AMORPHISATION PROCESS DURING MECHANICAL ALLOYING OF Al-Fe-Ti POWDERS AND CRYSTALLISATION OF THE MILLING PRODUCTS

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Abstract. In the present work, an elemental equiatomic powder mixture of Al, Fe, and Ti was mechanically alloyed in a high-energy ball mill. The phase transformations occurring in the material during milling and during subsequent heating in a calorimeter were studied with the use of X-ray diffraction. The results obtained show that an amorphous phase is formed during performed mechanical alloying process. However, some differences in the diffraction halo profile of the amorphous phase at different stages of the milling process were observed. It was also found that the products of crystallisation of the amorphous materials characterised by dissimilar diffraction halo were different. Crystallisation product of 10 h-milled sample was identified as a mixture of τ_2 phase and Fe(Al,Ti) solid solution, while of 30 h-milled sample – as a nanocrystalline AlFeTi intermetallic phase with B2 structure and the lattice parameter 2.951 Å. These results, as well as dissimilarity between calorimetric curves of the powders after 10 and 30 h of milling, indicate that different amorphous phases were formed at the different stages of the mechanical alloying process.

1. INTRODUCTION

A great advantage of the mechanical alloying (MA) process originates from the fact that it allows one to obtain materials far from their thermodynamic equilibrium. In particular, nanocrystalline, quasicrystalline or amorphous structures can be formed by the MA process [1,2]. In the latter case, it has been noted that it is easier to produce an amorphous phase, and it has a wider composition range, in an alloy system by MA than by rapid solidification process (RSP) [2]. There are some systems in which it is possible to produce an amorphous phase by MA but not by RSP techniques [2].

Al-Fe-Ti alloys have received attention over the last years [3]. The Al-Fe-Ti system in equilibrium state has recently been investigated [3], whereas works devoted to non-equilibrium alloys from this system are scarce. The formation of an amorphous phase was found in the case of mechanical alloying of Al50%Fe25%Ti25% (all compositions are given in at.% throughout this paper) powder mixture [4]. It was also found that creation of an amorphous phase took place at the middle stage of mechanical alloying process of an elemental equiatomic Al-Fe-Ti powder mixture, performed under nitrogen atmosphere [5]. The aim of this work was to study the structural and phase transforma-

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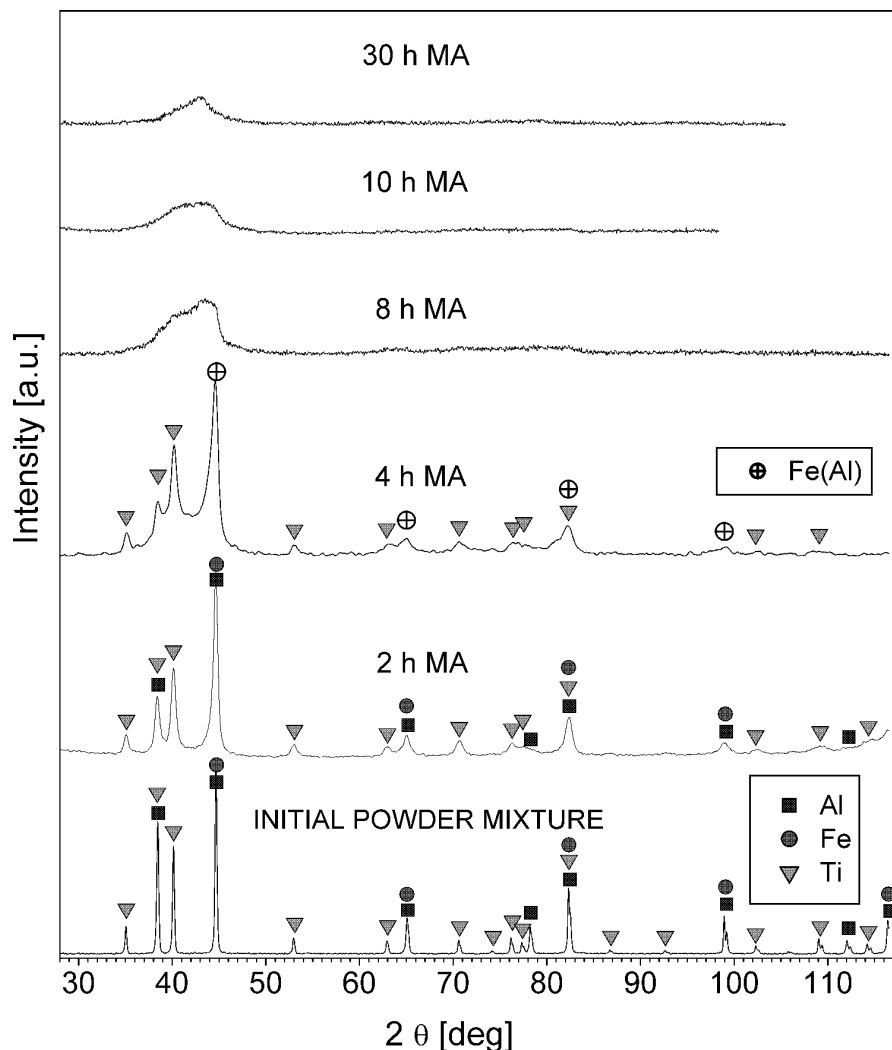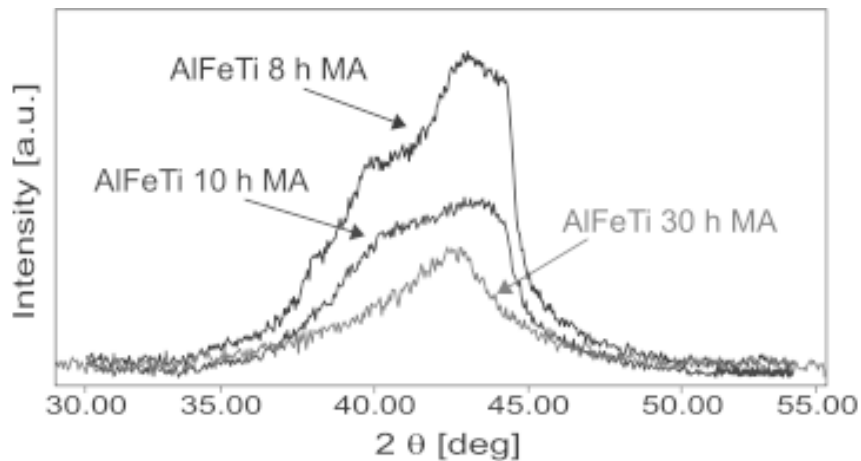Corresponding author: M. Krasnowski, e-mail: makr@inmat.pw.edu.pl

Fig. 1. XRD patterns of Al-Fe-Ti powder mixture at indicated milling times.

tions taking place during the mechanical alloying of an elemental equiatomic powder mixture of Al, Fe and Ti under argon atmosphere and during subsequent heating of the milled powders.
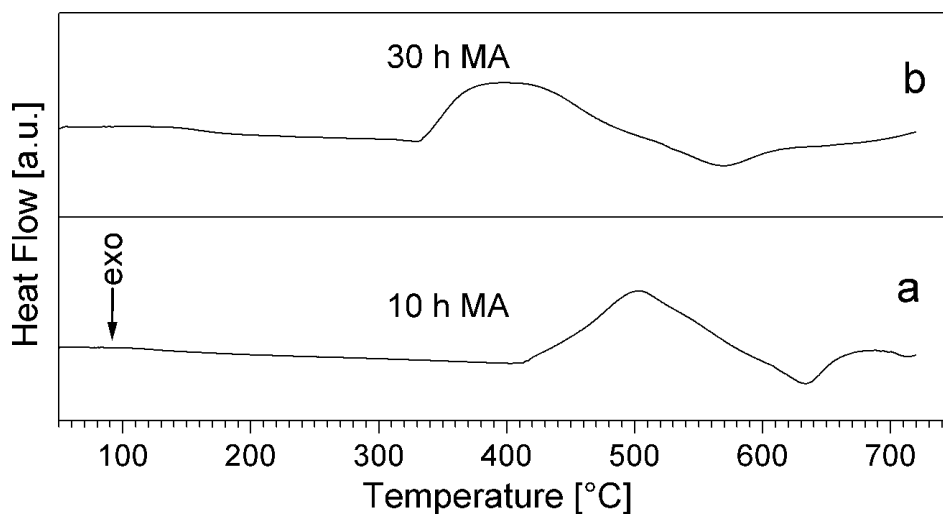
2. EXPERIMENTAL PROCEDURE

Pure Fe, Al and Ti elemental powders of composition Al 33.3%, Fe 33.4% and Ti 33.3% (at.%) were mechanically alloyed in a SPEX 8000 D high energy shaker ball mill under argon atmosphere. The ball-to-powder weight ratio was about 8:1. The phase changes that occurred in the material during milling were investigated by X-ray diffraction (XRD) method using a Philips PW 1830

diffractometer with a CuK_α radiation. The thermal behaviour of the milled material was examined by differential scanning calorimetry (DSC) using a Perkin Elmer DSC7 calorimeter in a temperature range from 50 to 720 °C at a constant rate of 20 °C/min. Specimens after heating in the calorimeter were investigated by XRD. The lattice parameters, the mean crystallite size and the mean lattice strain (the latter two estimated by the Williamson-Hall method) were calculated from the XRD data. The instrumental broadening was determined using a Si standard and subtracted from the experimental breadth to obtain physical broadening of each diffraction line, which was then used for the Williamson-Hall calculations.

Fig. 2. Enlarged fragments of the diffraction patterns in the range from 30 to 55°, for the 8, 10, and 30-h milled powders.
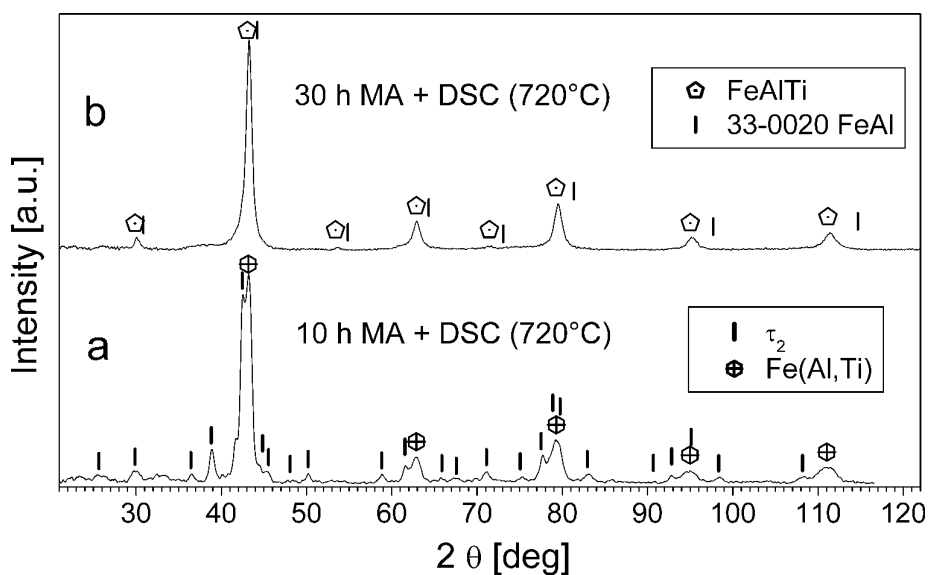

Fig. 3. DSC curves of the amorphous powders after: a) 10 and b) 30 h of mechanical alloying.

3. RESULTS AND DISCUSSION

In Fig. 1 the XRD patterns of the investigated powder mixture in the initial state and after various milling times are shown. On the basis of these patterns, one can perceive phase transformations occurring in the material during milling, however superposition of some peaks related to the constituent elements introduces some difficulties in detailed analysis. The XRD results reveal that at the early stage of the MA process (up to 4 h) the intensity of the Al diffraction peaks decreases progressively with respect to that of the Fe and Ti ones. In the XRD pattern of the powder after 4 h of the MA process, the Al (311) peak that is free from overlaps is not present (in the standard card it has

a relative intensity of 24% (JCPDS 04-0787)), while Fe and Ti peaks are still present. Therefore, we can assume that after 4 hours of the MA process all Al atoms become dissolved, most probably in the Fe lattice. Formation of Fe(Al) solid solution at the first stage of mechanical alloying of powder mixtures consisted of 3 or 4 elements was found for Al50Fe25Ti25 [4], Al25Fe25Ti25C25 [6], Al30Fe30Ti15C15 [7], Al45Fe45Ti5C5 [8] compositions and for equiatomic Al-Fe-Ti powder mixture milled under nitrogen atmosphere [5]. The XRD pattern for 8 h milled powder is significantly different than the previous one. There are no more well defined diffraction lines of previously existing phases, while a broad, asymmetric diffraction pro-

Fig. 4. XRD patterns after DSC examination of: a) 10 h-milled and b) 30 h-milled sample.

file is present. This kind of pattern indicates the appearance of an amorphous phase and very considerable grain refinement and high density of defects in the still remaining crystalline one. The next diffraction pattern, after 10 h of milling, indicates absence of any crystalline structure and the presence of an amorphous one. However, the visible diffraction halo is not like typical one originating from an amorphous phase and it looks like two overlapping haloes, one with a maximum intensity at 2θ of about 41.5°, and the second – of about 43.6°. The XRD pattern after 30 h of milling exhibits one halo and is typical for the amorphous phase. Fig. 2, which shows enlarged parts of the diffraction patterns in the range from 30 to 55°, for the 8, 10 and 30-h milled powders, illustrates differences in the diffraction halo profile of the amorphous material at the different stages of mechanical alloying. Basing on XRD results, we can speculate that after 10 h of milling, when amorphisation process is completed, the material is, most probably, not homogeneous and there are regions differing in chemical composition. Hence, possibly, at this step of milling two amorphous phases, which differ in chemical composition, coexist within the material and this supposition may explain the appearance of two overlapping diffraction haloes.

DSC experiments followed by XRD investigations can provide more information regarding dif-

ferences between amorphous material after 10 h and 30 h of mechanical alloying. The DSC curves of 10 h and 30 h-milled samples are shown in Fig. 3, while XRD patterns of these powders after heating in the calorimeter – in Fig. 4. In both cases two overlapping broad peaks: the first one associated with endothermic effect, and at higher temperature the second – an exothermic one are visible. However, there is a difference between both DSC scans – for 10 h-milled sample the peaks are recorded at higher temperature than for sample after 30 h of the MA process. The exothermic effect is certainly related to crystallisation of amorphous material. In the case of 10 h-milled sample the temperature of exothermic peak is equal to 633 °C, while for the second sample is of 570 °C. In the Fig. 4 one can see that the XRD patterns of the materials after heating in the calorimeter differ significantly from each other. Regarding the 30 h-milled sample after heating, in the XRD pattern, instead of the halo, the diffraction lines assigned to a cubic phase with ordered B2 structure and the lattice parameter equal to 2.951 Å appeared. The relative intensities of these lines are analogous to those of the FeAl phase with B2 structure and lattice parameter equal to 2.895 Å (JCPDS 33-0020). Taking into account this similarity of relative intensities and some difference of lattice parameter we can infer that an ordered AlFeTi intermetallic phase is the product

of crystallisation of the amorphous phase obtained after 30 h of milling. The mean crystallite size and the mean lattice strain in the crystallised AlFeTi intermetallic phase is 23 nm and 0.24% respectively. Whereas in the case of the sample milled for 10 h and heated in the calorimeter, some of the XRD peaks are found to be related to τ_2 phase with D8a structure ($Mn_{23}Th_6$ type), which exists in the Al-Fe-Ti system over a wide range of compositions [3]. The lattice parameter of the crystallised τ_2 phase is equal to 12.038 Å. The other peaks in the XRD pattern in Fig. 4a can be attributed to a bcc phase with the lattice parameter equal to 2.961 Å. This value is close to the lattice parameter of the FeTi phase, which is equal to 2.976 Å (JCPDS 19-0636), however the relative intensities of diffraction lines of this phase are quite different from those of the cubic phase, observed in Fig. 4a. Hence, we do not expect that this cubic phase is a FeTi intermetallic. On the other hand, the relative intensities of the peaks of the cubic phase are very similar to those of the FeAl phase (except superlattice lines which are absent in Fig. 4a) or of Fe(Al) solid solution [9] and meanwhile the lattice parameter of the cubic phase is larger than that of Fe(Al) [9]. Assuming that the crystallised cubic phase is a Fe based solid solution, this difference of lattice parameter can be due to the presence of not only Al atoms, but also Ti atoms as a solute. Hence, we suppose that the cubic phase, which crystallised beside the τ_2 phase, is a Fe(Al,Ti) solid solution. The creation of a τ_2 phase and a Fe(Al,Ti) solid solution as crystallisation products has been found when the amorphous phase which was formed throughout mechanical alloying of the Al50Fe25Ti25 powder mixture was heated in the calorimeter [4].

Basing on DSC experiments followed by XRD investigations, we can say that the different crystallisation products, as well as dissimilarity between DSC curves of the powder after 10 and 30 h of milling, support our conclusion concerning formation of different amorphous phases at the different stages of the MA process.

4. CONCLUSIONS

We investigated the phase development during mechanical alloying of the equiatomic Al-Fe-Ti pow-

der mixture and during subsequent heating of the milling product. On the basis of the XRD results we conclude that an amorphous phase is formed during the mechanical alloying process. However, some differences in the diffraction halo profile of the amorphous phase at different stages of the milling process (after 10 and 30 h) were observed. We also found that the products of crystallisation of the amorphous materials characterised by dissimilar diffraction halo were different. The crystallisation product of the 10 h-milled sample was identified as a mixture of τ_2 phase and Fe(Al,Ti) solid solution, while for the 30 h-milled sample it was an AlFeTi intermetallic phase with B2 structure, the lattice parameter 2.951 Å and mean crystallite size of 23 nm. Some dissimilarity between calorimetric curves of the powders after 10 and 30 h of milling were observed. The obtained results indicate that different amorphous phases were formed at the different stages of the mechanical alloying process.

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