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Fe (In) solid solution formation during mechanical attrition

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Abstract

The purpose of this work was to analyze interactions of Fe and In (immiscibile at equilibrium) during mechanical attrition in high energy planetary type activator. The structure of the samples with Fe + 10%In and Fe + 20%In mixture powders, processed during different times was studied. The experiments were performed by means of Mossbauer spectroscopy in wide temperature range (4–300 K) and X-ray diffraction. These experiments revealed changes in structural (Debye temperature, unit cell parameters) properties of the samples under investigation with the increase of mechanical attrition time. After 60 min of attrition, Fe (In) solution was formed.

Keywords: Mechanical alloying; Immiscible metals; X-ray diffraction; Mossbauer spectroscopy

1. Introduction

Fe (In) solid solution formation in the grain boundary region of milled Fe + 10 at%In sample was predicted in previous works [1,2]. The purpose of the present paper is to study stages of mechanical activation in Fe–In. These immiscible elements have a large positive value of interfacial enthalpy (+43 kJ/mol) according to Miedema model [3], different lattice structure and different atomic size. It is well known [4] that temperature of milling bodies can rise by several hundred degrees in high energy activators of the planetary mill type. It can be assumed that mechanical activation of such a pair can allow forming a morpholocically metastable structure [5]. To study samples at various stages of milling, we used X-ray diffraction and Mossbauer spectroscopy.

2. Experimental

Ball milling of Fe with 10 at%In and Fe with 20% In powder mixtures was performed in AGO planetary ball mill during different time intervals from 2 to 120 min. Vial (sealed under Ar) volume was 250 cm^3. Balls diameters and mass were 5 mm and 200 g, respectively. The speed of drum rotation was ∼1000 rpm. Elemental 10 g powders of iron with particle sizes of 50–60 μm and indium small lumps of 2–4 mm were used.

XRD was performed on Rigaku DX/Max diffractometer with Cu Kα radiation. The ^{57}Fe Mossbauer spectra were obtained at room temperature using constant acceleration spectrometer with ^{57}Co(Rh) radiation source. The Mossbauer spectra parameters with reconstruction of hyperfine magnetic fields distribution functions were analyzed by means of MSTools software [6].

3. Results and discussion

X-ray diffraction patterns of processed mixtures Fe + 10 at%In and Fe + 20 at%In are shown in Fig. 1. The patterns of both mixtures after 2 min treating consist of Fe and In elemental simple mixtures. But the patterns of products processed longer show that the Bragg peak intensities of indium decrease with increasing time of mechanochemical treatment, as broadened iron peaks are shifted to the lower angles. Under the activation conditions applied in our studies indium peaks disappear completely within 15 min for mixture Fe + 10 at%In and 60 min for Fe + 20 at%In. The detailed analysis of peak form has not revealed any asymmetry. The pattern reflects only the decrease of the average crystallite size from 42 nm after 2 min of grinding down to ∼20 nm after 120 min. The observed crystallite refinement is accompanied by an increase of the internal inhomogeneous microstrain introduced by mechanical deformation and structure imperfection. The nonmonotonous increase of the lattice parameter value with time of grinding from 0.28693 to 0.28975 nm testifies the gradual indium dissolution in iron. It may be ascribed to easy-melting of (In) which

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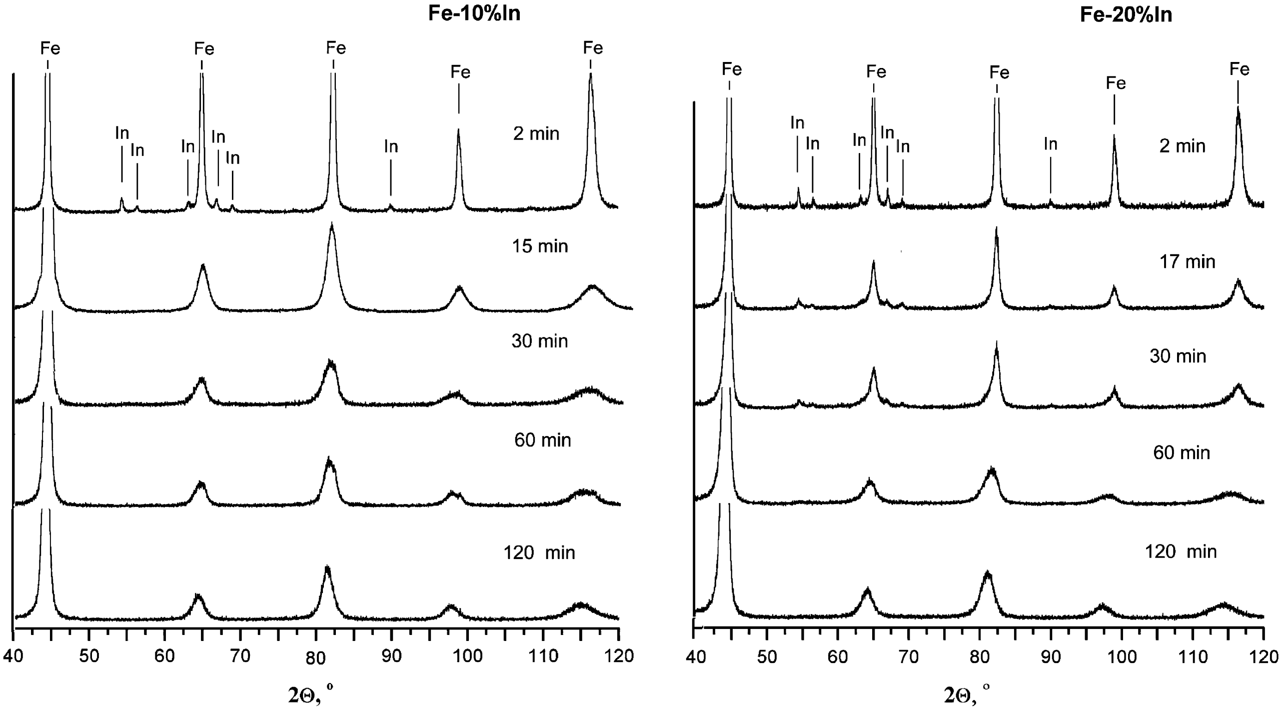

Fig. 1. X-ray diffraction patterns of Fe + 10 at%In and Fe + 20 at%In powder mixtures after milling for different time (from 2 up to 120 min).

spreads along the boundaries of particles formed by crushing of the solid component (Fe) and structural defects developing during plastic deformation [7]. The thickness of In spreading layer becomes thinner as grinding time increases. That's why disappearing of In lines in the Fe + 20 at%In system patterns comes later than in Fe + 10 at%In. As X-ray diffractometry is not sensitive for detection of such thin grain-boundary layers, to prove this suggestion, Fe^{57} Mossbauer spectroscopy sensitive to changes in local solute concentrations in the iron phases was used.

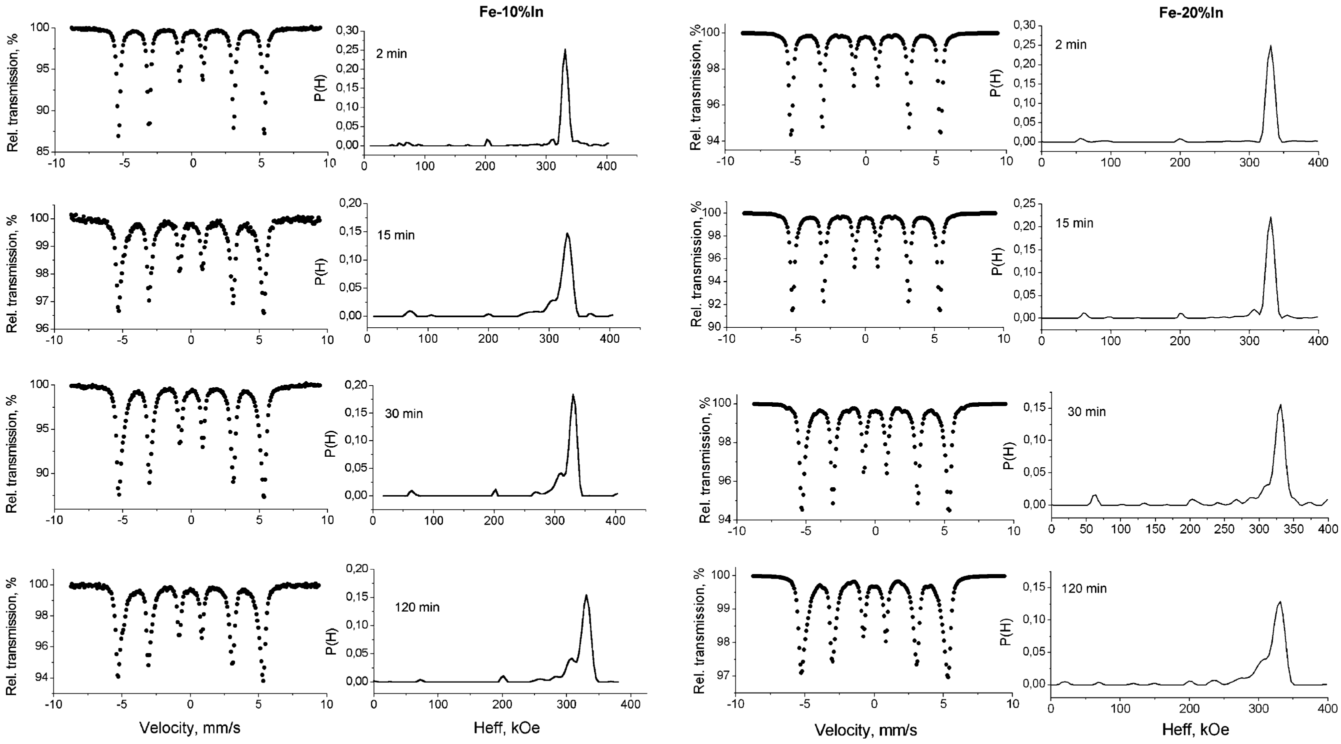

Fig. 2. Mossbauer spectra of Fe + 10 at%In and Fe + 20 at%In powder mixtures after milling for different time (from 2 up to 120 min) and corresponding hyperfine fields distribution functions.

The Mossbauer spectra obtained after various milling times and derived hyperfine magnetic fields distributions (Fig. 2) show evolution of mixture microstructures in the course of attrition. The Mossbauer spectra after 2 min show only sextet with Mossbauer hyperfine parameters associated with well known α-Fe at room temperature. Correspondingly, single peak at $H = 330$ kOe appears on P(H) distribution functions (Fig. 2). Anisotropy in Mossbauer spectra line intensities is also observed. The deviation from the usual intensity ratio $I_{1,6}$:$I_{2,5}$:$I_{3,4} = 3$:2:1 which is characteristic for isotropic polycrystalline iron is caused by the high deformation level and the grain crushing [8] during ball milling.

The Mossbauer spectra of milled powders processed longer show asymmetric broadening of lines. Analysis of hyperfine fields distribution functions for these spectra revealed existence of several peaks on them. The main intense high field peak on the curve is due to α-Fe grain. This peak shows intensity decrease and broadens in comparison to the single peak observed after 2 min of grinding. The additional peaks appearing in this picture at small hyperfine magnetic fields ($H \sim 305$ kOe) correspond to effects of impurity neighbors in different iron coordination shells as in random binary solid solutions of transition elements [9]. Hyperfine field peculiarities reflect changes of conduction electron polarization and have a linear response to the d moment changes induced by the impurity. In that case isomer shift changes are ascribed primarily to the variations in the density of d-electrons at the iron neighbour sites [9]. The correlation with isomer shifts of corresponding components must be observed if we imply In dissolution in Fe. The Mossbauer spectra fitting in our case revealed the consistent Fe (In) subspectra isomer shifts change towards their positive values corresponding to spin-electron density decrease.

Such spectra are typical also for milled powders when sufficient grain boundaries appear during refinement and numerous defect formation leads to a decrease in density [10]. But to obtain such intensive subspectra of grain boundary the value of grain size must be about twice as smaller as is observed in our samples.

To compare the forms of hyperfine magnetic structure of milled powders at equal time (during15 min) for Fe + 10%In and α-Fe samples, their hyperfine fields distribution functions are shown in Fig. 3. One can see that additional peak due to interface region appears after that time only in the hyperfine fields distribution of Fe–In sample.

The other parameter of Mossbauer spectrum testifying In dissolution in Fe is spectral intensity. It is well known that at definite temperatures this parameter depends on quantity of Fe atoms in the sample (n) and on probability of Mossbauer effect for it structure—f':

$$I \sim nf'' \tag{1}$$

Where f'' is the exponential function of Debye temperature:

$$f'' = \exp\frac{-6RT}{k\Theta^2} \tag{2}$$

R is recoil energy constant for Fe^{57} nucleus, T the temperature of experimental measurements, k Boltzman constant.

If the Mossbauer spectra temperature and iron concentration are the same for all the samples under investigation, the magnitude of their spectral intensity remains constant. But its changes may confirm some new structural state in the samples.

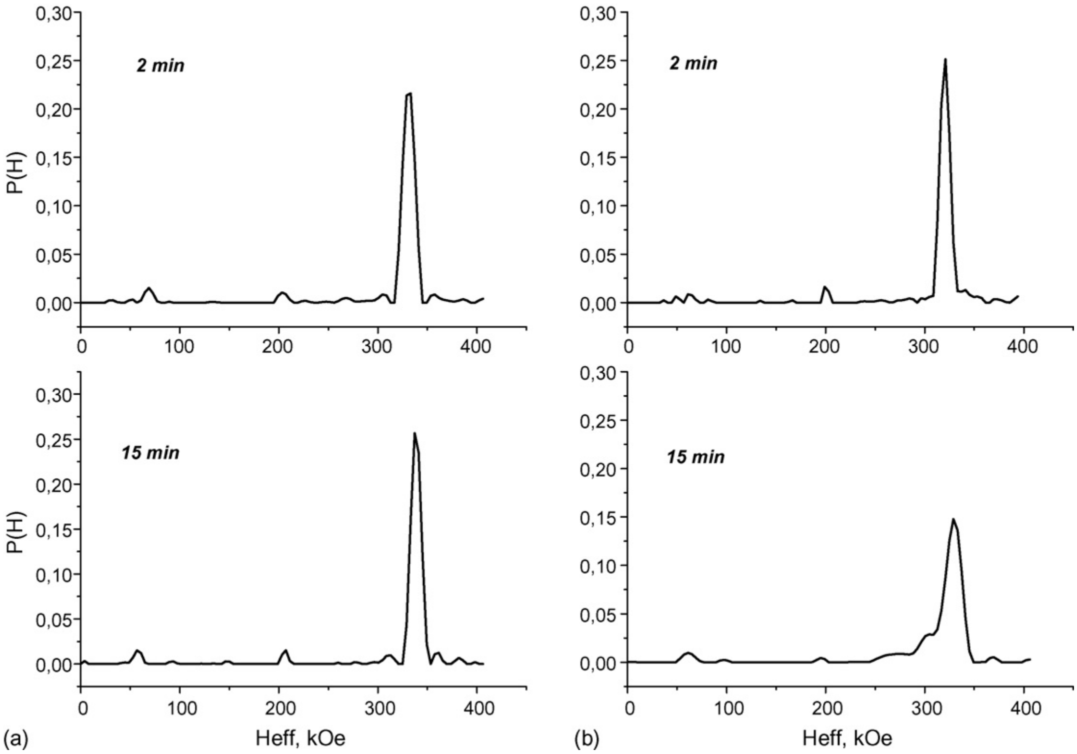

Fig. 3. Hyperfine fields distributions from Mossbauer spectra (a) pure α-Fe and (b) Fe + 10%In mixture after 2 and 15 min of milling.

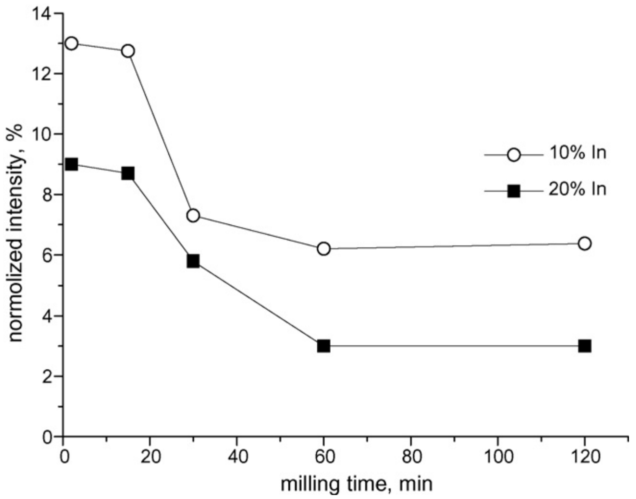

Fig. 4. The values of Mossbauer spectrum intensity for Fe + 10%In and Fe + 20%In mixtures obtained after different milling time.

In our case the Debye temperatures for Fe is 429.7 K and 108 K for In. It is clear that In dissolution in the grain boundary regions of Fe and solid solution Fe(In) formation lead to decrease of Debye temperature. If there is not any indium dissolution in the grain boundary regions of iron, the structure (and Debye temperature) of the sample not change but the obtained data shown in Fig. 4 refute this suggestion. One can see from this picture that the Mossbauer spectra intensities for both samples (Fe + 10%In and Fe + 20%In) decrease significantly: twice for Fe + 10%In and three times for Fe + 20%In mixture. This fact may be explained in the following way. The sample with Fe + 20%In contains more In atoms in mixture in comparison with Fe + 10%In. Thus their spreading along the iron grain boundaries is more significant and involves more Fe atoms in the process of solid solution formation. The results confirm the new structural state in the samples: coexistence of iron grains with their specific Debye temperature and grain boundary regions with significantly lower Debye temperature of Fe (In) solid solution. It must be mentioned that there are no changes in Mossbauer spectra intensities after 60 min of mechanical activation. In our opinion after this time the process of indium spreading along the iron grain boundary and Fe(In) solid solution formation is finished. The dynamics of this process corresponds to observed changes in X-ray patterns of processed mixtures.

4. Conclusion

The results allow us to conclude that slim layers of Fe(In) solid solution formed in the grain boundary regions after 60 min of high energy mechanical activation of non-interacting Fe and In elements powder mixture.

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