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Phase transformations during mechanical alloying and subsequent heating of Fe–Al–B powders

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Elemental powder mixtures of $(Fe50Al50)_{100-x}B_x$ ($x = 5$, 10, 20 and 30 vol%) were subjected to mechanical alloying. The thermal behaviour of the milled powders was examined by differential scanning calorimetry. Structural and phase transformations occurring in the powders throughout mechanical alloying and during subsequent heating in the calorimeter were investigated by X-ray diffraction. It was found that for all the powder mixtures, a nanocrystalline Fe(Al) solid solution was formed during milling. For the powders containing 20 and 30% of B, an amorphous phase was also present in the ball milled product and for the latter one it was the prevalent phase. Thus, the content of B in the powder mixture affects phase transformations which take place during mechanical alloying of Fe–Al–B powders. It was also found that the increase of B content in the mixtures causes more intense decrease of the Fe(Al) grain size during milling. Microscopy examinations revealed that the produced powders have composite structure with B particles embedded in the nanocrystalline Fe(Al) solid solution matrix or in the two phase amorphous and nanocrystalline matrix, depending on B content. Upon heating of the ball milled products containing 5 and 10% of B, the Fe(Al) solid solution transformed into the ordered FeAl intermetallic phase. During heating of the ball milled products containing 20 and 30% of B, the amorphous phase crystallised and a phase isomorphic with the $AlFe_2B_2$ one was formed.

1. Introduction

Mechanical alloying (MA) is a widely used method for the preparation of nanocrystalline or amorphous powders [1]. It is known that the reduction of the grain size to the nanometer scale can improve physical and mechanical properties comparing to those of materials with the micrometer grain size range [2–7]. An advantage of MA, besides ability of nanocrystalline structure formation, is that during this process alloys are formed by solid-state reaction [1]. MA processes are usually carried out by ball milling that involves repeated welding, fracturing and rewelding of powder particles. In the case that ductile and hard, brittle components are milled together, usually, the latter ones get fragmented and refined and tend to become trapped in the ductile particles [1]. Consequently, the resulting powder can have a composite structure with clear contamination-free boundaries between the matrix and the strengthening particles, which will result in good adhesion between constituents. The product of the described process will be therefore an *in situ* composite. The use of milling should also enable attaining a homogeneous distribution of trapped reinforcing particles in the matrix. The use of low-density strengthening particles such as boron will cause decrease of the material density.

By means of the MA process of metal powders mixtures with composition corresponding to intermetallic phases stoichiometry, alloys with the structure of disordered or partially ordered solid solutions are usually produced [1,8]. Over the last few years, a number of studies have been reported on mechanically alloyed Fe–%50Al powder mixture [9–13]. The disordered Fe(Al) solid solution [9–12] or partially ordered FeAl intermetallic phase (B2 structure) [13] were obtained in the mentioned works. Disordered Fe(Al) solid solution produced by MA can be ordered and transformed to FeAl intermetallic phase by heat treatment [9–12].

It is well established that a very small addition of boron (~0.1 at %) improves mechanical properties in number of intermetallics, among others the FeAl one [14]. The beneficial role of boron is caused by its segregation to the grain boundaries and the enhancement of their cohesion [15]. Fe–Al alloys with larger boron addition, up to 20 at%, were prepared by MA [16,17]. There is an evidence that when boron is milled with ductile components, the

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powder particles of MA product contain built-in boron inclusions [18]. In the works mentioned above on mechanical alloying of Fe–Al–B powders [16,17], no composite structure with boron inclusions embedded in powder particles was reported. However, composite structures with boron particles embedded in an amorphous $Al_{85}Fe_{15}$ alloy [19] or in amorphous $Al_{60}Fe_{15}Ti_{15}(Co/Mg/Zr)_5$ alloys [20] have been obtained recently by MA. Composite powders consisting of Fe(Al) matrix reinforced with TiC, NbC, VC, TiN or Al_2O_3 prepared by MA have been reported [5,21–23]. However, no works devoted to the production of composite powders consisting of Fe(Al) or FeAl alloy reinforced with boron particles (which have lower density than the reinforcements mentioned above) have been found in the literature.

In this work, we studied structural and phase transformations taking place during mechanical alloying of the Fe–Al–B system and during heating of the MA products. It was assumed that during milling processes boron particles will be built into the matrix being formed *in situ*. We examined the role of boron content in the phase formation during milling.

2. Experimental

In this study, the starting elemental powders were Al (99.7% purity, 325 mesh), Fe (99.9% purity, 200 mesh) (ABCR products) and crystalline B (99.4% purity, 100 mesh) (Chemsavers product). The initial materials for mechanical alloying processes were powder mixtures of Fe-50at.%Al with addition of 5, 10, 20 and 30 vol% of B (abbreviated in the text as B5, B10, B20 and B30 respectively). The quantity of added boron was calculated assuming the measured densities of the Fe, Al and B powders. Mechanical alloying processes were performed in a SPEX 8000 D high-energy shaker ball mill. The ball-to-powder weight ratio was about 10:1. To minimize oxygen contamination, powder sampling and the milling processes were carried out under argon atmosphere. Fe-50at.%Al powder mixture without addition of B was also mechanically alloyed under the same conditions as a reference sample (B0).

The thermal behaviour of the mechanical alloying products was examined by differential scanning calorimetry (DSC) using a Perkin Elmer DSC7 calorimeter. The DSC scans were performed under protective Ar atmosphere in a temperature range from 50 to 720 °C at a constant heating rate of 40 °C/min.

The phase changes that occurred in the material throughout the mechanical alloying processes and the structure of the materials after heating in the calorimeter were investigated by X-ray diffraction (XRD) method using a Rigaku MiniFlex II diffractometer operated with a CuK_α radiation. The DHN-PDS software was used for $K_{\alpha 2}$ component stripping from the XRD patterns (Rachinger method), indexing the peaks and calculation and refinement of unit-cell parameters. To assess the mean crystallite size, the Williamson-Hall method was applied. The instrumental broadening was adjudicated using a Si standard, and subtracted from the experimental breadth to obtain the “physical” broadening of each diffraction line.

A Hitachi S-3500N scanning electron microscope (SEM) equipped with EDS system was used for observations of the milled powders and for determination of chemical composition. Cross-section samples for SEM examinations were prepared by embedding the powder in a conducting resin and subsequent polishing.

The density of the loose powders was measured using a helium pycnometer Accupyc 1330.

3. Results and discussion

Fig. 1 illustrates XRD patterns of the Al–Fe–B powder mixtures in the initial state and after selected milling times. For the mixtures containing 5 and 10 vol% of boron (Fig. 1a and b), the diffraction peaks related to this element are not present in the pattern of the initial powders, while for two other mixtures some very weak boron peaks are visible. This is due to the low scattering factor of boron, its small amount in the mixture and high X-ray mass absorption coefficient of Fe [24]. For each phase present in a polyphase mixture, a limit of detection depends, among others, on the structure of this phase and on the character of coexisting phases. Intensity of diffraction lines of a phase present in a mixture depends not only on its concentration, but also on its structure (phase that consists of light atoms exhibits smaller peaks intensity than the one built of heavier atoms – the effect of structural factor) and on mass absorption coefficients of mixture and phase. For the intensity $I_{(hkl)\alpha}$ of a *hkl* line of a phase α in a mixture and for the intensity $I^0_{(hkl)\alpha}$ of the same *hkl* line in pure phase α, there is a dependence [25].

$$I_{(hkl)\alpha} = I^0_{(hkl)\alpha}\frac{\mu_\alpha}{\mu_m}X_\alpha, \tag{1}$$

where μ_α and μ_m are mass absorption coefficients of phase α and of mixture respectively, and X_α is the weight fraction of phase α. The mass absorption coefficient of polyphase mixture is the weighted average of the mass absorption coefficients of its components [24] and is given by

$$\mu_m = \sum_i \mu_i X_i, \tag{2}$$

where μ_j and X_j are mass absorption coefficient and weight fraction of component j respectively. For Cu K_α radiation, the mass absorption coefficients of Fe, Al and B are 304.4, 50.23 and 2.14 cm^2/g respectively [26]. Hence, in Equation (1) for the initial B10 mixture, the $\frac{\mu_\alpha}{\mu_m}X_\alpha$ term related to boron is equal to 0.00052. Thus, it can be expected that diffraction peaks of boron could be of negligible intensity and lost in background. Although undetected by XRD, the balance of B must have been present in each mixture throughout the performed mechanical alloying processes.

In the XRD patterns in Fig. 1, for all powder mixtures, the Al diffraction peaks intensity decreases with respect to that of the Fe ones as the milling proceeds. In the patterns after 6 h of milling the Al peaks are not present, except the for the sample with the lowest content of B, where a trace of the most intense Al line (111) is visible. At the same time the Fe diffraction peaks become asymmetric, broader at low-angle shoulders. Such a change in the shape of peak profiles can be due to appearance of broad, low intense peaks on the left side of the Fe peaks. The new peaks contributing to the profiles are related to a new phase with the same structure as the bcc Fe and a slightly larger unit cell parameter. These observations indicate the formation of Fe(Al) solid solution. We found analogous features in the case of mechanical alloying of Al–50% Fe [11], Al–40%Fe and Al–35% Fe [8] powder mixtures and analysed them in more details in terms of Fe(Al) solid solution formation [11]. In the pattern of B5 powder after 10 h of milling (Fig. 1a), the Al (111) line disappears and for all milled compositions the diffraction lines of Fe(Al) solid solution are no more asymmetric. Another observation in Fig. 1 is a broadening of the diffraction peaks with the milling time extension. This broadening is due to the decrease in the mean crystallite size and/or the increase in the lattice strain. The extent of the broadening increases with the increase of the B content in the milled mixtures. For the B30 samples milled for 20 and 30 h (Fig. 1d), in the XRD pattern only a broad peak with a maximum intensity at 2θ of about 44° and weak, very broad peaks at higher angular positions are visible. This kind of diffractograms can be considered as overlapping of the pattern of a nanocrystalline