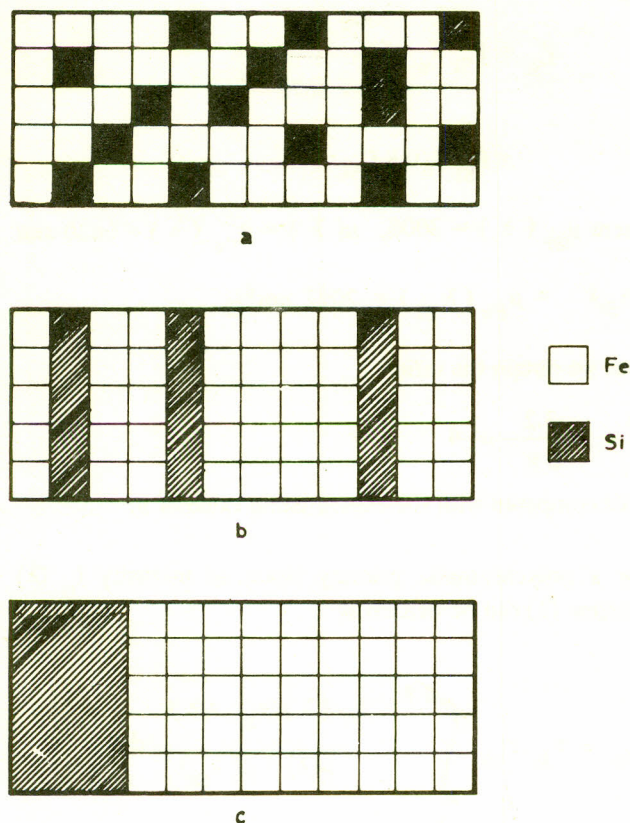


Fig. 2. Distributions of iron and silicon grains of equal size.

tion of the intensities requires not only a more accurate determination of the primary spectrum, but also knowledge of the grain size.

Although the grain size is probably smaller than the critical thickness so that the distribution a and b of Fig. 2 are not equivalent, but nevertheless the main portion of the intensity comes from a thin surface layer. If all the atoms in a pure silicon specimen are irradiated by the same primary beam, only 10% of the total intensity would come from silicon atoms at a greater depth than $30\mu\text{m}$. Since the primary radiation is also absorbed, the active layer is even thinner. Distributions a and b will thus be approximately equivalent. Thus, we may conclude that calibration curves obtained from samples prepared by mechanically mixing Fe and Si would generally give a significantly different slope than what we get for the case of alloyed samples.

EXPERIMENTAL DETAILS

Set (1). The accurately weighed silicon and iron powder mixtures were thoroughly mixed in a tungsten

carbide ball-mill grinder and pressed in a disc on cellulose backing with a pressure of 5 tons/cm^2 to form 2.5 cm dia tablets with a semi-smooth surface. Three tablets were prepared for each sample, to avoid heterogeneity effects.

Set (2). The mixtures of silicon (in the form of ingot polycrystalline) and iron rods (reference number JM 848 Specure Lab. Nr W7800) were melted in an arc furnace on water-cooled copperheath in argon atmosphere of pressure 40 KPa. The alloy buttons were flattened in a Plattner diamond mortar and cut by hand cutter into small pieces before ball-milling in the grinder. About 0.1 g of the ground material, in the form of tiny thin foils, was spread on a cellulose tablet of 2.5 cm dia and pressed at 5 tons/cm^2 , to give semi-smooth layer on a cellulose tablet.

The X-ray fluorescence intensity measurements were carried out on a Philips PW1410 manual vacuum spectrometer under the following conditions:

1. Au-radiation unfiltered at 45 kilovolts and 40 milliamperes.
2. Gas Flow proportional counter voltage = 1780 volts.
3. Window reading = 220 and Low Level reading = 300, corresponding to the acceptance of signals between 1.1 volts and 1.5 volts.
4. Pressure = 70–140 Pa.
5. Analysing crystal PENTA ERYTHRITOL (002), $2d = 8.742\text{ \AA}$
6. Collimator = coarse
7. Spinner = on
8. Fixed time = 100 s

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