

SILICON IN Fe-Si ALLOYS: CORRECTION OF X-RAY INTENSITIES FOR PREFERRED ORIENTATION

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A texture effect in the silicon phase of industrial Fe-Si alloys was noticed in the X-ray diffraction patterns through the reinforcement of the 111 reflection. A similar effect was also apparent in a commercial silicon standard pellet used as reference material and supposed to be texture-free.

A quick correction procedure to account for preferred orientation effects was developed, based on a previous algorithm currently applied for the automatic profile fitting of powder diffractometer data. "Modified Wilson plots" are established for visualizing the efficiency of texture correction according to the proposed method.

KEY WORDS: Silicon, preferred-orientation, ferrosilicon-alloys, X-ray diffraction, microstructure.

INTRODUCTION

Powdered samples for X-ray diffraction (XRD) analysis are seldom free from preferred orientation of the crystallites (texture) even when the material is cubic and the specimen is carefully prepared (Parrish and Huang, 1983; Will, Parrish and Huang, 1983; Schreiner and Kimmel, 1987; Will, Masciocchi, Parrish and Hart, 1987). Therefore, it was not surprising to notice a texture effect in silicon during a phase composition study of ferrosilicon alloys by XRD and scanning electron microscopy (SEM) (Margarido and Figueiredo, 1988; Margarido and Figueiredo, 1989).

In the case of ferrosilicon composites, it is important to ascertain the presence of such preferred orientation effect arising from non-equiaxed powder particles producing alignment during specimen preparation in XRD analysis. In fact, cleavage during powder production may possibly influence alloy behaviour during hydrometallurgical processing for silicon refining (Margarido, Figueiredo, Martins and Bastos, 1994).

A study was therefore undertaken to discern the preferred orientation plane and to evaluate the texture effect on silicon grains in industrial ferrosilicon alloys.

Table 1 Alloy composition.

Alloy	1	2
<i>Elements</i>	<i>Weight (%)</i>	
Si	75.59	80.22
Fe	20.83	16.19
Ca	1.05	0.97
Al	1.30	1.32
<i>Phase (normative)</i>	<i>Weight(%)</i>	
Silicon	54.8	63.3
"FeSi ₂ "	41.7	33.8
total	96.5	97.1

MATERIALS AND EXPERIMENTAL

Two different ferrosilicon alloys (nominally "75% Si", labelled 1 and 2) were studied, their chemical composition and normative phase constitution being listed in Table 1.

As Fe-Si alloys are quite friable, their manipulation and transportation gives rise to a fine fraction (powder) of material resulting from spontaneous disaggregation. This fraction, with a grain size less than 10 μ m, may present a texture effect differing from the remanent material, and consequently two size fractions were analysed from each ferrosilicon composite.

Samples from both fractions – coarse, $\phi > 10 \mu$ m, and fine, $\phi < 10 \mu$ m – were crushed and ground in an agate mortar to a grain size under 325 mesh and front-loaded into a cavity-type sample holder for XRD study.

Powder diffraction spectra were collected in a continuous scan mode using a non-automated Philips goniometer equipped with a curved graphite-crystal monochromator and fixed slits. A highly stabilized Philips PW 1732 generator was used with a broad focus copper tube operating at 50 kV, 40 mA.

For sake of comparison, a reference silicon powder pellet (Philips standard, assumed to be texture-free) was measured under the same instrumental conditions.

X-ray diffraction patterns of studied alloy samples (Figure 1) showed no significant differences concerning the major phases – silicon and α -FeSi₂ (tetragonal). However, detailed scans of coarse fractions revealed different contents of minor phases, namely CaSi, CaSi₂, β -FeSi₂ (orthorhombic), CaAl₂Si_{1.5} and Al-Fe-Si, beyond a quaternary defective phase structurally akin to α -FeSi₂ named CAALSIFER (Margarido and Figueiredo, 1988).

Typical SEM micrographs are reproduced in Figure 2 showing a dominating silicon phase with the form of elongated large grains in a matrix of iron disilicide and concentrations of chemically heterogeneous phase aggregates.

Globules of α -FeSi₂ are frequently retained inside the Si grains which quite often present sharp linear boundaries.

For the measurement of diffracted intensities, low-speed scans ($1/4^\circ 2\theta \cdot \text{min}^{-1}$) of silicon X-ray reflections were graphically recorded under carefully optimized instrumental conditions. Three records were performed in order to improve statistics. Intensity data were obtained by weighing the recording paper subtended under each diffraction peak, after suppressing the background contribution.

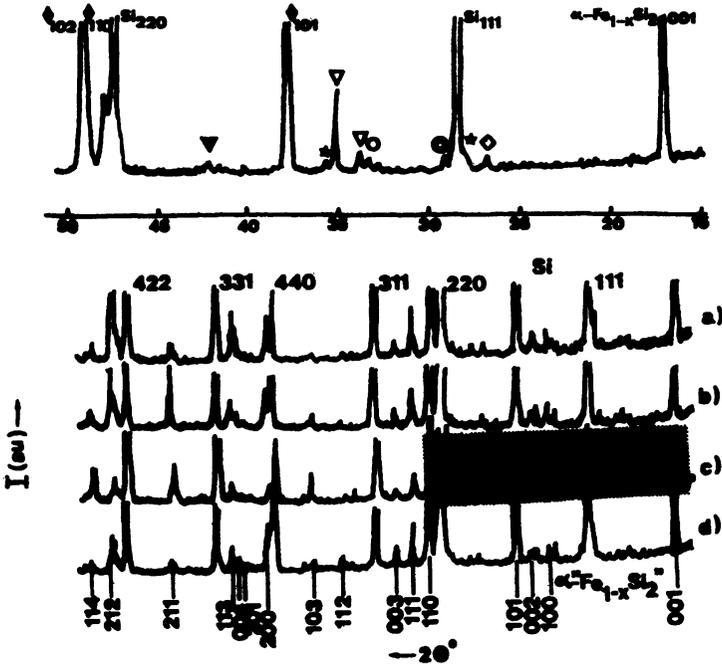


Figure 1 X-ray diffraction powder patterns (Cu $K\alpha$ radiation) of alloy 1 (a and b) and alloy 2 (c and d) respectively, coarse and fine fractions. Detailed scan of X-ray diffraction spectra (Cu $K\alpha$ radiation) of industrial ferrosilicon composites (coarse fraction). Identification of phases are indicated: $CaSi_2$ - ∇ ; $CaSi$ - ∇ ; $CaAl_2Si_{1.5}$ - \star ; $Al-Fe-Si$ - \circ ; $\alpha-Fe-x-Si_2$ - \diamond ; $\beta-FeSi_2$ - \bullet ; SiO_2 - \diamond .

THEORETICAL APPRAISAL

The correction for preferred orientation of the crystallites in a powder specimen is made along with the calculation of integrated diffraction-line intensities when applying the Rietveld method for data processing. In single-phase substances, the application of automatic profile fitting procedures has been very successful for structural characterization purposes, namely, for extracting information on elemental ordering schemes, assessing residual stresses and evaluating the crystallinity degree and the extension of the ordered (crystalline) domains in quite amorphous solids. The validity of applying such analytical procedure critically depends on careful sample preparation, particularly for assuring that surface roughness and porosity are significantly reduced. Additional difficulties arise when working on composites. Constraints induced by phase formation under solid state reaction or simultaneous crystallization from the melt, may hinder a correct structural interpretation of diffracted intensities through automatic data processing. Subtraction of intensity contributions from overlapping reflections in multi-phase substances may further compromise the accuracy of derived results. As a

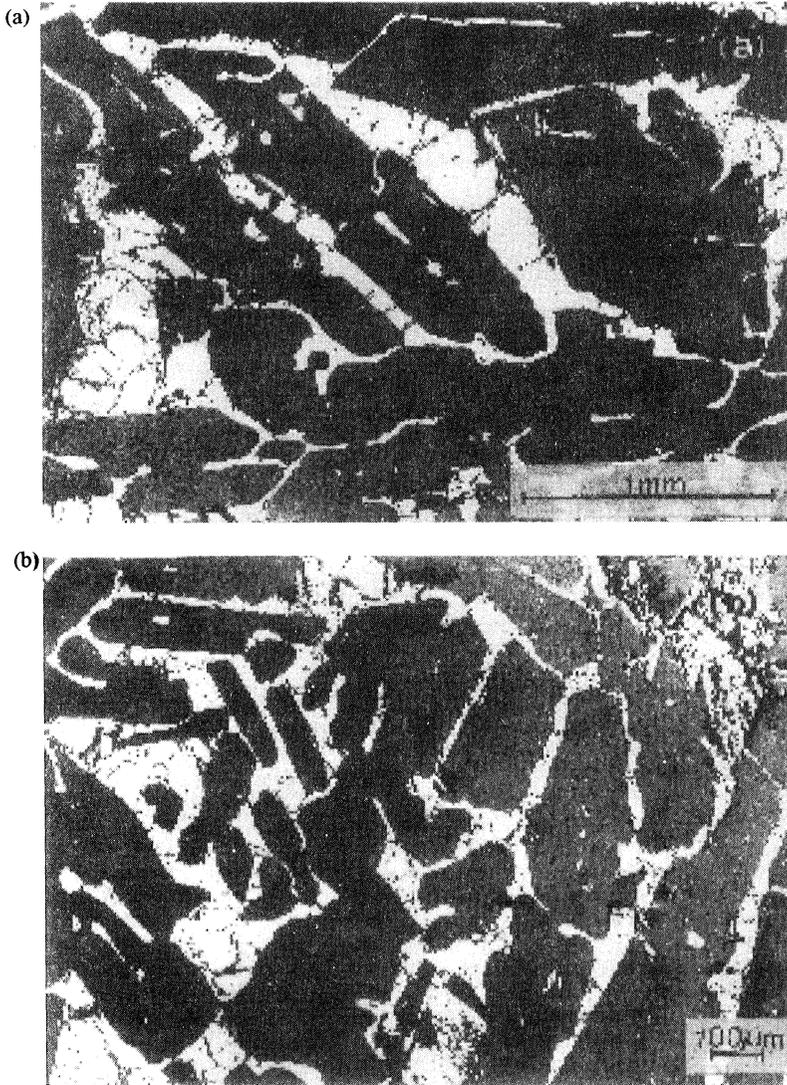


Figure 2 SEM/EDS micrographs of ferrosilicon composites. Left, general view showing large elongated silicon grains in a matrix of $\alpha\text{-Fe}_{17}\text{Si}_2$; (a) alloy 1; (b) alloy 2. Right, clusters of minor phases in samples 1(c) and 2(d). Chemical elements in the phases: 1) Si, Ca, Al; 2) Si; 3) Si, Ca; 4) Al, Si, Ca, Fe; 5) Si, Fe, Al; 6) Al, Si, Ca, Fe, Mg; 7) Al, Si, Ca, Ni, Cu.

consequence, hand-made calculations will become useful and profitable in particularly disadvantageous cases, like the ferrosilicon composites (Margarido and Figueiredo, 1988).

Because the absolute value of diffracted intensities is beyond experimental access, various attempts were made to establish a derivation method concerning the scale factor for correcting intensity data collected with powder diffractometers. If no preferred orientation effects are noticed, the scaling parameter can be deduced as shown by Wilson (1942), that is, by plotting the ratios of the experimental intensities (I) versus the corresponding calculated values (I_c) expressed in a logarithmic scale, against the angular variable ($\sin^2 \theta/\lambda$); the intercept of the resulting straight line on the $\ln(I/I_c)$ axis will be the value of the scale factor while the slope of the graph gives the isotropic Debye-Waller or temperature factor.

Jarvinen, Merisalo, Pesonen and Inkinen (1970) developed a correction procedure to account for the preferred orientation of crystallites in cubic powders based upon the examination of the polar axis density distribution; however, the attachment of a texture goniometer is required for data collection. For the Bragg-Brentano powder diffractometer alone, Valvoda (1987) has established a linear regression method for intensity rescaling in quantitative phase analysis, based on the above reported "Wilson plots" and requiring the previous knowledge of the relative intensities collected from a random specimen.

Silicon samples are very seldom free from texture (Parrish and Huang, 1983) and the disturbing effect of preferred orientation on diffracted intensities may occasionally be magnified by the crystallite sizes. Despite the efforts to produce a reference powdered material (Hubbard, Swanson and Mauer, 1975), such a silicon standard is not easily available. For silicon hosted by composites, it is furthermore necessary to ascertain if the actual texture effect is confined to the usual $\langle 111 \rangle$ orientation. However the identification of the so-called "preferred orientation plane" can only be performed by trial.

The quick procedure developed for hand-performing the estimation and correction of texture effects in silicon is based on the recognized fact that texture can be described by a simple function expressing the orientation alignment probability in terms of angular distances between any crystal direction and a reference one. The simplified exponential expression due to Will, Parrish and Huang (1983) is used,

$$I_{cor} = I_{obs} \bullet \exp [-G (\pi/2 - \alpha)^2] \quad (1)$$

where G is called the "preferred orientation parameter" and α (expressed in radians) is the acute angle between the diffracting plane with indices (h, k, l_i) and the selected preferred orientation plane $(h_0 k_0 l_0)$:

$$\alpha = \theta_{h, k, l_i} - \theta_{h_0 k_0 l_0} \quad (2)$$

In order to overcome the difficulty of simultaneously deducing the scale factor, the isotropic temperature factor and the preferred orientation parameter, a modified version of Valvoda's analytical procedure (Valvoda, 1987) was developed. Instead of single experimental intensity data, collected on a random specimen as used by the latter author, ratios of the actual silicon diffracted intensities [I_{obs}] against the published intensity values [I_{rand}] from a reference material (Will, Parrish and Huang, 1983) are applied.

Because such standard is practically texture-free ($G_{111} = 0.06$), from equation (1)

$$I_{rand - cor} = I_{rand - obs} \bullet \exp [-0.06 (\pi/2 - \alpha)^2] = I_{rand} \quad (3)$$

Assuming that the isotropic temperature factor is approximately constant for silicon in industrial ferrosilicon alloys produced according to a fixed technology, the ratios $[I_{obs}/I_{rand}]$ will only depend on the degree of preferred orientation of the silicon phase in those composites. Indeed, after correcting for texture effects, the intensities actually diffracted by an industrial silicon sample $[I_{cor}]$ can be adequately rescaled (up or down) to the corresponding intensity values published for the reference material:

$$I_{cor} = S \cdot I_{rand} \tag{4}$$

Then, again from equation (1):

$$S \cdot I_{rand} = I_{obs} \cdot \exp [-G (\pi/2 - \alpha)^2] \tag{5}$$

that is,

$$I_{obs}/I_{rand} = S \cdot \exp [G (\pi/2 - \alpha)^2] \tag{6}$$

A graphical representation of I_{obs}/I_{rand} in a logarithmic scale against the squared angular hkl -dependent variable $[\pi/2 - \alpha]$ in radians will give the G-parameter (slope of the resulting straight line) and the approximate value of the scaling factor relatively to the reference material (intercept on the Y-axis), as illustrated in Figure 3.

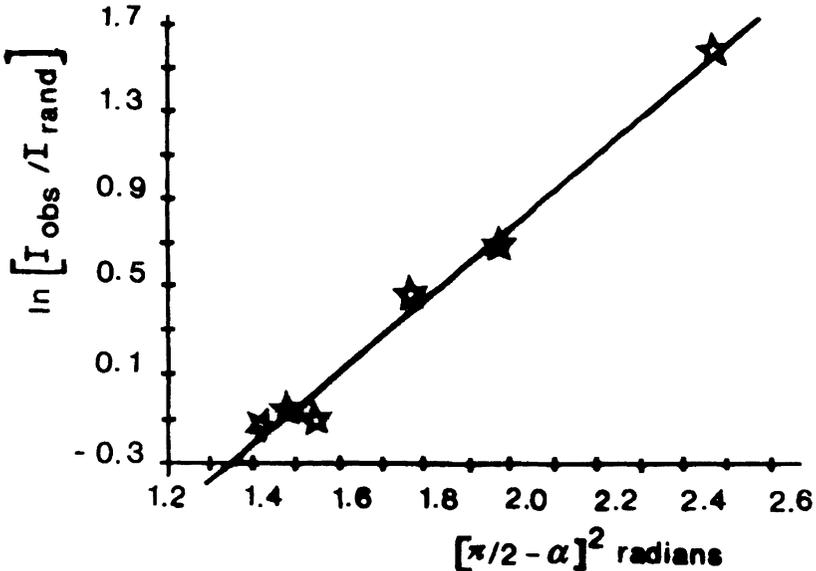


Figure 3 Graphical plotting of $\ln [I_{obs}/I_{rand}]$ vs $[\pi/2 - \alpha]^2$ (in radians) for deducing G-parameter illustrated through fine fraction of alloy 1.

MODIFIED WILSON PLOTS

The correction of diffracted intensities, I_{obs} , through the derived G_{hkl} parameter in order to obtain I_{cor} must be performed even when a small deviation from a completely random distribution of the crystallites is noticed.

A modification of the usual "Wilson plots" for deducing the temperature and the scale factors was devised in order to visualize the efficiency of the preferred orientation correction. Two sets of differentials (Δ_{obs} and Δ_{cor}) are plotted versus the angular variable $[(\sin \theta/\lambda)^2]$. The first set (Δ_{obs}) represents the differences between the value of $[\ln I_{obs}/I_{rand}]$ for each individual reflection $h_i k_i l_i$ and the corresponding mean value, excluding the preferred-orientation reflection $h_0 k_0 l_0$. The second set (Δ_{cor}) is obtained in a similar way but now considering the intensity values after correction according to the *a-priori* selected preferred orientation plane and taking into account all the observed reflections ($h_i k_i l_i$ plus $h_0 k_0 l_0$).

When plotting these differentials for one silicon sample in the same graph, the values Δ_{obs} will be spread relatively to an horizontal line (constant value) with a peak or deviation maximum for the preferred-orientation reflection. Conversely, the distribution of Δ_{cor} values is expected to approach linearity and converge towards a minimum value.

A measure of the efficiency in correcting for texture is displayed by such plot through the relative trend for alignment of the differentials after preferred-orientation correction as illustrated later on (see Figure 4).

RESULTS AND DISCUSSION

Normalized diffracted intensities for six silicon reflections in the two studied alloys, prior and after correcting for preferred orientation according to a calculated G_{hkl} parameter, are listed in Table 2, along with the published values for the reference material and the experimental data from a Philips standard silicon pellet. The experimental value $G = 0.34$ (Table 2) clearly indicates that the Philips standard silicon pellet is not free from texture along $\langle 111 \rangle$ as it might be.

The more common preferred orientation direction detected in the present experiments is $\langle 111 \rangle$, as usual for silicon in industrial ferrosilicon alloys. However, the texture effect is less pronounced in alloy nr. 2 (richer in silicon phase) when comparing to

Table 2 Normalized diffracted intensities for silicon, before (a) and after (b) correction.

<i>hkl</i>	Powder (*) NBS 640a $G_{111} = 0.06$		Philips Standard $G_{111} = 0.34$		Alloy 1 $\phi < 10 \text{ mm}$ $G_{111} = 1.66$		Alloy 1 $\phi > 10 \text{ mm}$ $G_{111} = 0.44$		Alloy 2 $\phi < 10 \text{ mm}$ $G_{111} = 0.84$		Alloy 2 $\phi > 10 \text{ mm}$ $G_{331} = 0.45$	
	(a)	(b)	(a)	(b)	(a)	(b)	(a)	(b)	(a)	(b)	(a)	(b)
111	100	100	100	100	100	100	100	100	100	100	100	100
220	59	60	40	47	24	54	20	25	17	26	42	35
311	35	37	27	34	12	37	14	19	9	17	39	30
400	9	9	6	8	2	9	3	4	5	11	6	4
331	14	15	10	15	3	14	13	20	8	18	28	17
422	21	22	13	19	4	22	8	12	7	16	32	21

*Data from Will, Parrish and Huang (1983).

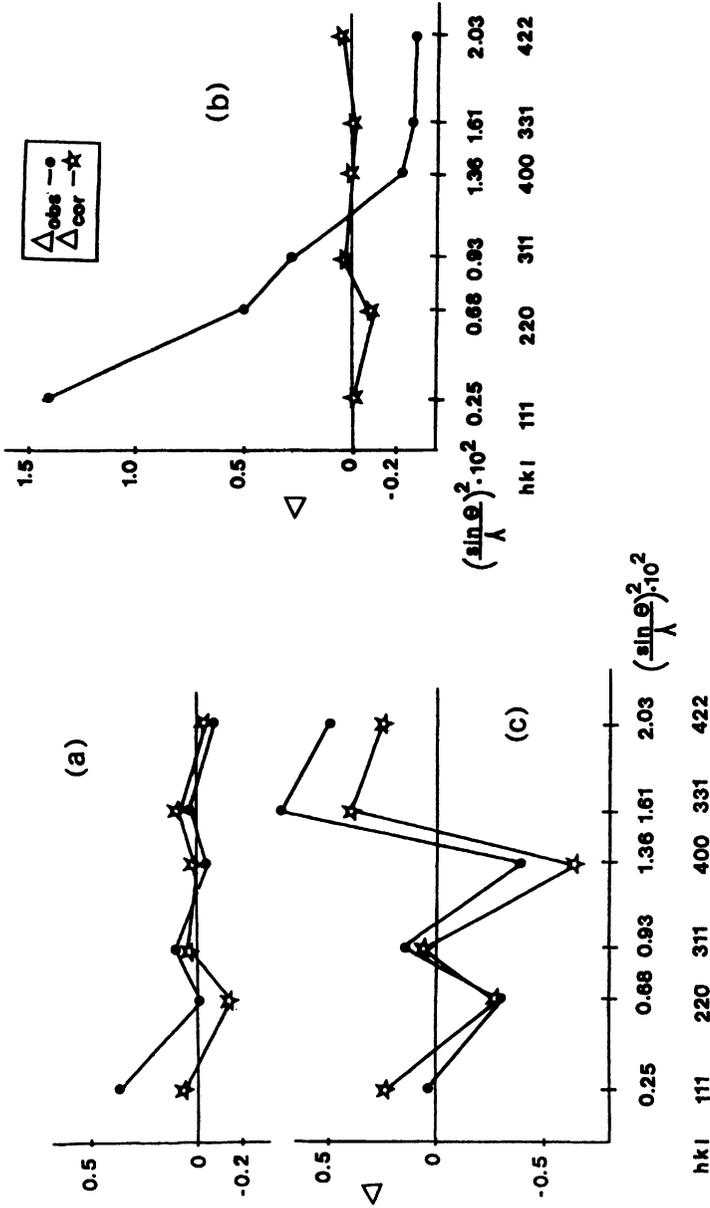


Figure 4 "Modified Wilson-plots" for: (a) Philips silicon standard and (b) fine fraction of alloy 1, both textured along $\langle 111 \rangle$, and (c) coarse fraction of alloy 2, with preferred-orientation along $\langle 331 \rangle$.

Table 3 Residuals Δ_{obs} and Δ_{cor} .

	$(\sin \theta/\lambda)^2$	Alloy 1				Alloy 2					
		Philips Standard		$\phi < 10 \text{ mm}$		$\phi > 10 \text{ mm}$		$\phi < 10 \text{ mm}$		$\phi > 10 \text{ mm}$	
		Δ_{obs}	Δ_{cor}	Δ_{obs}	Δ_{cor}	Δ_{obs}	Δ_{cor}	Δ_{obs}	Δ_{cor}	Δ_{obs}	Δ_{cor}
111	0.02543	0.365	0.063	1.407	0	0.860	0.468	0.978	0.217	0.044	0.227
220	0.06781	-0.007	-0.142	0.506	-0.08	-0.193	-0.433	-0.235	-0.583	-0.300	-0.301
311	0.09324	0.097	0.034	0.292	0.05	-0.048	-0.213	-0.339	-0.503	0.148	0.053
400	0.13562	-0.037	-0.003	-0.223	0.01	-0.368	-0.411	0.389	0.467	-0.385	-0.628
331	0.16105	0.032	0.075	-0.283	0	0.720	0.748	0.343	0.437	0.722	0.392
422	0.20343	-0.084	-0.028	-0.29	0.05	-0.111	-0.158	-0.159	-0.033	0.491	0.255

alloy nr.1, and also from fine to coarse fractions in both alloys. Furthermore, the coarse fraction of alloy 2 had to be corrected for texture along $\langle 331 \rangle$ instead of $\langle 111 \rangle$. It is also noteworthy that texture correction may occasionally be less efficient (e.g., in the coarse fraction of alloy 1 and fine fraction of alloy 2).

Modified Wilson plots – based on Δ_{obs} and Δ_{cor} , as listed in Table 3 – are illustrated in Figure 4 for the Philips silicon standard, for the fine fraction of alloy 1 and for the coarse fraction of alloy 2, before and after correcting for preferred orientation effect. The minimization of the residuals Δ (or linearization effect) resulting from preferred orientation correction is evident in Figure 4b. Indeed, texture was remarkably accounted for by the correction procedure in the case of alloy 1, fine fraction – just the sample presenting the highest degree of texturing along $\langle 111 \rangle$. Conversely, the standard silicon pellet shows only incipient texturing along the same direction, as clearly displayed by Figure 4a.

The results obtained so far prove the efficiency of the proposed procedure in assigning the preferred orientation plane and correcting for texture effects in the silicon phase hosted by industrial ferrosilicon composites.

The validity of the described method stands on the assumption that the isotropic temperature factor remains approximately constant for all the samples and its reliability when extended to cubic phases other than silicon depends on the availability of suitable, texture-free reference materials.

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