JOURNAL OF MATERIALS SCIENCE 39 (2004) 5421–5423

Nanosized mechanocomposites and solid solution in immiscible metal systems

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Mechanical alloying is the most perspective method for preparation of nanosized mechanocomposites in non-mixed liquid and solid metals. It is known that plastic metals get fragile in the presence of the liquid metal phase, and this phase spreads over the surface of solid metal due to good wettability. Temperature of milling bodies can rise by several hundred degrees in the high-energy planetary ball mill. Low melting metals, such as gallium, indium, tin, and bismuth can melt on the surface of the balls. So, a pair composed of liquid and solid metal can form in an activator. In such cases, it can be assumed that mechanical activation of metal systems with positive mixing enthalpies, can allow forming a morphologically metastable structure with unusually high concentration of inter-phase boundaries due to easy-melting component spreading along the boundaries of particles formed by comminution of the solid component.

Nanosized mechanocomposites were prepared for Cu-Bi and Fe-Bi systems. The content of Bi in these systems must be lower than 3 at. (10 wt.)%. The obtained mechanocomposites represent nanosized particles of copper (or iron) coated with a layer of bismuth in 2–3 atoms. Mechanical activation of the formed composites leads to the formation of supersaturated solid solutions.

1. Introduction

Large number of solid solutions is known to be obtained in the systems with positive enthalpy of mixing, for which the solid-phase mechanism of interaction is mainly considered. No investigations have been carried out into the mechanochemical formation of solid solutions in the systems of solid and liquid metals. The aim of the present investigation was to study the mechanochemical formation of solid solutions from a solid and a liquid metal in systems with positive enthalpy of mixing.

2. Experimental

An AGO-2 ball planetary mill was used in the laboratory experiments. In order to avoid oxidation, all experiments were performed in argon medium. The X-ray phase analysis was performed using URD-63 diffractometer equipped with graphite monochromator, using Cu-K_α radiation. Mössbauer spectra were recorded using YaGRS-4 spectrometer with ^{57}Co. X-ray photoelectron spectra (XPE) were obtained using ES-2401 spectrophotometer with Mg anode. The vacuum in the chamber of analyzer was 10^{-6} Pa. The spectrometer was calibrated using the Au4$f_{7/2}$ line with 84.0 eV. The accuracy of determination of line positions was $0.1 \div 0.2$ eV, relative error of line intensity determination as not more than 10%. The expansion of the spectra was performed using the procedure described in [1]. The profiles of concentrations of the lines over the depth were obtained by means of etching with argon ions. Spraying rate was 10 A/min. The O1s, Bi4$f_{7/2}$, Fe3p spectral peaks were analyzed.

3. Results and discussion

The mechanochemical interaction between a solid and liquid metals in the systems with positive enthalpy of mixing, Cu-Bi and Fe-Bi, was investigated. The enthalpies of mixing in Cu-Bi and Fe-Bi systems, calculated by Miedema's method, are +1.1 and +7.1 kJ/mol, respectively. According to the equilibrium diagrams, these systems do not contain intermetallics, nor mutual solubility.

Mechanochemical synthesis was performed in high-energy AGO-2 ball planetary mills using the mode in which the milling bodies get heated to 300–400°C very rapidly [2–4]. This mode of mechanical activation provides melting of bismuth on balls, thus realizing the system composed of a solid metal and a liquid one.

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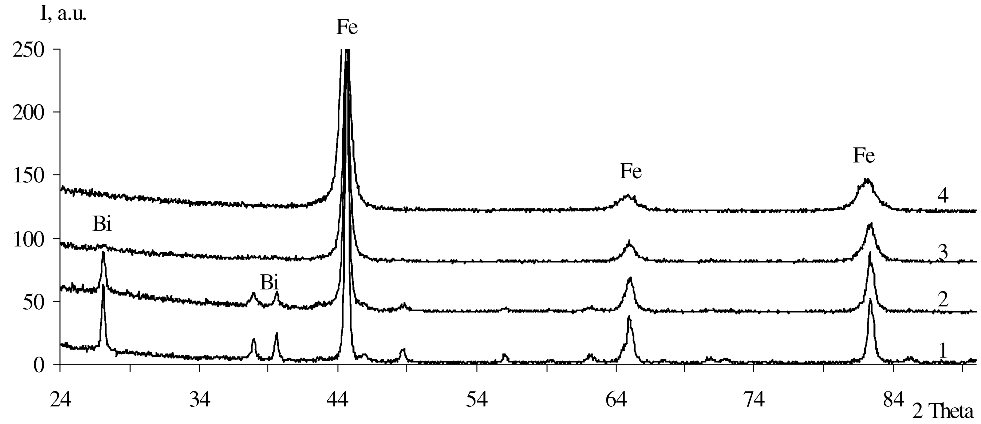

Figure 1 X-ray diffraction patterns of the Fe 3 at.% Bi mixtures taken after MA for 40 s (1), 5 min (2), 20 min (3), and 40 min (4).

It has been revealed that for immiscible systems with the same second component, i.e., bismuth, the behavior of mechanical alloying is different for low and high bismuth contents. For example, the process changes drastically if bismuth content of the system is less then 3 at.%.

X-ray diffraction studies of MA products in the system Cu + 3 at.% Bi show that the peak intensities of bismuth decrease with the time of mechanochemical treatment, as the copper peaks are not shifted. Bismuth peaks disappear practically completely within 10 min of milling; peaks corresponding to copper broaden substantially but do not change their positions.

In the Fe-Bi system with bismuth concentration less than 3 at.%, its unusual behavior is observed. The X-ray diffraction patterns of the activated system do not contain intermetallides; no solid solutions are observed till a definite moment of time ($a = 2.8672$ nm after MA for 3 min and $a = 2.8688$ nm after MA for 20 min); however, bismuth becomes invisible in diffraction patterns after the activation time of 20 min, both X-ray (Fig. 1) and electron diffraction patterns are evidences for this fact. Mössbauer spectra also indicate the absence of interaction within this time interval (Fig. 2). The X-ray photoelectron spectra provide an evidence that bismuth is on the surface of iron; the thickness of bismuth-enriched layer is 2–3 nm (Fig. 3). Bismuth concentration profiles over the depth of the iron particle were obtained by means of etching with the argon ions at the spraying rate of 10 Å/min, while a sharp decrease in bismuth concentration occurs within 2–3 min.

According to the data of chemical analysis, bismuth content of these samples after MA is 9.8 wt% in mixture with copper, and 9.6 wt% in mixture with iron, while the initial mixture contained 10 wt (3 at.)% Bi.

Under the subsequent mechanical activation, bismuth starts to intrude itself into iron lattices (Fig. 4). The formation of solid solution on the basis of the α-Fe lattice is reliably detected by Mössbauer spectroscopy after activation for 40 min (Fig. 2). At this moment, nanostructure ($l < 10$ nm) is formed in α-iron particles. Insertion of bismuth into iron grains from the boundaries immediately leads to an increase in the number of microdistortions.

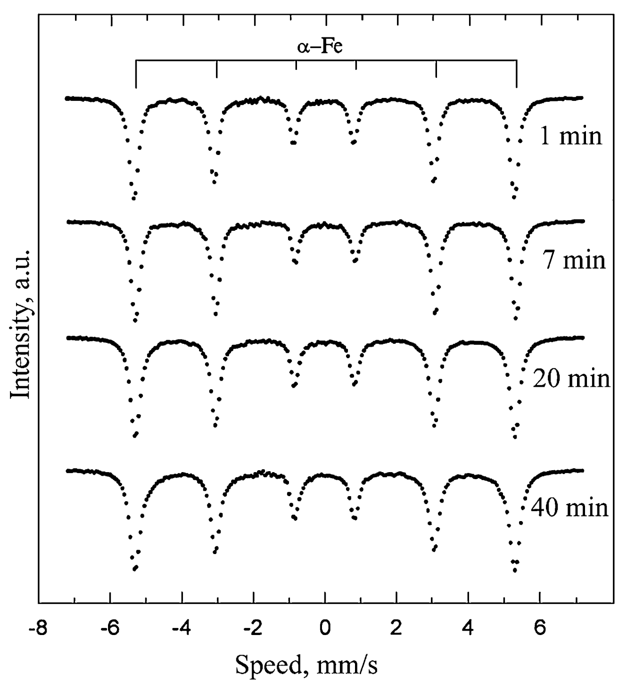

Figure 2 Mössbauer spectra of the Fe 3 at.% Bi mixtures taken after various milling times.

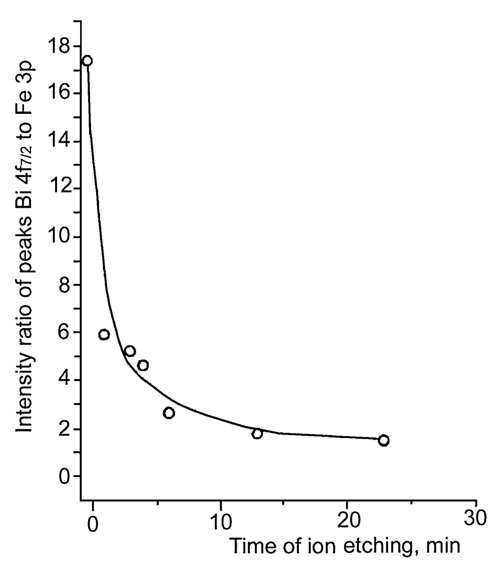

Figure 3 The profiles of Bi concentration over depth of particle.

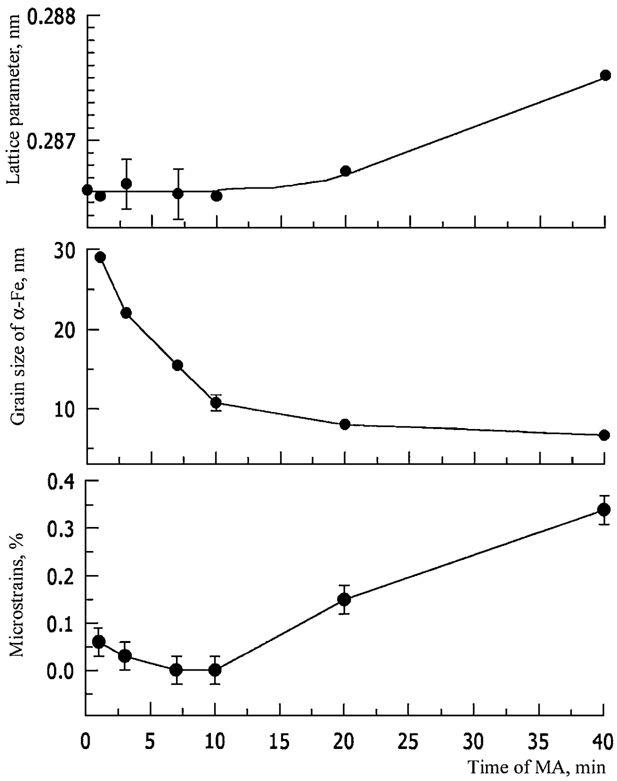

Figure 4 Structure change in the Fe 3 at.% Bi mixture during MA.

4. Conclusion
The obtained experimental data showed that under mechanical alloying in the systems with positive enthalpy of mixing, composed of a solid and a liquid metal, the first stage results in the formation of a mechanocomposite in which the solid-phase component has nanometer size, while the liquid phase is spread over the surface of the solid one in a very thin layer due to good wettability. Mechanical activation of the formed nanocomposites leads to the formation of non-equilibrium solid solutions.

Acknowledgments
The investigation has been performed within the Integration Program of Russian Academy of Science I-8.15 "Fundamental problems of physics and chemistry of nanosized systems and nanomaterials."

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Received 11 September 2003
and accepted 27 February 2004