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# Bulk amorphous and nanocrystalline Al83Fe17 alloys prepared by consolidation of mechanically alloyed amorphous powder

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ABSTRACT

In the present work, bulk amorphous and nanocrystalline Al83Fe17 alloys were obtained by consolidation of mechanically alloyed powders. Mechanical alloying of Al–17% Fe powder mixture yielded powder with an amorphous structure. Thermal behaviour of the milling product was examined using differential scanning calorimetry. This investigation revealed that the amorphous phase crystallised above 380 °C. The amorphous powder was compacted under a pressure of 7.7 GPa in different conditions: at 380 °C for 600 s and at 1000 °C for 180 s. Structural investigations of the bulk material revealed that the amorphous structure was retained after consolidation process applied at 380 °C. Compaction under high pressure at 1000 °C caused crystallisation of the amorphous phase and appearance of metastable nanocrystalline phases, different to those which crystallised during heating in the calorimeter under atmospheric pressure. The microhardness of the bulk amorphous sample is 760 HV0.2, whereas that of bulk nanocrystalline one is 630 HV0.2. The density of the bulk amorphous material is 3.505 g/cm$^3$ and is ~3% lower than that of the nanocrystalline one. The open porosity of both consolidated materials is 0.4%. The results obtained show that the quality of compaction preserving amorphous structure as well as of the one yielding nanocrystalline structure is satisfactory and the products' microhardness is relatively high. The results also indicate that application of high pressure affects crystallisation of amorphous alloy influencing the phase composition of the products of this process.



## 1. Introduction

The main advantages of aluminium based alloys are low density and a good corrosion resistance. Among the aluminium alloys, iron aluminide intermetallics seem to be of technological interest [1]. This is due to their advantageous properties, in particular a high specific strength (strength-to-density ratio), high specific stiffness, good strength at intermediate temperatures and excellent corrosion resistance at elevated temperatures under oxidizing, carburizing and sulfidizing atmospheres [1]. A new class of Al-based alloys, which has received a great deal of attention over the last few years, are amorphous as well as nanocrystalline ones. Amorphous alloys can have unusual combination of properties such as high strength, good ductility, high fracture toughness and good corrosion resistance [2]. Nanocrystalline materials exhibit enhanced properties, such as high strength and hardness [3,4], compared to the materials with conventional grain size. Mechanical alloying (MA) is a widely used processing route for synthesis of amorphous and nanocrystalline materials [5]. However, MA products are in the form of a powder, thus consolidation is a necessary step for milled powders for possible practical applications. Consolidation of amorphous powders into bulk, full-density material providing amorphous structure's maintenance or creating nanocrystalline one is not easy to achieve. Crystallisation of amorphous phase and extensive grain growth occur during conventional consolidation at elevated temperature. High temperature is required for good consolidation of powders into bulk materials, i.e. to remove all porosity and to obtain good interparticle bonding, this is why the serious challenge of compaction processes is to retain the amorphous structure or to preserve nanocrystalline structure if such was formed during consolidation. To fulfil this, the applying of a high pressure during consolidation as well as limiting of the high temperature exposure time should be taken into account. High pressure hot-pressing method has been successfully used for producing bulk nanocrystalline samples [6–11]. Recently, we demonstrated that application of a high pressure influences grain growth at elevated temperature by hindering it [8–10].

Amorphous aluminium-rich Al–Fe powder alloys have been prepared using the MA process [12,13]. However, works devoted to consolidation of these powders are not plentiful [14].

In the present work, we obtained bulk amorphous as well as bulk nanocrystalline Al–17% Fe alloys by consolidation of amorphous powders. The structural and phase transformations taking place

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during the mechanical alloying, during subsequent heating of the final milling product and during consolidation were also studied.

## 2. Experimental

Pure Al and Fe elemental powders of composition Al–17% Fe (all compositions are given in at.% throughout this paper) were mechanically alloyed in a SPEX 8000 D high-energy shaker ball mill. The ball-to-powder weight ratio was about 10:1. In order to minimize oxygen contamination the milling process was performed under argon atmosphere.

The thermal behaviour of the milling product was examined by differential scanning calorimetry (DSC) method using a PerkinElmer DSC7 calorimeter in a temperature range from 50 to 720 °C at a constant rate of 40 °C/min.

A press equipped with a toroid-type high pressure cell was used for consolidation of the milled powder. The shape of the cell and the material of the gasket ensure that the compacting conditions were close to isostatic ones. The compaction process was performed under a pressure of 7.7 GPa at a temperature of 380 °C for 10 min and at a temperature of 1000 °C for 3 min. The heating and cooling rate was 1000 °C/min.

The phase changes that occurred in the powder during milling as well as the structure of the materials after heating in the calorimeter and after consolidation were investigated by X-ray diffraction (XRD) method using a Philips 1830 diffractometer using $CuK_\alpha$ radiation. The lattice parameter, the mean crystallite size and the mean lattice strain, the latter two determined by the Williamson–Hall method, were calculated from the XRD data taking into account $CuK_{\alpha1}$ radiation, after $K_{\alpha2}$ stripping using the Rachinger method. The instrumental broadening was determined using an Si standard and subtracted from the experimental breadth to obtain a "physical" broadening of each diffraction line, which was then used for the Williamson–Hall calculations.

A Hitachi S-3500N scanning electron microscope (SEM) as well as a Reichert MeF2 light microscope was used for observation of the surface of the bulk samples. Samples for SEM and light microscopy were prepared using standard polishing techniques.

The hardness of the compacts was measured using a ZWICK microhardness tester under a load of 200 g imposed for 15 s. Vickers microhardness value was the average of at least 25 indentations. The density of bulk samples was determined using a Gibertini E154 balance equipped with a device for measuring the density of solids (Archimedes method). The error in density determination was 0.5%. Basing on mass measurements performed during density determination, open porosity of bulk samples was calculated.

## 3. Results and discussion

Fig. 1 shows the XRD patterns of the powder mixture of Al–17% Fe in the initial state, after various milling times and after DSC examination (up to 720 °C) of the final MA product. On the basis of these patterns, phase transformations occurring in the powder samples during the MA process and during heating in the calorimeter can be analysed. The XRD results demonstrate that with the increase of milling time, the intensity of the fcc Al diffraction peaks decreases progressively with respect to that of the bcc Fe ones. Simultaneously, the Fe diffraction lines become slightly shifted towards lower angles, which indicates that the lattice parameter of Fe has increased. These changes suggest that a bcc Fe(Al) solid solution forms during this stage of the process. Another feature which can be seen in this pattern is a broadening of the diffraction lines due to the reduction in grain size and the increase in lattice strain. In the XRD pattern obtained after 25-h milling, one can see broad Fe-based solid solution peaks, the residual Al peaks and a small broad halo due to an amorphous component seeming to overlap the most intense peak. After 35 h of MA, the Al peaks vanish completely and only an amorphous halo and very weak Fe(Al) peaks are visible. The next XRD pattern reveals amorphous halo only, which indicates that further milling up to 50 h induces complete amorphisation of the milled material. Thus, the product of performed mechanical alloying of Al–17% Fe powder mixture is an amorphous alloy. According to the Fe–Al phase equilibrium diagram, for the concentration of 83% of Al there is a two-phase $FeAl_3$ + Al field. However, mechanical alloying is a non-equilibrium processing technique, hence the phase composition of its products can differ from that expected taking into account phase equilibrium diagrams. For example, an almost complete amorphisation

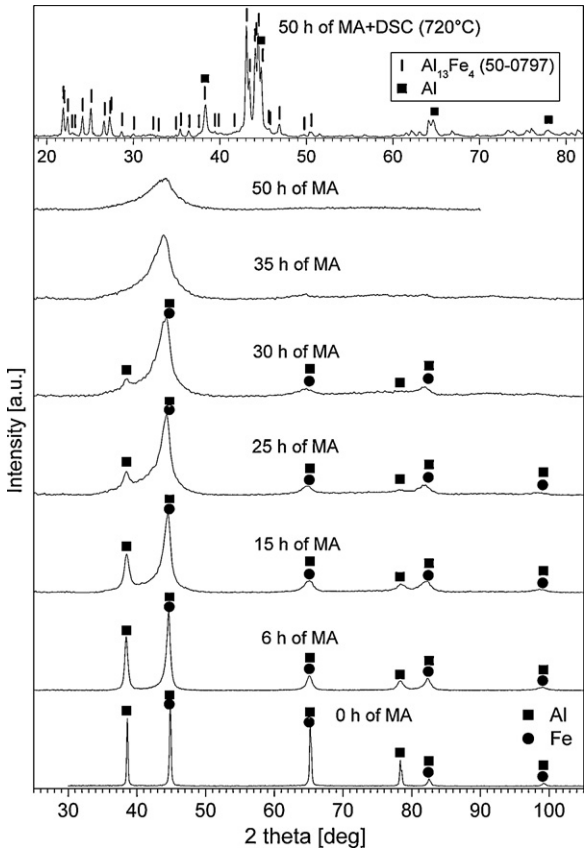


**Fig. 1.** XRD patterns of the Al83Fe17 powder mixture after various milling times and after DSC examination of the final MA product.

was found in compositions with Al concentration ranging from 67% to 83% during mechanical alloying of Al–Fe alloys in low-energy conventional ball mill [12].

In order to study the thermal behaviour of the milling product, the powder sample was examined in the calorimeter. Fig. 2 shows the DSC trace for the powders after 50 h of the MA process. The DSC curve reveals three exothermic peaks at temperature between about 380 and 650 °C and endothermic one at 670 °C. The exothermic effects, or at least one of them, can be related to crystallisation of amorphous phase, while the endothermic one to Al melting.

The powder sample after DSC examination was investigated using the XRD method in order to define the phase changes that occurred during heating. The diffraction spectrum of the final milling product after heating in the calorimeter is shown at the top of Fig. 1. Comparing this spectrum with the one obtained before heating, one can see that diffraction lines appear, which confirm the origin of the exothermic effects. These lines are attributed to the $Al_{13}Fe_4$ phase (50-0797 ICDD card) and to fcc Al.

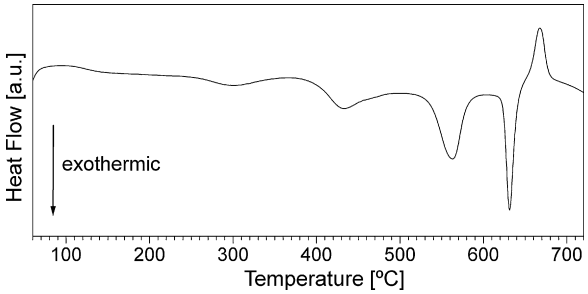


**Fig. 2.** DSC curve of the final milling product after 50 h of MA.

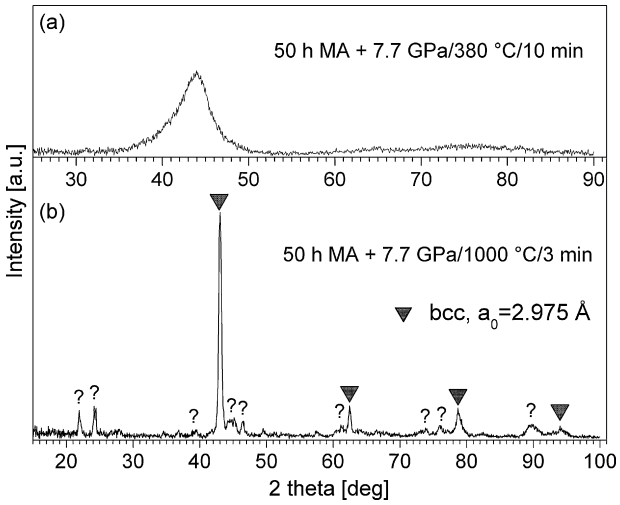


**Fig. 3.** XRD patterns of the bulk samples after consolidation of the final milling product at (a) 380 °C and (b) 1000 °C.

The final MA product was subjected to high pressure consolidation. Two temperatures were chosen for this process: 380 °C for the purpose of providing amorphous structure's maintenance during compaction, and 1000 °C, which was usually used in our previous works for consolidation of nanocrystalline powders [8–11,14]. The XRD patterns of the consolidated materials are shown in Fig. 3. In Fig. 3a, for the sample processed at 380 °C, only an amorphous halo is visible. This indicates that amorphous structure of the material was retained during compaction. In Fig. 3b, for the sample processed at 1000 °C, diffraction peaks are present, which indicates that crystallisation of amorphous phase occurred during consolidation. However, the diffraction lines in Fig. 3b cannot be assigned to any phase in Al–Fe system [15] nor to any Al–Fe phase in the ICDD PDF4 database, hence products of the crystallisation under high pressure of the amorphous Al83Fe17 alloy are metastable phases. Some of the peaks of the pattern in Fig. 3b can be indexed in cubic system and attributed to a phase with bcc structure and unit cell parameter of 2.975 Å. The estimated crystallite size and the mean lattice strain of this phase are 36 nm and 0.1%, respectively. It is worthwhile to comment on the pressure's effect on crystallisation of the amorphous Al83Fe17 alloy. During heating in the calorimeter, when material was under atmospheric pressure, the crystallisation products were the $Al_{13}Fe_4$ phase and fcc Al, while during heating throughout the consolidation process, when high pressure was applied, crystallisation yielded metastable phases different from the ones mentioned above. Hence, in our case, we can infer that application of high pressure affects crystallisation of amorphous alloy influencing the phase composition of the products of this process.

Compacted samples were investigated using light microscopy and SEM in order to verify the quality of consolidation. Fig. 4 shows the images of the polished samples' surface. One can see that the surface is smooth and free of pores between bound powder particles, which evidences good quality of consolidation.

The consolidated material was also characterised using microhardness, density and open porosity measurements. The average Vickers microhardness value of the consolidated samples is equal to 760 HV0.2 with a standard deviation of 23 (3.0%) and 630 HV0.2

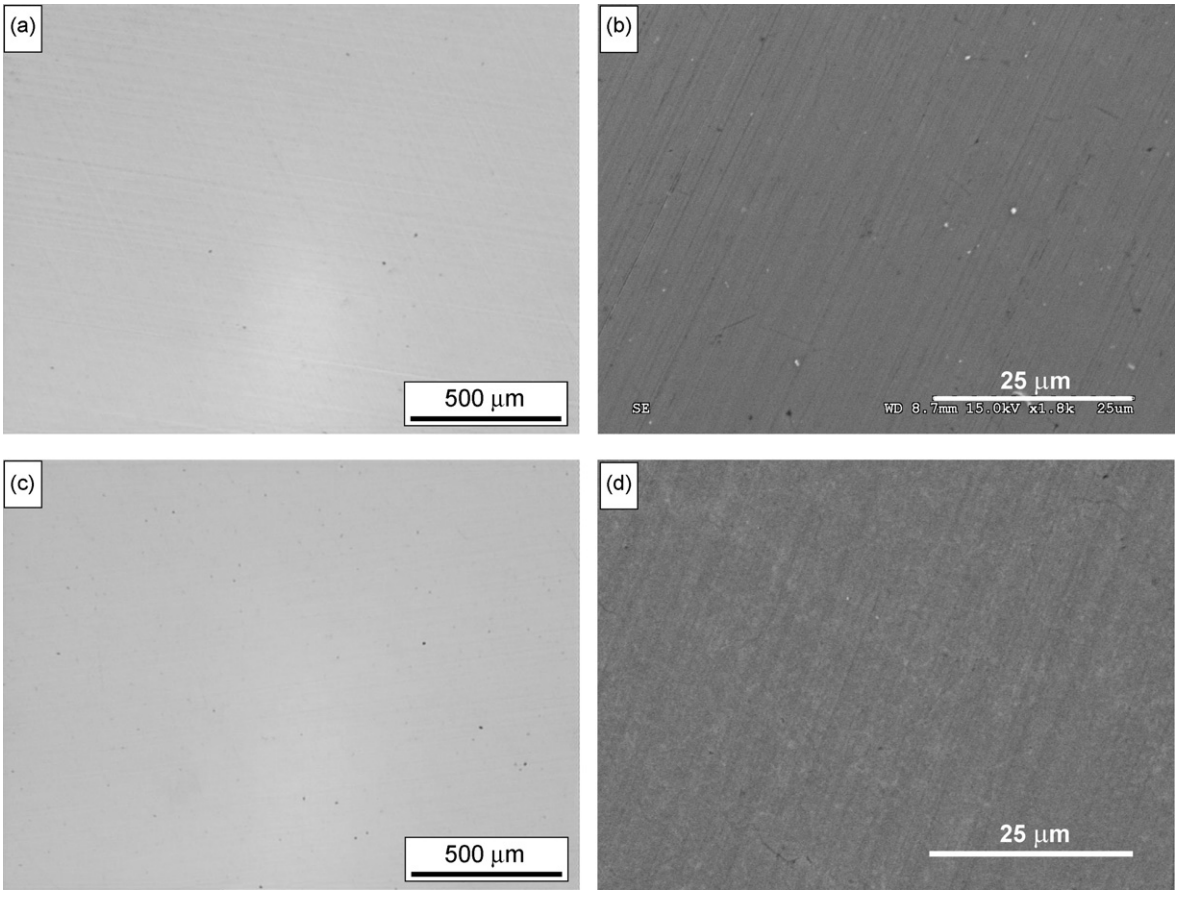


**Fig. 4.** Micrographs of the polished surface of the consolidated samples: (a, b) amorphous material; (c, d) nanocrystalline material; (a, c) light microscopy images; (b, d) SEM images.

with a standard deviation of 37 (6.0%) for bulk amorphous and nanocrystalline sample, respectively. No information about hardness of a bulk amorphous or nanocrystalline Al–Fe alloys with similar content of Al to that in this study has been found in literature. However, data for some Al-based alloys are available and can be quoted for comparison. For example, a microhardness 540 HV0.1 for the Al88Mm5Ni5Fe2 alloy with mixed amorphous-nanocrystalline structure, consolidated using the same equipment as in our work, has been reported [16]. For the hot-pressed Al85Ni5Y8Co2 alloy with mixed amorphous-nanocrystalline structure, a microhardness value around 500 HV was obtained [17], while for the hot-extruded Al88.7Ni7.9Mm3.4 alloy microhardness 253 HV was achieved [18]. On the basis of the quoted results, we can assume that the microhardness of the bulk samples obtained in this work is relatively high.

The density values of the bulk samples are 3.505 and 3.604 g/cm$^3$ for amorphous and nanocrystalline material, respectively. It is known that the density of an amorphous phase is often a few percent lower than its corresponding crystalline phase. This is because the transformation from an amorphous to a crystalline phase involves a negative total volume change due to excess volume in an amorphous phase. In our case, the density of the amorphous material is ~3% lower than that of the nanocrystalline one. The open porosity of both consolidated samples is 0.4%.

## 4. Conclusions

An amorphous alloy was the product of mechanical alloying of Al–17% Fe powder mixture in SPEX 8000 D high-energy ball mill. Calorimetric study revealed that this amorphous alloy crystallised above 380 °C. After heating of the amorphous milling product in the calorimeter up to 720 °C, the $Al_{13}Fe_4$ and fcc Al phases were identified in the material. The mechanically alloyed powder was successfully consolidated under a pressure of 7.7 GPa at 380 °C for 600 s and at 1000 °C for 180 s. During compaction of the powder at 380 °C, the amorphous structure was retained. Consolidation at 1000 °C caused crystallisation of the amorphous phase and appearance of metastable nanocrystalline phases, different to those which crystallised during heating in the calorimeter under atmospheric pressure. The microhardness of the bulk amorphous sample is 760 HV0.2, whereas that of bulk nanocrystalline one is 630 HV0.2. The density of the bulk amorphous material is 3.505 g/cm$^3$ and is ~3% lower than that of the nanocrystalline one. The open porosity of both consolidated materials is 0.4%. The results obtained show that the quality of compaction preserving amorphous structure as well as of the one yielding nanocrystalline structure is satisfactory and the products' microhardness is relatively high. The results also indicate that application of high pressure affects crystallisation of amorphous alloy, influencing the phase composition of the products of this process.

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