



# Mechanical alloying of Fe–Si and milling of $\alpha$ - and $\beta$ -FeSi<sub>2</sub> bulk phases

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## ABSTRACT

Iron disilicide synthesis by mechanical alloying was performed.  $\epsilon$ -FeSi,  $\alpha$ -Fe<sub>1-x</sub>Si<sub>2</sub>, amorphous FeSi<sub>2</sub> were formed with relative intensities depending on the milling period.  $\beta$ -FeSi<sub>2</sub> phase was formed after annealing the gridded powder at the temperature where this phase is stable. Mössbauer spectroscopy and X-ray diffraction methods were applied to determine the different phases formed. The morphology of the resulting particles was observed by high resolution scanning electron microscopy. The effect of the milling on bulk iron–silicide samples was and studied chemical effects of the ball milling on Fe–Si<sub>2</sub> systems have been studied.

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## 1. Introduction

The combination of pressure and shear in solids creates mechanical effect and plays a key role in solid state physics and chemistry. Earlier, the mechanical alloying of iron and silicon were studied in case of low silicon concentration [1,2]. Recently, the Si/Fe component ratio was increased up to 70/30 [3,4]. After milling different iron–silicide phases were formed depending on the milling methods applied. Up till now, no systematic studies were performed on the relative intensities of the different phases depending on the milling periods. Also no final “equilibrium state” could be determined. Mostly X-ray diffraction method was applied to determine the structures.

Our aim was to determine the phases formed after long time mechanical alloying of Fe 2Si powders and synthesize  $\beta$ -FeSi<sub>2</sub> phase. Also, the effect of milling on stable phases of  $\alpha$ -Fe<sub>0.8</sub>Fe<sub>2</sub> and  $\beta$ -FeSi<sub>2</sub> were studied. Mössbauer spectroscopy is a very sensitive method to observe the changes of the short range structure of iron containing materials and recognize the different phases formed. Therefore, Mössbauer spectroscopy, X-ray diffraction and electron microscopy methods have been applied simultaneously to

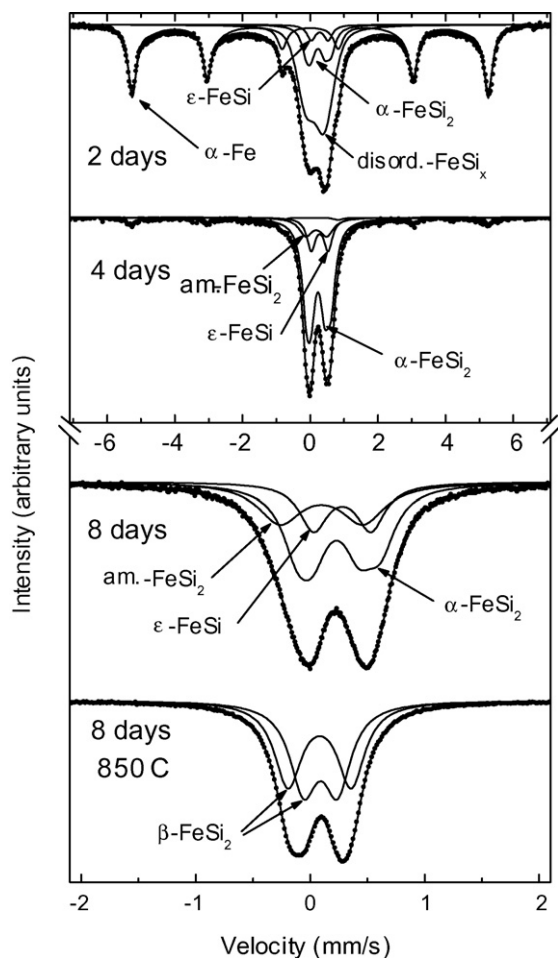
determine the phases and grain sizes after the different mechanical treatments depending on the milling time.

## 2. Experimental details

Iron and silicon were properly cleaned for mechanical alloying. Fe powder with a purity of 4N was heated in pure H<sub>2</sub> atmosphere at 900 K for 10 h to reduce some oxide layers possibly formed on the surface. Si crystals of high purity were immersed in 5 at. percent HF aqueous solution to remove any oxide layer on their surface. Bulk  $\alpha$ -Fe<sub>0.8</sub>Si<sub>2</sub> was synthesized by induction melting the components in water cooled copper crucible. Bulk  $\beta$ -FeSi<sub>2</sub> was also synthesized by melting Fe and Si in stoichiometric quantity in induction oven and then annealed at 1143 K being stable at this temperature. The mechanical milling of Fe powder and Si granulate in atomic ratio of 1:2 (denoted by Fe 2Si) was carried out in a vibrating frame single ball vial using a hardened steel ball (60 mm diameter, 870 g) that oscillates on the top of a 70-mm diameter, 5-mm thick hardened steel bottom plate. The oscillation frequency of the vibrating table was 50 Hz. The amplitude of the ball movement was 1–6 mm, and the frequency was 14–33 Hz. The vial was continuously pumped during milling by a turbomolecular pump system. The typical pressure in the vial was  $3 \times 10^{-6}$  mbar. For this arrangement 1 g powder charge was used to get high enough milling intensity and low impurity concentration. For X-ray diffraction and electron microscopy measurements the powders were used just as were obtained after milling. Transmission Mössbauer measurements were carried out by using a conventional constant acceleration-type spectrometer. For the analysis of the spectra, a least-squares fitting program was used. Also, using this program, spectra with histogram distributions of parameter values could be fitted. Spectra with quadrupole splitting distributions were fitted by 35 subspectra. The linear correlation of the quadrupole splitting with isomer shift was included. The isomer shift values are given relative to that of  $\alpha$ -Fe at room temperature. A STOE STADI-P system with germanium monochromatized MoK $\alpha$  radiation and a position sensitive detector

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**Fig. 1.** Mössbauer spectra of the alloyed and annealed Fe 2Si sample measured at 300 K.

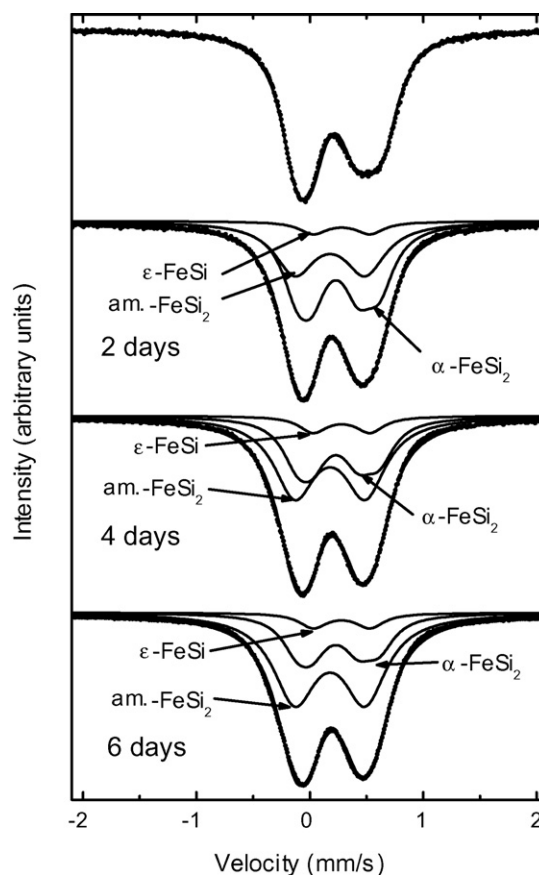
with 6° aperture in transmission mode was used for X-ray powder diffraction measurements.

For study of the sample topography a Philips XL 30 FEG high resolution scanning electron microscope was used.

### 3. Results

The Mössbauer spectra of the ball milled Fe 2Si alloyed and annealed samples are shown in Fig. 1.

The intensity of the spectral components shows that the relative intensity of the resulting phases between Fe and Si strongly depends on the milling time. The obtained spectra showed the formation of four different iron–silicide components. Among these components disordered  $\text{FeSi}_x$  and  $\epsilon\text{-FeSi}$  appeared.  $x$  means that the composition is not exactly known. Other components appear for longer milling time with higher relative intensities. Their hyperfine parameters are in good agreement with literature values published earlier [5,6] for amorphous  $\text{FeSi}_2$  and [7,8] for  $\epsilon\text{-FeSi}$ . At longer milling period, the relative intensity of  $\alpha\text{-FeSi}_2$  further increased.  $\alpha\text{-FeSi}_2$  shows an asymmetric doublet similar to that published earlier [9]. The analysis of this spectrum is presented in next caption.  $\beta\text{-FeSi}_2$  was formed after annealing the milled sample at 1120 K for 10 days. The spectrum shows two doublets with parameter values agreeing to those published in Ref. [10] Recently, we have implanted crystalline  $\beta\text{-FeSi}_2$  by  $\text{Kr}^+$  ions with an energy of 130 keV by  $1.5 \times 10^{17}$  ions/ $\text{cm}^2$  fluence to produce an amorphous surface layer on its surface and measured the Mössbauer spectrum by CEMS. The hyperfine parameters were in good agreement with

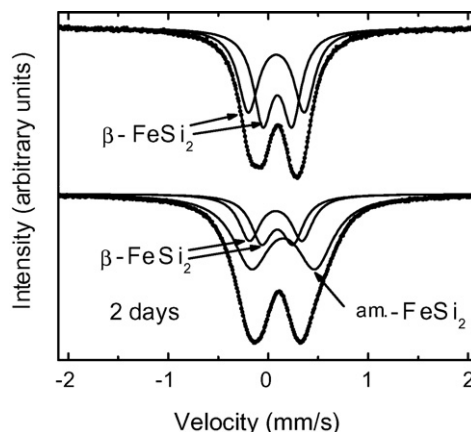


**Fig. 2.** Mössbauer spectra of milled  $\alpha\text{-Fe}_{0.8}\text{Si}_2$ .

the values published in Refs. [5,6]. The measured parameters are included in Table 1 (last line). In the tables, the  $\alpha$  phases are shown as  $\alpha\text{-FeSi}_2$ . The correct compositions may be different as it will be explained in the next caption.

The  $\alpha\text{-Fe}_{0.8}\text{Si}_2$  and  $\beta\text{-FeSi}_2$  stable phases were milled and the obtained spectra are shown in Figs. 2 and 3.

The hyperfine parameter values are compiled in Table 2. In the complex doublet spectrum  $\epsilon\text{-FeSi}$  and amorphous  $\text{FeSi}_2$  were formed. The relative intensity of the latter phase increased with longer time of milling. In order to get more information on the milling effect X-ray diffraction measurements were performed on the samples with different compositions. In Fig. 4, the X-ray diffraction patterns of Fe 2Si alloyed sample is shown. The same and



**Fig. 3.** Mössbauer spectra of milled  $\beta\text{-FeSi}_2$ .

**Table 1**

Mössbauer parameters of milled Fe 2Si sample measured at room temperature. Isomer shift ( $\delta$ ), quadrupole splitting (QS), standard deviation of QS (STD) in mm/s, internal magnetic field in Tesla, width (W) in mm/s and relative intensities in percent. Average values are denoted by <>.

Milling days	Component	$\delta$	QS	STD QS	$B_{hf}$	W	Rel. int.
2	$\alpha$ -Fe	0.01(1)	0.00(1)		32.0(2)	0.37(2)	47.4(3)
	$\varepsilon$ -FeSi	0.28(1)	0.49(1)			0.30(2)	3.7(2)
	Disord.-FeSi <sub>x</sub>	<0.15>	<0.54>	0.29(1)		0.26	37.4(3)
	$\alpha$ -Fe <sub>0.8</sub> Si <sub>2</sub>	<0.23>	<0.58>	0.19(1)		0.26	11.5(2)
4	$\alpha$ -Fe	0.01(1)	0.00(1)		32.0(2)	0.37(2)	7.7(2)
	$\varepsilon$ -FeSi	0.28(1)	0.49(1)			0.30(2)	14.3(2)
	Am.-FeSi <sub>2</sub>	<0.18>	<0.56>	0.16(1)		0.26	12.4(2)
	$\alpha$ -Fe <sub>0.8</sub> Si <sub>2</sub>	<0.23>	<0.58>	0.19(1)		0.26	65.6(3)
8	$\varepsilon$ -FeSi	0.28(1)	0.49(1)			0.30(2)	22.6(2)
	Am.-FeSi <sub>2</sub>	<0.18>	<0.56>	0.16(1)		0.26	58.4(3)
	$\alpha$ -Fe <sub>0.8</sub> Si <sub>2</sub>	<0.23>	<0.58>	0.19(1)		0.26	19.0(2)
8 Annealed 1120K	$\beta$ -FeSi <sub>2</sub> a	0.08(1)	0.53(1)			0.28(1)	50.0(1)
	$\beta$ -FeSi <sub>2</sub> b	0.09(1)	-0.32(1)			0.28(1)	50.0(1)
Implanted	Am.-FeSi <sub>2</sub>	<0.18>	<0.56>	0.16(1)		0.26	100.0

**Table 2**

Mössbauer parameters of milled  $\alpha$ -Fe<sub>0.8</sub>Si<sub>2</sub>,  $\beta$ -FeSi<sub>2</sub> and amorphous FeSi<sub>2</sub> samples measured at room temperature. Isomer shift ( $\delta$ ), quadrupole splitting (QS), standard deviation of QS (STD) in mm/s, width (W) in mm/s and relative intensities in percent. Average values are denoted by <>.

Sample	Milling days	Component	$\delta$	QS	STD QS	W	Rel. int.	
$\alpha$ -FeSi <sub>2</sub>	0	$\alpha$ -FeSi <sub>2</sub>	<0.23>	<0.58>	0.19(1)	0.26	100.0	
	2	$\varepsilon$ -FeSi	0.28(1)	0.49(1)		0.30(2)	6.1(2)	
		Am.-FeSi <sub>2</sub>	<0.18>	<0.56>	0.16(1)	0.26	36.3(3)	
	4	$\alpha$ -Fe <sub>0.8</sub> Si <sub>2</sub>	<0.23>	<0.58>	0.19(1)	0.26	57.6(3)	
		$\varepsilon$ -FeSi	0.28(1)	0.49(1)		0.30(2)	7.7(2)	
		Am.-FeSi <sub>2</sub>	<0.18>	<0.56>	0.16(1)	0.26	54.9(3)	
	6	$\alpha$ -Fe <sub>0.8</sub> Si <sub>2</sub>	<0.23>	<0.58>	0.19(1)	0.26	37.4(3)	
		$\alpha$ -FeSi	0.28(1)	0.49(1)		0.30(2)	7.0(2)	
		Am.-FeSi <sub>2</sub>	<0.18>	<0.56>	0.16(1)	0.26	62.6(3)	
	$\beta$ -FeSi <sub>2</sub>	0	$\beta$ -FeSi <sub>2</sub> a	0.08(1)	0.53(1)		0.28(1)	50.0(1)
		0	$\beta$ -FeSi <sub>2</sub> b	0.09(1)	-0.32(1)		0.28(1)	50.0(1)
		2	$\beta$ -FeSi <sub>2</sub> a	0.08(1)	0.53(1)		0.28(1)	21.6(2)
$\beta$ -FeSi <sub>2</sub> b			0.09(1)	-0.32(1)		0.28(1)	21.6(2)	
Am.-FeSi <sub>2</sub>			<0.18>	<0.56>	0.16(1)	0.26	56.8(3)	
6		$\beta$ -FeSi <sub>2</sub> a	0.08(1)	0.53(1)		0.28(1)	21.2(2)	
		$\beta$ -FeSi <sub>2</sub> b	0.09(1)	-0.32(1)		0.28(1)	21.2(2)	
		Am.-FeSi <sub>2</sub>	<0.18>	<0.56>	0.16(1)	0.26	57.6(3)	

milling time dependence were observed as measured by Mössbauer spectroscopy.

The diffraction patterns of milled  $\alpha$ -Fe<sub>0.8</sub>Si<sub>2</sub> and  $\beta$ -FeSi<sub>2</sub> are shown on Figs. 5 and 6, respectively. In Fig. 5,  $\alpha$ -FeSi<sub>2</sub> and  $\varepsilon$ -FeSi appear. In Fig. 6,  $\beta$ -FeSi<sub>2</sub> is present.

From the elevated base-line intensities in the last two figures the formation of amorphous FeSi<sub>2</sub> can be concluded. The lines shown in the figures are in good agreement with those published earlier in the literature,  $\alpha$ -Fe<sub>0.8</sub>Si<sub>2</sub>: [11],  $\beta$ -FeSi<sub>2</sub>: [12],  $\varepsilon$ -FeSi: [13]. The SEM image of the alloyed powder (Fig. 7) shows

agglomerated grains with typical diameter between 100 and 500 nm.

#### 4. Discussion

After mechanical alloying of Fe 2Si powders for 2 days the <sup>57</sup>Fe Mössbauer spectrum shows considerable changes. In the center region of the velocity a broad doublet-like component appears. This component can be fitted by three doublets of  $\varepsilon$ -FeSi,  $\alpha$ -Fe<sub>1-x</sub>Si<sub>2</sub> and

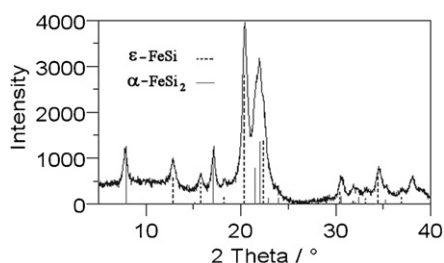


Fig. 4. X-ray diffraction pattern of Fe 2Si powder alloyed for 8 days.

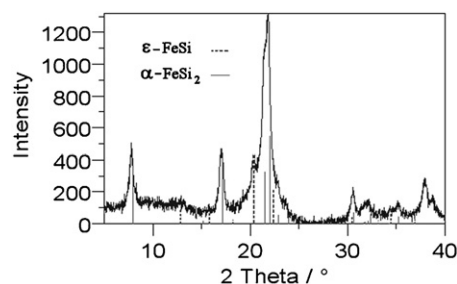


Fig. 5. X-ray diffraction pattern of  $\alpha$ -Fe<sub>0.8</sub>Si<sub>2</sub> milled for 6 days.

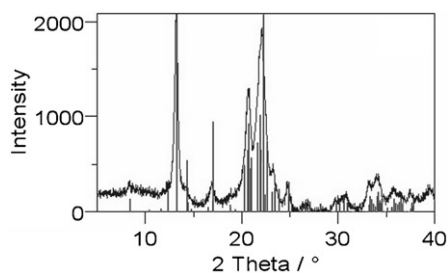


Fig. 6. X-ray diffraction pattern of  $\beta$ -FeSi<sub>2</sub> milled for 6 days.

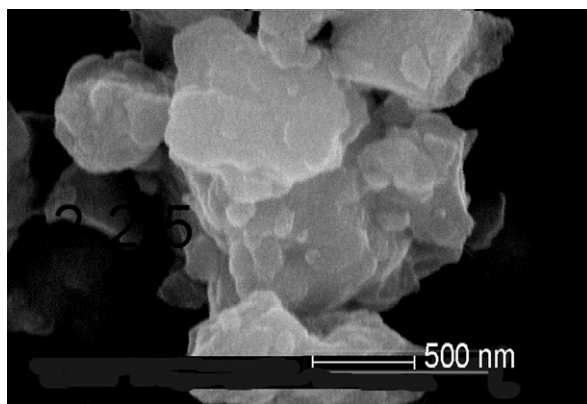


Fig. 7. SE image of the Fe 2Si powder milled for 8 days.

disordered FeSi<sub>2</sub>. After milling times of four and 8 days, the relative intensities of these components are increased.  $\alpha$ -FeSi<sub>2</sub>,  $\epsilon$ -FeSi and a third component with the characteristic hyperfine parameter of amorphous FeSi<sub>2</sub> can be identified. Considering the Si-Fe phase diagram, the  $\epsilon$ -FeSi phase has the maximum heat formation value as calculated in Ref. [14]. It is interesting to notice that  $\alpha$ -FeSi<sub>2</sub> phase appears in spite of the fact that it is stable at higher temperatures (between 1208 and 1496 K) than the  $\beta$ -FeSi<sub>2</sub> phase which is stable below 1208 K [15]. It is known that mechanical alloying is not an equilibrium process. In the case of metals lamellae in brittle crystals fragments are forming during the milling. Between the component atoms cold welding and friction chemical reaction take place [16,17]. The brittle small fragments of Si react with the ductile iron and form finally complete Fe-silicide phases. The crystal structure of  $\alpha$ -FeSi<sub>2</sub> is tetrahedral ( $P/mmm.D_{4h}^1$ ) and can be derived from the fluorite type lattice. The main feature is the completeness of the Si sublattice and the presence of a large number of equilibrium structural vacancies at the iron sites [18]. These vacancies are filled by Si atoms. The hyperfine parameter values depend on the composition. The iron content can decrease within the range of ~20 percent. The correlation between the hyperfine parameters and the composition was determined [19]. The applied method was used to analyze the vacancy filling by Si atoms resulting in asymmetric broad doublet spectra appearing always in this phase as it was also observed by us. Our spectrum was fitted applying a histogram distribution and obtained single doublet with parameter distribution. The average hyperfine parameters are included in Table 1. The obtained values indicate composition close to Fe<sub>0.8</sub>Si<sub>2</sub>. Increasing milling time reduces the particle size and increases the intensity of the amorphous component. This finding was confirmed

by X-ray diffraction. The FWHM of the reflections are increased due to a smaller particle size and the background is increased due to a larger amorphous content. After annealing the gridded powder it transformed to orthorhombic  $\beta$ -FeSi<sub>2</sub> at the temperature where this phase is stable. This material can be compressed and annealed to get different shapes and can be used for practical purposes e.g for thermocouple production which is concerned as a promising material for thermoelectric devices [20].

Milling the  $\alpha$ -Fe<sub>0.8</sub>Si<sub>2</sub> phase, some  $\epsilon$ -FeSi appears but mostly the intensity of the amorphous phase increases depending on the period of milling. The reason is that the  $\alpha$  phase contains atomic disorder and forms preferably amorphous structure by forming more disorder and decreasing the powder particle size. The milling of bulk particles of  $\beta$ -FeSi<sub>2</sub> results in some amorphous FeSi<sub>2</sub>.

## 5. Conclusions

Iron disilicide synthesis was observed by applying mechanical alloying.  $\epsilon$ -FeSi,  $\alpha$ -Fe<sub>1-x</sub>Si<sub>2</sub>, amorphous FeSi<sub>2</sub> were formed their relative intensities depend on the milling period. The SE image showed small particle and laminated structures, which have been formed after milling the Fe 2Si powder for long time period.  $\beta$ -FeSi<sub>2</sub> phase was formed after annealing the gridded powder at the temperature where this phase is stable. The total quantity of the alloyed powder was transformed to this phase. Bulk  $\alpha$ -Fe<sub>0.8</sub>Si<sub>2</sub> and  $\beta$ -FeSi<sub>2</sub> phases were also milled. In this case of  $\alpha$ -Fe<sub>0.8</sub>Si<sub>2</sub>,  $\epsilon$ -FeSi and amorphous phases were formed. No  $\beta$ -FeSi<sub>2</sub> was observed after milling. The milling of pure  $\beta$ -FeSi<sub>2</sub> resulted partly in amorphous FeSi<sub>2</sub>.

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