MECHANICALLY INDUCED CHANGES IN A BINARY Fe-Si MIXTURE DURING ENERGY - INTENSIVE MILLING

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Abstract

Changes in particle size, morphology, specific surface area, structure and composition during high - energy planetary milling of a binary mixture of an elemental Fe25%at.Si mixture have been investigated. Based on the obtained results, the course of milling can be divided into two main stages. The first stage, of milling up to 25 min, is associated with the particle aggregation and crystallite refinement of both components. Complete amorphization of silicon and a formation of tight contacts between Fe and Si particles facilitates the successive formation of a solid solution in advanced stages of milling. The second alloying period includes partial formation of a disordered bcc solid solution.

Keywords: milling, mechanical alloying, mechanically induced changes, disordering, bcc solid solution

Introduction

Mechanically and thermally induced changes in the Fe - Si binary system are of great interest in physics and material science [1-11]. During the last few years, the possibility of preparing materials with soft - magnetic properties has been proven and information about the nature of individual processes occurring during mechanical treatment has been gained. According to literature data, the preparation of Fe - Si alloys by energy - intensive milling includes the structure disordering of both silicon and iron, the creation of a large interfacial area and formation of solid solutions [8-11]. The mechanism of the mechanical alloying, however, has not been fully explained yet. In order to contribute to solving the mentioned problem, the time sequence of the individual processes during discontinuous conditions of planetary milling of a Fe - Si binary mixture have been studied, and the mutual relations between the mechanically induced changes have been analyzed. The results obtained are reported in this paper.

Material and methods

A homogenized mixture of elementary iron (99.5% purity, particle size < 10 μm) and silicon (99.5% purity, particle size < 150 μm) (3:1 in atomic proportion) was milled in a planetary mill AGO-2 (URF Technology, Budapest) in a stationary argon atmosphere using a steel vial and balls. The following conditions were listed: ball - to - powder weight ratio 20:1, rotation speed of planet carrier 700 r.p.m., centrifugal acceleration on thimble axes 1000 ms^{-2}. The vial temperature during milling was kept constant by water cooling.

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A scanning electron microscope (SEM) (Tesla BS-340, Brno) equipped with an EDX unit (LINK ISIS 300) was used to observe the morphology of the powders and the individual particle size. The particle size distribution was measured by the method of laser radiation scattering on the granulometer Helos LA (Sympatec GmbH, Clausthal-Zellerfeld). The mean particle diameter d_m was calculated as the first moment of density of the volume size distribution function. The specific surface area S_A was determined by the standard B.E.T. method using the apparatus Gemini 2360 (Sy-Lab, Vienna).

X-ray diffraction measurements were carried out using an automatic SIEMENS-D500 diffractometer equipped with a graphite crystal monochromator (in the diffracted beam) and controlled by an AUTOCOMPT computer using DIFFRACT-AT software (developed by SOCABIM) and ICDD - JCPDS database. A stabilised voltage of 35 kV and a current of 26 mA were used. Vertical divergence of the X-ray beam (CoK_α radiation) was restricted using two Soller diaphragms. Horizontal divergence was 1°. Measurements were carried out in a vacuum of 10^{-2} Pa. Samples were measured on a platinum support at room temperature. The crystallite size, microstrains and lattice parameters were calculated by harmonic analysis method of the XRD line profiles. The amount of alloy content was calculated by evaluation of the integral peak intensities fitted by the last - square method.

Results and discussion

The traditional aim of milling is particle size reduction, resulting in an increase in specific surface area. It is well known that fragmentation by milling of individual substances proceeds up to a critical particle diameter, at which the finely dispersed particles stick together to form secondary aggregates. The critical particle size depends on the external and internal conditions of stress [12]. However, under intensive milling of a powder mixture containing ductile particles of iron, aggregation occurs from the very beginning of the milling process (Fig.1). This fact is demonstrated by an increase in mean particle diameter, and a decrease in specific surface area in the initial period of up to 25 min of milling, as well as by comparing the SEM micrographs of the starting powder with that of the milled one (Figs.2 A and B). After this first period, regular fragmentation proceeds as it is known for the milling of individual substances.

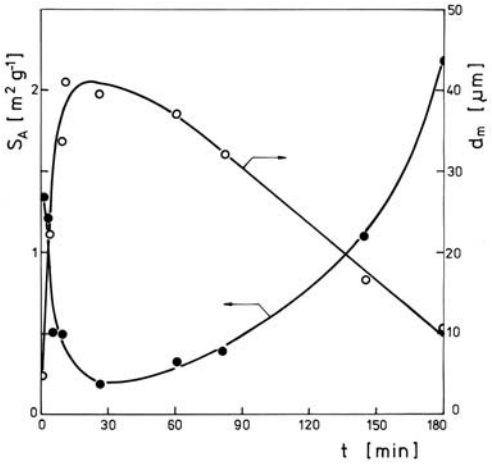

Fig.1.Mean particle diameter, dm, and specific surface area, SA, vs. milling time, t.

Aggregation of primary particles during mechanical alloying is assumed to be a consequence of cold welding and/or the creation of layered structures. Formation of numerous intimate point contacts and their possible changes to interfaces by plastic flow [13] creates favourable conditions for intimate mixing between the Fe and Si components on an the atomic level. This process known in mechanochemistry as "transport effect", takes place in the advanced stage of milling, followed by a renewal of the surfaces due to particle size reduction and flaking of the product from the contact sites between interacting particles ("fresh surface effect").

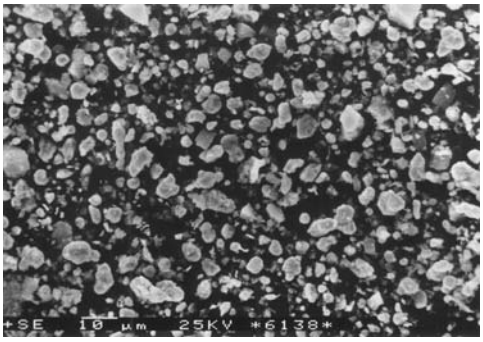

Fig.2a.Scanning electron micrograph of the starting mixture.

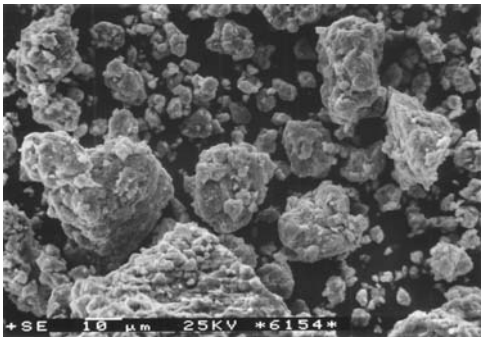

Fig.2b.Scanning electron micrograph of the sample milled for 25 min.

Using XRD analysis, a gradual diminishing of the XRD intensity of the Si (111) peak was observed in the initial stage of milling. As it has been shown in [9], the amorphization of the brittle silicon was completed after 25 min of milling. The changes of iron during milling have been detected from the broadened and asymmetric Fe (110) diffraction peak, corresponding to the α - Fe reactant and created product. The peak broadening and asymmetry was observed in diffraction peaks of up to 80 min of milling (Fig.3), however, the above mentioned changes become remarkable after 25 min of milling when the amorphization of silicon is completed.

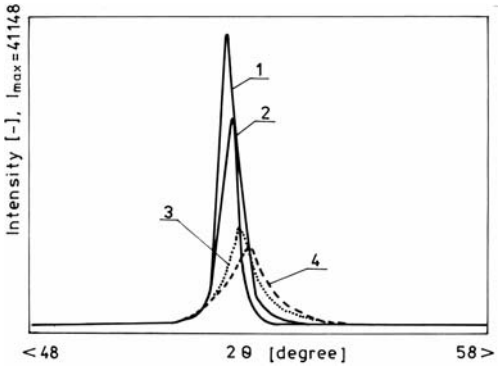

Fig.3.Comparison of the XRD Fe (110) line profile of the initial mixture (1) with that of samples milled for 5 min (2), 25 min (3) and 80 min (4).

Crystallite size and lattice microstrain in the milled samples, estimated on the basis of physical line broadening of Fe (110) peak, are summarized in Table 1. While in the

initial milling period line, broadening results from the reduction of crystallite size, in the advanced stage of milling the local lattice strain, dominates line broadening.

The formation of the bcc solid solution indicated by shifts of the reflection angles 2θ of the Fe (110) peaks from 52.326 to 52.84, proceeds gradually in a time interval from 10 to 80 min of milling. In this interval Fe and Si are converted into the Fe_3Si bcc-crystalline solid solution with a maximum conversion degree of 88%. A sharp decrease of lattice parameters from 0.2868 nm to the minimum value at 0.2847 nm was determined in the above mentioned time interval (see again Table 1). The XRD peak asymmetry, changes in lattice parameter and microstrain can be explained by local differences of Fe lattice parameters due to diffusion of Si into Fe followed by the formation of a mechanically alloyed solid solution. According to [8,9], a similar decrease in lattice parameters to 0.2847 nm was found. It has been interpreted by a mechanically stimulated disorder - order transition proceeding mechanical alloying. A decrease in lattice parameters of disordered Fe - Si alloys in the concentration range from 13 to 33 at.% of Si has been explained in the different number of the Si atom in the near environment of a Fe atom [14].

Tab.1. Changes of physical line broadening, b, crystallite size, D, lattice microstrains, $\Delta\sigma$, and lattice parameter, a, with increasing milling time, t.

t [min]	$b \cdot 10^4$ [-]	D [nm]	$\Delta\sigma.10^{-3}$ [MPa]	a [nm]
0	25.1	262	1.01	0.28678
2	28.9	202	1.15	0.28674
5	32.6	149	1.24	0.28669
10	39.8	92	1.31	0.28669
25	63.2	44	2.35	0.28644
60	94.6	19	2.55	0.28517
80	100.2	18	3.20	0.28467
140	96.7	19	2.85	0.28511
180	77.5	17	2.48	0.28579

After 80 min of milling, an increase of lattice parameter and a decrease of lattice microstrain occur. This can indicate a relaxation of lattice contraction and/or can correspond to that observed for thermally induced ordering of the Fe - Si solid solution to a thermodynamic stable DO_3 structure [10]. The explanation of changes in structure and in chemical and phase composition of mechanically alloyed samples requires a more precise estimation of the Fe - Si system milled in the planetary mill, with tools and vials made of different materials and annealed to an ordered state by Mössbauer spectroscopy.

Conclusion

The time sequence of the mechanically induced changes during high - energy milling of the binary mixture of an elemental Fe25at.%Si, enables one to divide the duration of milling into two stages differing in the nature of prevailing processes. In the first stage, the aggregates are created consisting of structurally disordered or even amorphized particles of Fe and Si. Amorphization of silicon and the formation of tight contacts between Fe and Si particles greatly facilitates the successive formation of Fe - Si solid solution in the advanced stages of milling. The solid solution originates in the second stage in a non-equilibrium disordered state. The precision of the disordered structure before completion of the mechanical alloying, and of ordered structure after annealing, will be investigated in our following work.

Acknowledgement

The authors are grateful to the Slovak Grant Agency for Sciences (Grant No. 2/7040/20) for financial support of this work.

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