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In many applications at high temperature, the semiconducting compound β - $Fe Si_2$ has been already proposed for power generation. The goal of this part of the study is to obtain pure semiconducting (β) - $Fe Si_2$ phase as a material of reference for thermoelectric properties.

To start with, we elaborated the material, by the melting of elemental Iron and Silicon powders at 1250 °C and the transition of the metallic (α) to semiconducting (β) phase is obtained by annealing. This classical preparation of β - $Fe Si_2$ was time consuming and because of the phase diagram results in the production of inhomogeneous alloys.

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We then considered mechanical alloying as an alternate method of producting β - Fe Si_2. This method for elaborating the compound from lower temperature must avoid the difficulties of sublimation and evaporation of the components. It also allows the optimization of β - Fe Si_2.

We compare the results of the two elaborating methods by x-ray diffraction measurements. These results on β - Fe Si_2 obtained by mechanical alloying, as far we know, were original. This process now appears to be a reliable method to introduce amounts of dopant in the material. It must now be developed.

AD

IMPROVEMENT STUDY OF IRON DISILICIDE THERMOELECTRIC MATERIALS.

Final Technical report

by

Stanislas and Hubert SCHERRER

January 1990

United States Army

EUROPEAN RESEARCH OFFICE OF THE U.S. ARMY

London England

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January 1990

IMPROVEMENT STUDY OF IRON DISILICIDE THERMOELECTRIC MATERIALS

This study concerns the first part of the program entitled *"Improvement study of iron disilicide thermoelectric materials"*.

In many applications at high temperature, materials for power generation must have a large figure of merit Z, a stability of surfaces with respect to oxidation, sublimation and evaporation, a low cost for elaboration. The semiconducting compound β - $Fe\ Si_2$ meets these requirements and has been already proposed for power generations. Iron disilicide is doped with cobalt to obtain the N-type material. The P-type is obtained either by manganese (used by KOMATSU commercially) or by aluminium (U. BIRKHOLZ - University of KARLSRUHE). The manganese gives a Z of around $0.5.10^{-4}\ K^{-1}$ while aluminium is supposed to give $Z = 1.5.10^{-4}\ K^{-1}$ (400° C).

The goal of this part of the study is to obtain pure semiconducting β - $Fe\ Si_2$ phase from elemental 325 mesh iron and silicon powder under the conditions of phase diagram (fig. 1). Thermoelectric properties of this material must be a reference for later studies. At once, we elaborate the material by the same classical method as KOMATSU or U. BIRKHOLZ ; the synthesis of elemental iron and silicon powder is achieved by melting at 1250° C and the transition of the metallic (α) to semiconducting (β) phase is obtained by annealing. Then, we find it is very difficult to maintain the stoichiometric composition during the $\alpha \rightarrow \beta$ phase transformation. Consequently to this method it is impossible to control adjustement of the doping material. Using the competence and the experiments of our laboratory, we elaborate with success β - $Fe\ Si_2$ by mechanical alloying. This method elaborating the compound from low temperature must avoid the difficulties of sublimation, evaporation of the components and allows the optimisation of β - $Fe\ Si_2$.

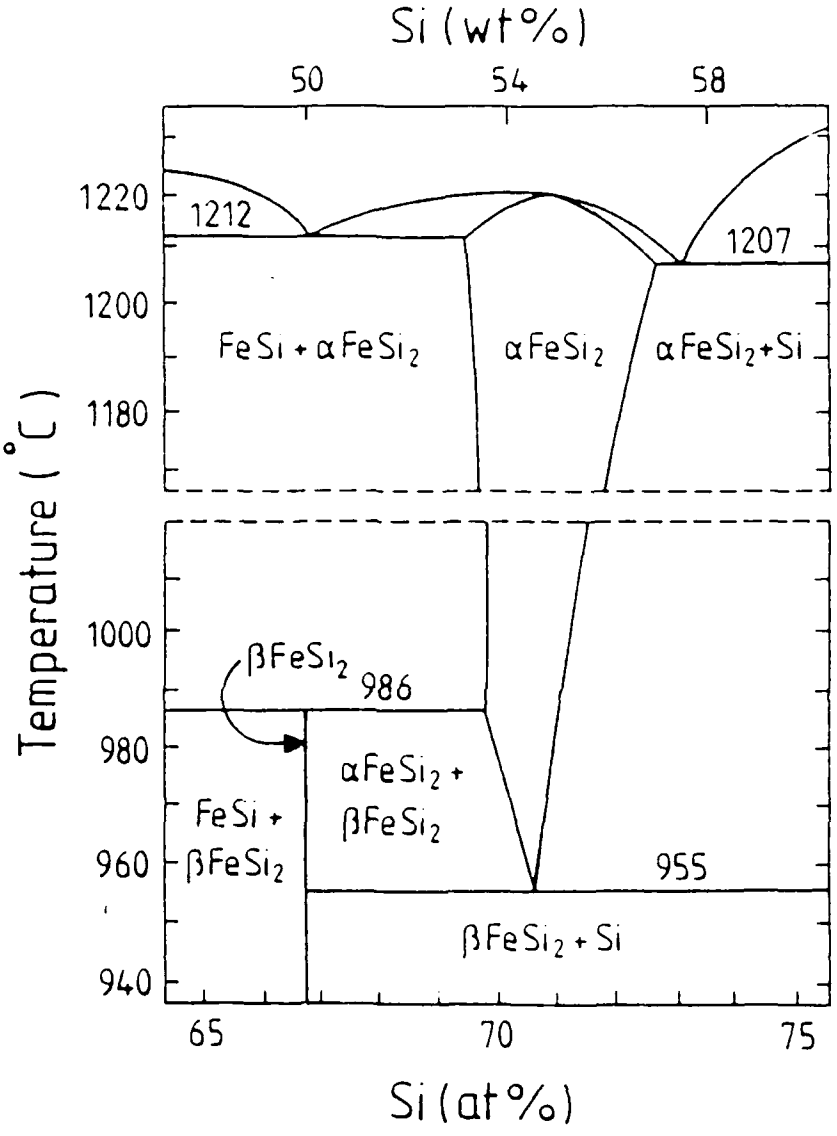


Figure 1 : Phase diagram of the binary system Fe-Si

I. - CLASSICAL SYNTHESIS OF PURE β IRON DISILICIDE (β - Fe Si_2). -

According to a classical process it can be obtained by annealing at 1075 K from the α metallic phase. Pure materials iron (ARMCO 99,995 %), silicon (CERAC 99,995 %) were purified in a reducing atmosphere. Then the compounds in a stoichiometric composition were melted by induction heating in a quartz ampoule under He-H_2 atmosphere. In this way we obtained the α - metallic phase of Fe Si_2 and then we must achieve the α → β phase transformation.

After cooling to room temperature the ingot was ground in a mill. The powder was filled into a cylindrical box of 10 mm in diameter and a ram pressure (70 MPa) was applied. The samples were annealed at 450 K under vacuum for several hours. The subsequent sintering process was performed for 3 hours at 1450 K under a stream of He-H_2 mixture. The transition to the semiconducting phase was achieved by annealing for several days at 1075 K under high vacuum. In the table below we show the measurement of thermoelectric power at room temperature.

N° sample	(1)	(2)	(3)	(4)	(5)
α in $\mu V/_o$	167,3	246,5	294,9	209,6	160,4

We noted that all samples were always n-types. The time needed for the phase transition from the metallic high temperature to the semiconducting phase is found to be very sensitive to the stoichiometric composition of the material. Thus thermoelectric power changed in the same manner.

Some measurements on electrical resistivity and thermal conductivity were performed. Samples had a very high resistivity about 50 m Ω .m. This value was not surprising because the samples were undoped and the thermal conductivity was found as a classical value $\lambda = 6.95\ w.m^{-1}.K^{-1}$.

X-ray diffraction measurements on these samples showed that α - $Fe\ Si_2$ line vanished but we noted the important presence of Fe Si lines (fig. 2).

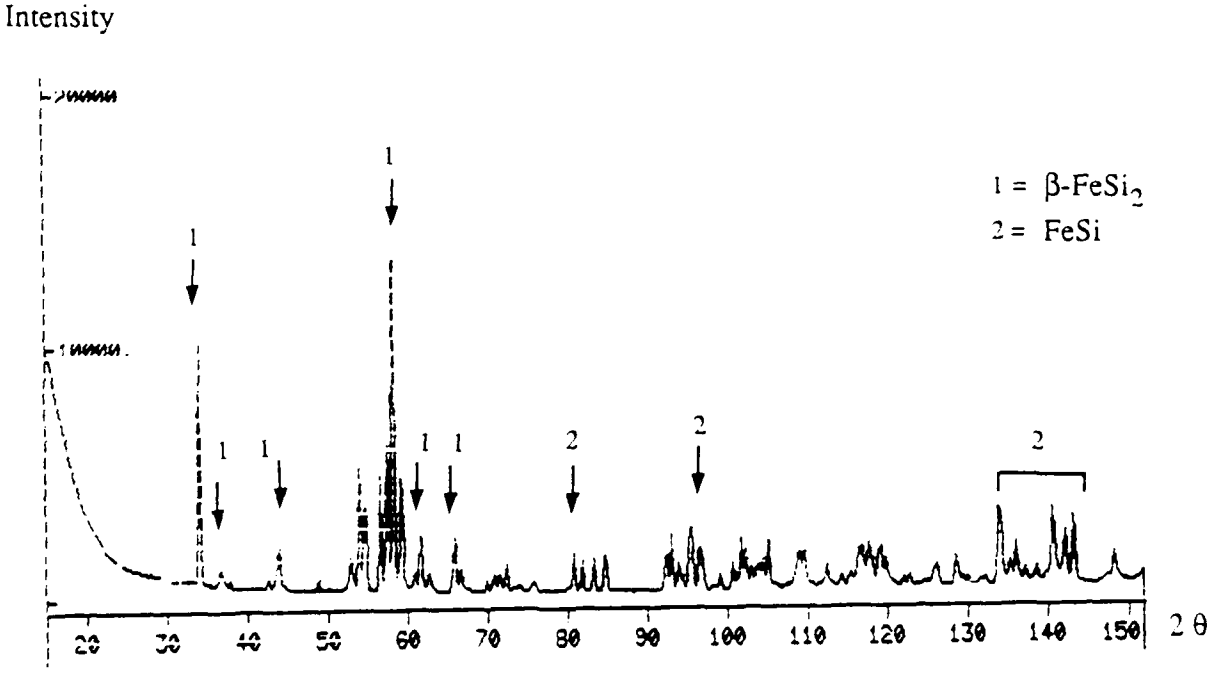


Figure 2 : X-Ray diffraction pattern of β-$FeSi_2$ Sample [classical synthesis]

From the phase diagram, it seemed that it was very difficult to keep the stoichiometric composition during the $\alpha \rightarrow \beta$ phase transformation. Consequently to this method it is impossible to control adjustement of the doping material.

II. - PREPARATION OF PURE β IRON DISILICIDE (β Fe Si_2) BY MECHANICAL ALLOYING. -

The classical preparation of β Fe Si_2 , as we saw, was time-consuming and difficult. Because of the phase diagram Fe Si or Si particles are present and therefore result in the production of inhomogeneous alloys. In addition, the high vapour pressure of aluminium (for example) at elevated temperatures makes the controlled addition of this dopant difficult in the melt. These difficulties with cast alloys led us to consider mechanical alloying as an alternate method of producing Fe Si_2 thermoelectric materials.

Mechanical alloying offers the possibility of minimizing compositional heterogeneity and grain size and of evaluating additions which are not amenable to the melting process. It is a technique in which crystalline intermetallic or elemental powders are alloyed through a sequence of collision events inside a high energy ball mill. On a macroscopic scale this process is accomplished through a repeated fracture and cold welding process. It is desirable to prepare thermoelectric materials with low thermal conductivity so that a temperature gradient can easily be maintained in a device, provided the electrical conductivity and Seebeck coefficient can be kept suitably large. Evidence suggests that mechanical alloying would produce a material with extremely small (< 1 μm) particle size which should result in a significant reduction in thermal conductivity. To achieve alloying we used a vibrating shaker and planetary types of mills with unequal success.

III. - MECHANICAL ALLOYING WITH A VIBRATORY SHAKER TYPE OF MILL. -

The Fe Si_2 samples wereprepared from elemental 325 mesh silicon and iron powder. The amounts of each component were weighed in anargon-filled glove box to obtain a nominal composition of Fe Si_2 and placed in a tungsten carbide vial along with a 8 gram 10 mm diameter WC ball and sealed under argon. In the initial attempts to achieve alloying these vials were loaded into a vibratory shaker type of mill (fig. 3).

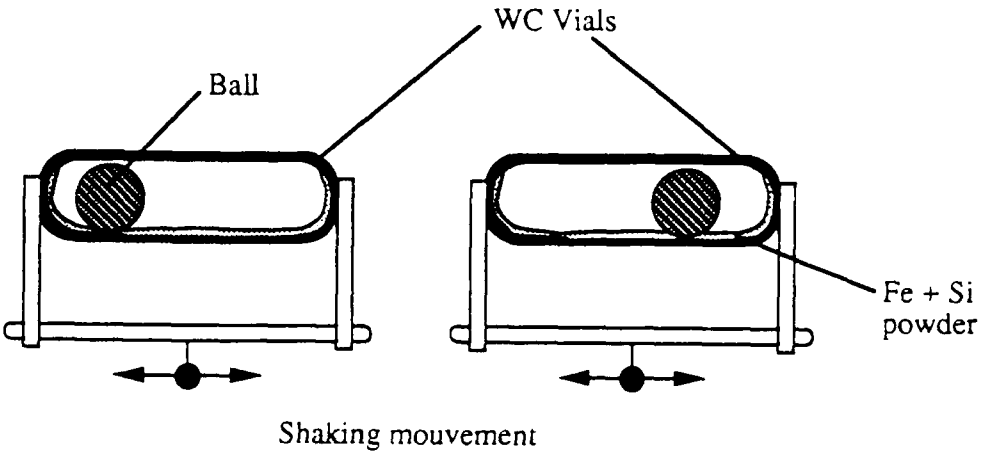
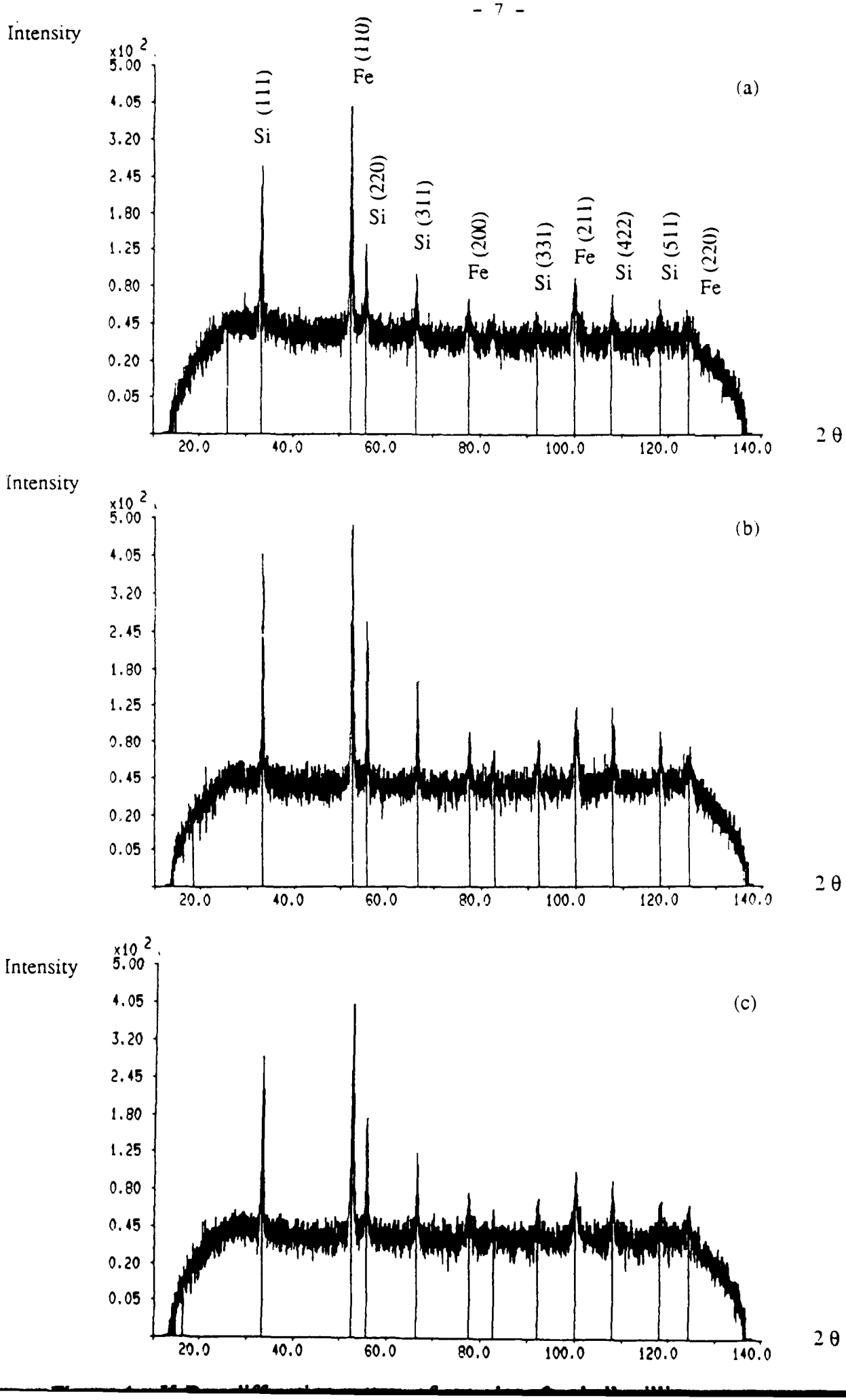


Figure 5 : Vibratory shaker type of mill

X-Ray diffraction measurements taken of the powder after 1 hour of processing showed that the Si and iron lines had no change indicating alloying had not occurred. In the figure 4 cliches a and b corresponded to powder respectively taken free in the vial and aggregated on the walls of the vial. No change could be observed as on cliche c for 3 hours of processing. Many other attempts were made up to 14 hours.

In the figures 5 a, b and c for 14, 15 and 30 hours respectively some changes appeared, enlarging of X-ray lines and appearance of 3 $Fe\ Si_2$ X-ray line.

It was felt that in this type of mill, insufficient energy was dissipated to cause alloying to occur.


Intensity
x10 2
5.00
4.05
3.20
2.45
1.80
1.25
0.80
0.45
0.20
0.05
Si (111)
Fe (110)
Si (220)
Si (311)
Fe (200)
Si (331)
Fe (211)
Si (422)
Si (511)
Fe (220)
(a)
20.0
40.0
60.0
80.0
100.0
120.0
140.0
2 θ
Intensity
(b)
Intensity
(c)

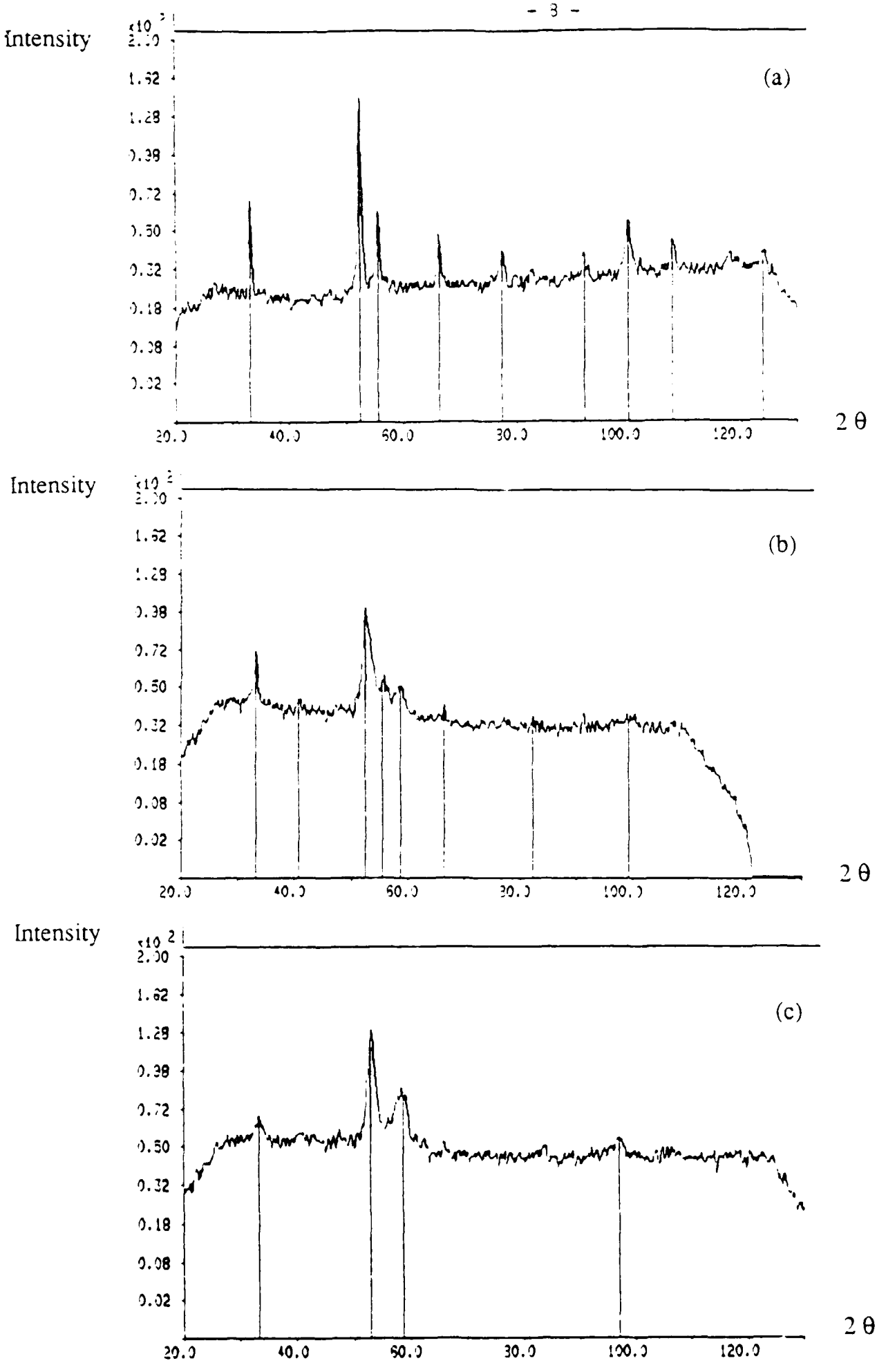


Figure 5 : X-Ray diffraction pattern of samples after ball milling

IV. - MECHANICAL ALLOYING WITH A PLANETARY TYPE OF MILL. -

The vials filled under the same conditions as before were loaded into a planetary mill which rapidly rotates each vial and is in opposition to the primary rotation axis of the platform (fig. 6). Some attempts were made to optimise the components mass, number of balls, and time of processing. For all the following attempts, the amounts of each component were weighed (10 gram) in an argon-filled glove box to obtain a nominal composition of $Fe\ Si_2$ and placed in a tungsten carbide vial 50 ml with seven, 8 gram 10 mm diameter WC balls and sealed under argon. The platform rotates at the rate of 340 rpm and the vials at 680 rpm. X-rays diffraction measurements taken of the powder after 2 hours of processing were shown in figure 7a.

We observe the existence of :

- α $Fe\ Si_2$ (quadratic) : lines 1 and 3
- β $Fe\ Si_2$ (orthomrombic) : line 2
- $Fe\ Si$ (cubic) : line 4
- the line 5 shows the simultaneous presence of α $Fe\ Si_2$ and β $Fe\ Si_2$.

After 4 hours of processing we noted in the figure 7b :

- lines 1 and 3 decrease in a significative manner
- line 2 (β $Fe\ Si_2$) increases considerably
- line 4 shows the disappearance of $Fe\ Si$
- the decreasing of line 5 confirms the transformation of β $Fe\ Si_2$ in relation with α $Fe\ Si_2$ and $Fe\ Si$.

We think that this is a good way to obtain β $Fe\ Si_2$.

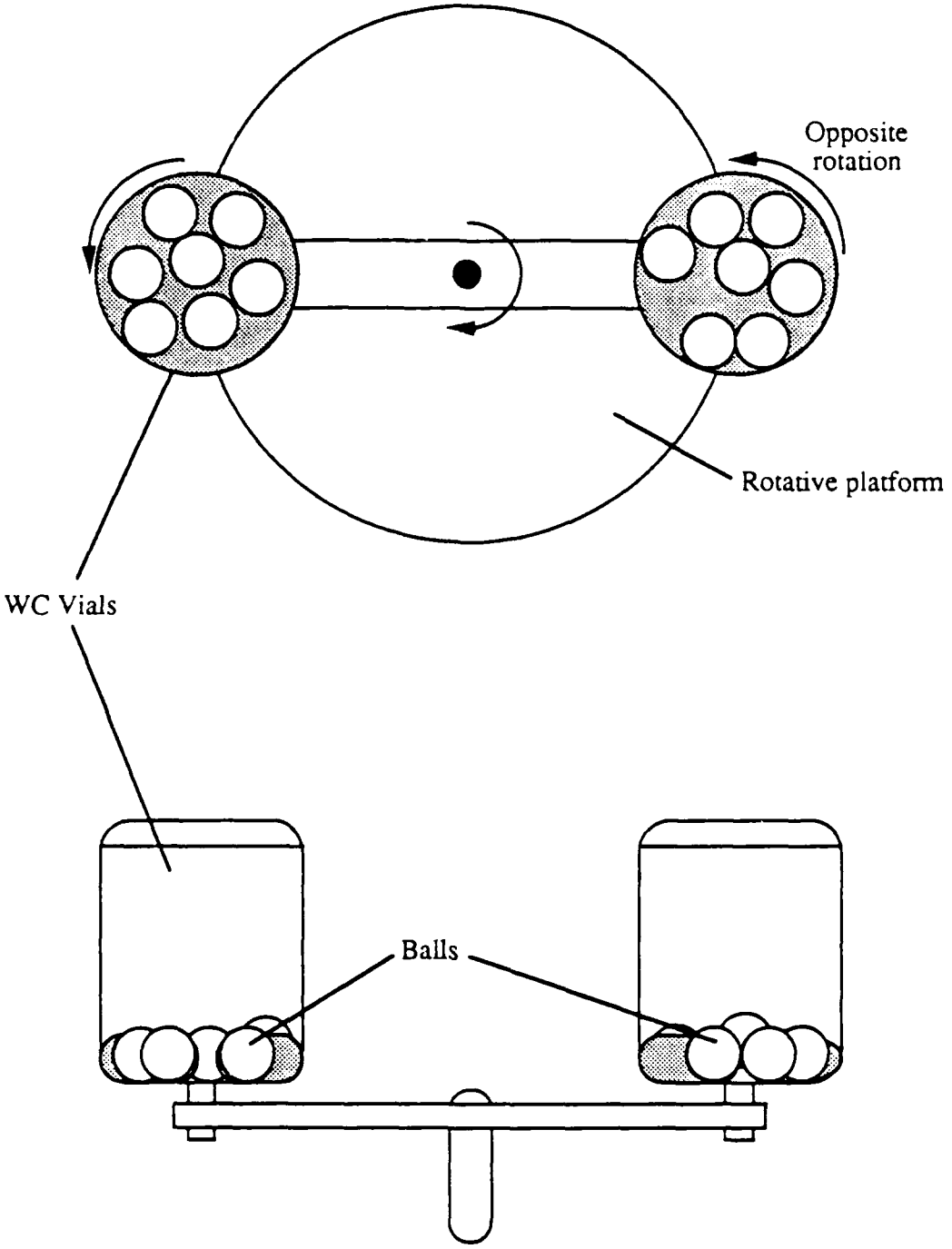
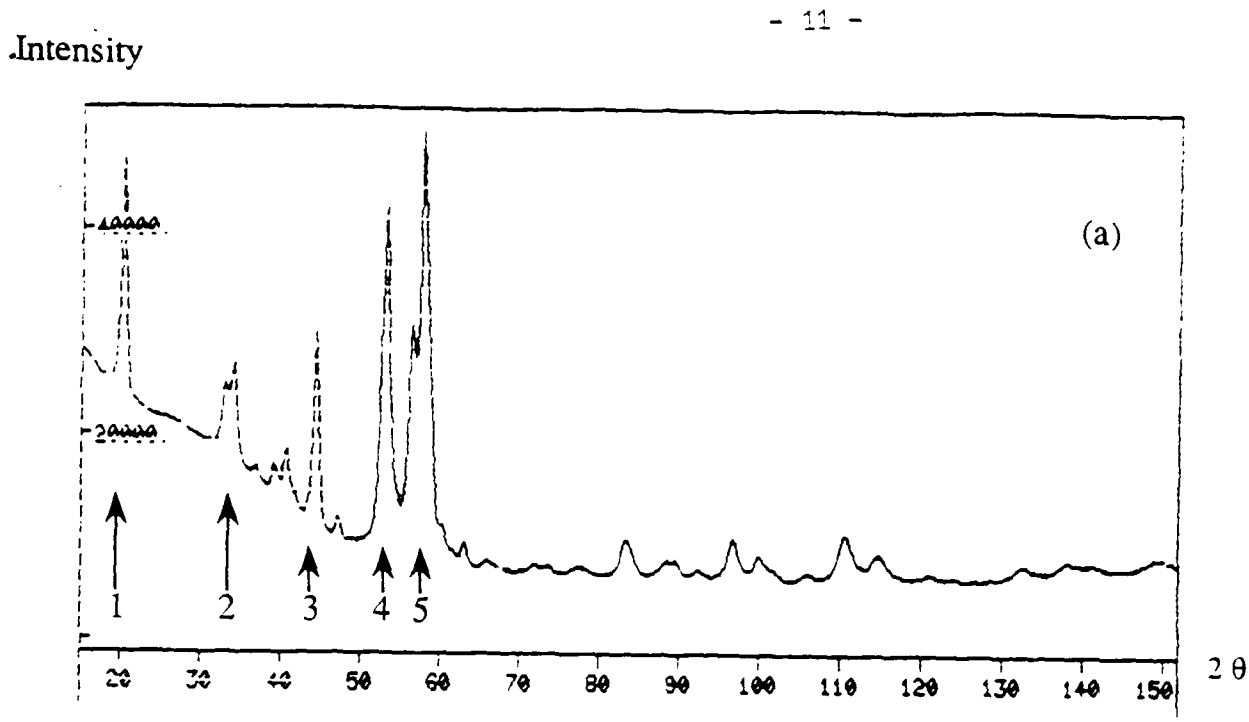


Fig 6 : Planetary type of mill



α - $FeSi_2$ = 1 ; 3 ; 5

β - $FeSi_2$ = 2 ; 5

FeSi = 4

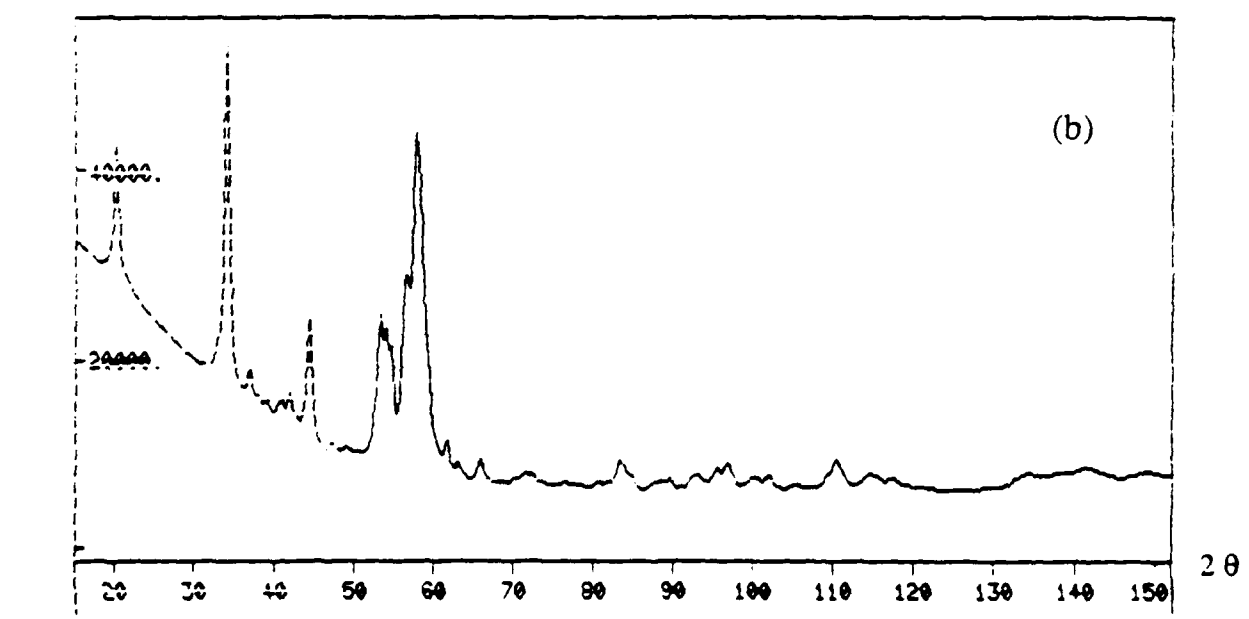


Fig 7 : X-Ray diffraction pattern of mechanical alloyed samples
(a) - after 2 hours
(b) - after 4 hours

The figure 8 shows an experiment of D. S. C. (Differential Scanning Calorimetry) with powder taken after 1 hour of processing. We note that the $\alpha \rightarrow \beta$ transformation takes place at a lower temperature (400-500° C) than the temperature predicted by the phase diagram. This is probably due to the existence of many energetic defects in the powder which are annealed quickly. These defects favourise certainly the phase transformations.

In the figure 9a are representated the X-rays lines of the powder after one hour of grinding. Then the powder is annealed (500° C) during one hour and the X-rays spectra are represented in figure 9b.

CONCLUSION. -

The results obtained from a planetary mill were found to be suitable to elaborate the semiconducting β Fe Si_2 phase. The rapidity of the process (about 2 hours of grinding and annealing) was noted.

Results about D. S. C. showed that the $\alpha \rightarrow \beta$ phase transition was at a lower temperature due to an anrealing of very energetic defects introduced during mechanical alloying.

These results on β Fe Si_2 obtained by mechanical alloying, as far as we know, were original. Then this process seems a reliable method to introduce amounts of dopant in the material and must be developed.

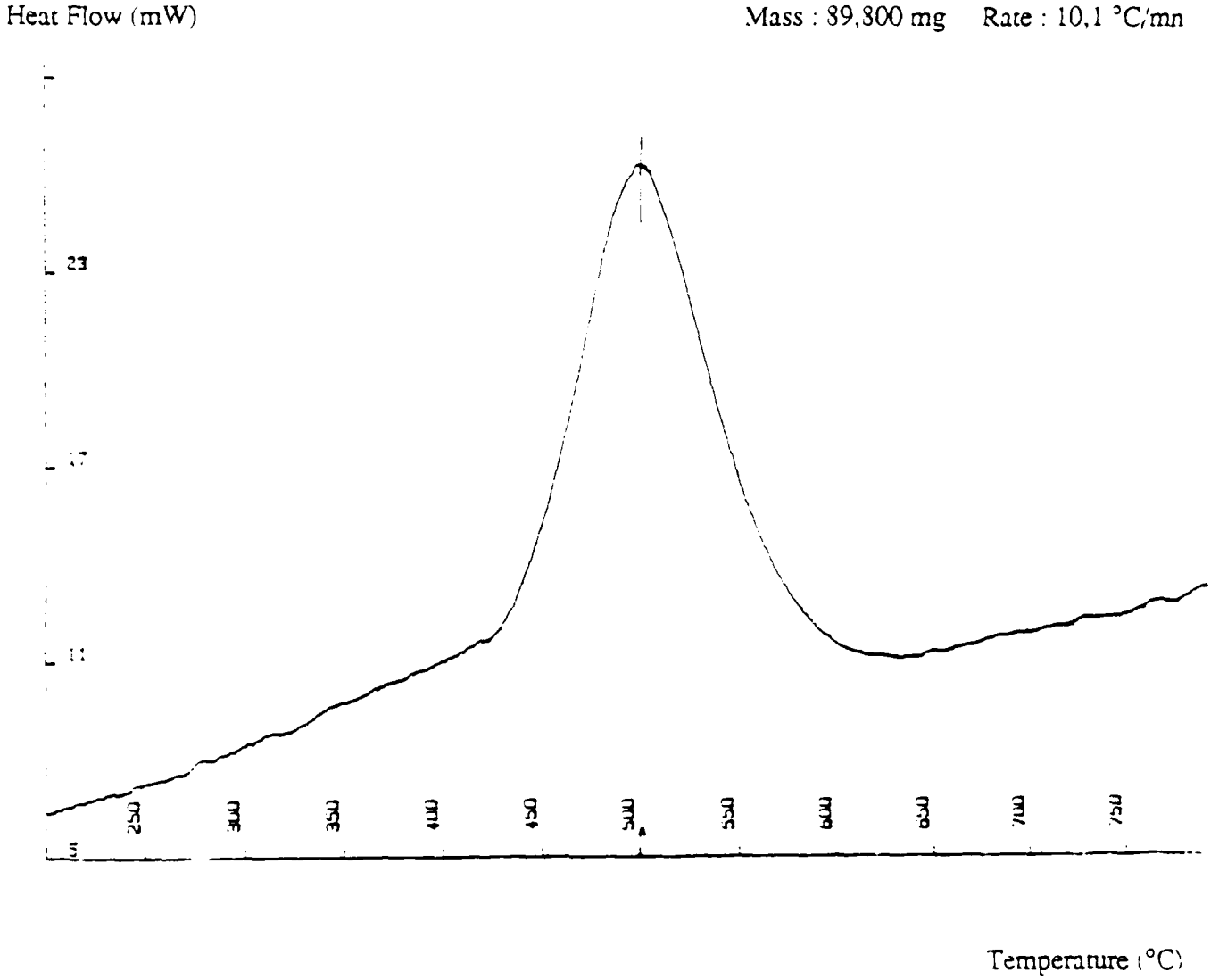
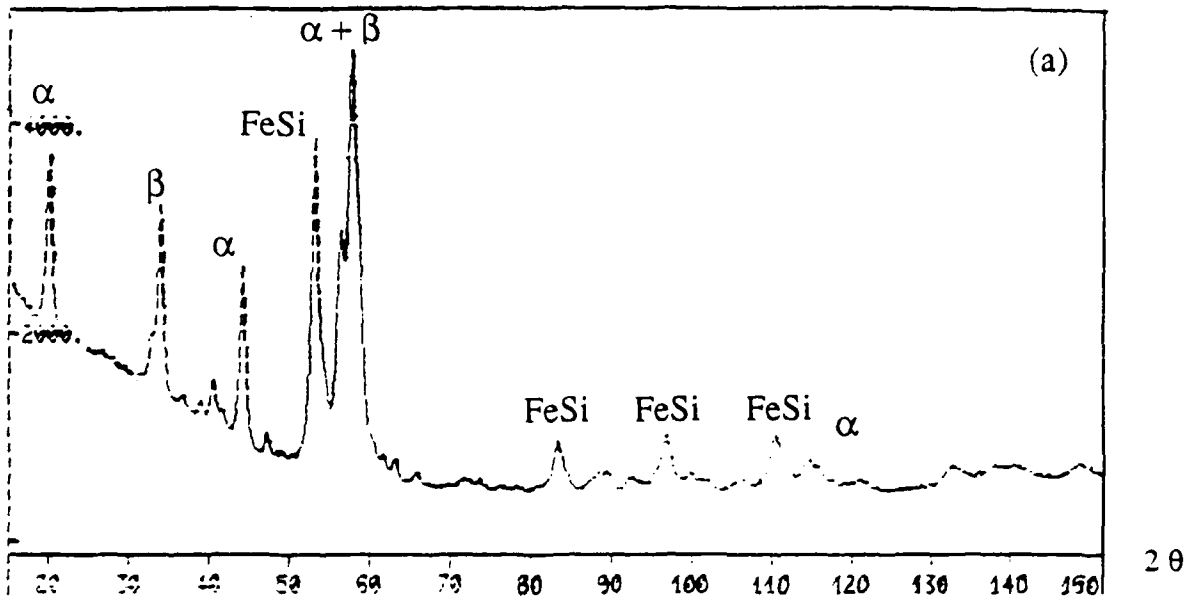


Figure 8 : $\alpha \rightarrow \beta$ transition observed by Differential Scanning Calorimetry

Intensity



Intensity

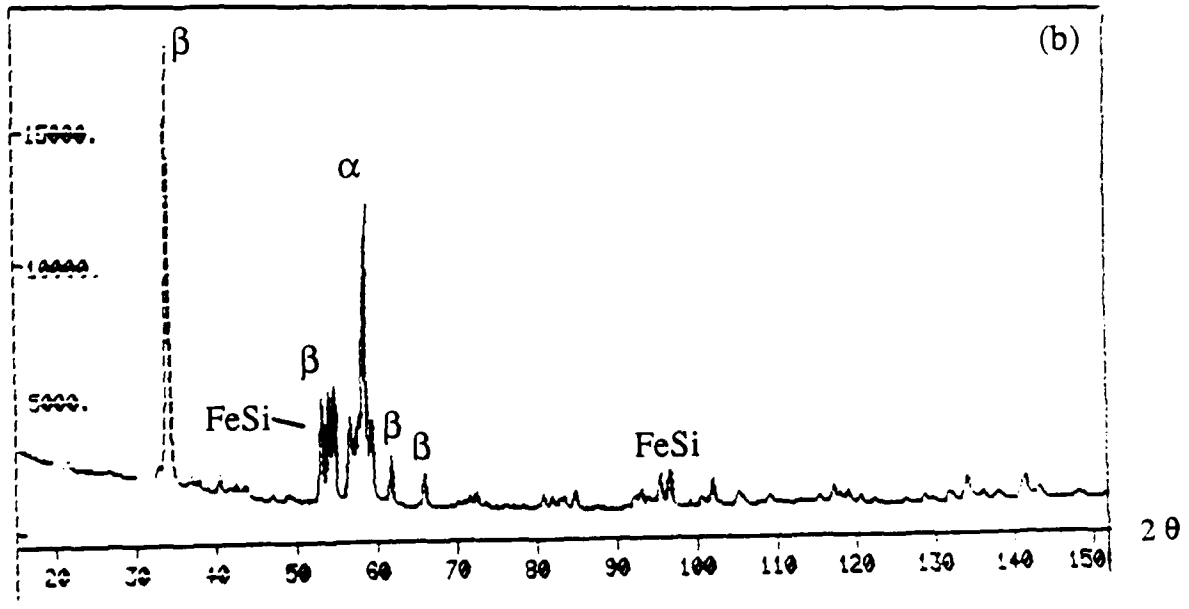


Figure 9 : X-Ray diffraction pattern of mechanical alloyed samples
(a) one hour of ball milling
(b) same plus one hour of annealing (500°C)