Al-Fe-Ni Metallic Glasses via Mechanical Alloying and Its Consolidation

Do Nam Binh, Nguyen Thi Hoang Oanh * and Nguyen Hoang Viet *

School of Materials Science and Engineering, Hanoi University of Science and Technology, No. 1 Dai Co Viet, Hai Ba Trung, Hanoi 100000, Vietnam
* Correspondence: oanh.nguyenthioang@hust.edu.vn (N.T.H.O.); viet.nguyenhoang@hust.edu.vn (N.H.V.)

Abstract: In this paper, the influence of mechanical milling on the microstructural evolution and magnetic properties of Al82Fe14Ni4 alloys prepared by mechanical alloying is investigated. The elemental powder mixture was processed under argon gas at 250 rpm and 350 rpm using a planetary ball mill. The powder particles experienced severe deformation, fragmentation and mutually cold-welding during the collisions of the balls. The diffraction peaks of the Al, Fe and Ni phases gradually disappeared during the milling process, and a halo peak corresponding to the amorphous phase formed. The amorphization of powders milled at 250 rpm was slower than that of 350 rpm. These alloys achieved a fully amorphous structure after milling for 60 h. The amorphous powder alloy milled at 350 rpm exhibited higher thermal stability compared with that of an alloy milled at 250 rpm. The saturation magnetization of the milled Al82Fe14Ni4 alloy powder were decreased following the formation of a para-magnetic amorphous phase. The highest compressive strength, about 710 MPa, was obtained for the Al82Fe14Ni4 alloy sintered at 600 °C by SPS.

Keywords: Al-based amorphous alloy; mechanical alloying; magnetic properties; spark plasma sintering

1. Introduction

Al-based metallic glasses have great potential in applications requiring high corrosion resistance, high wear resistance, high strength and relatively low density [1–5]. Al-based metallic glasses contain Al contents of higher than 80 at.% of the base component with a deep eutectic, which is a common factor for easy glass formation [4–9]. Due to a lack of regular long-range order within their atomic structures, amorphous materials have no detectable crystal structure [2]. Therefore, amorphous alloys possess superior properties than those of crystalline alloys [2,7]. It was reported that most Al-based amorphous alloys have a high tensile strength, as much as 1000 MPa, which is about twice as high as that of conventional high-strength aluminum alloys [1,10,11]. Among the Al-based amorphous alloys, Al-Fe alloys have attracted technological interest because they possess high specific strength and excellent corrosion resistance at elevated temperatures under sulfidizing, oxidizing and carburizing environments [12,13].

Generally, there are several preparation methods for Al-based amorphous alloys, such as melt-spinning [1,14–16], powder metallurgy [17] and casting [1,18] and mechanical alloying (MA) [19,20]. Among these methods, MA provides some advantages for producing amorphous alloys, such as a wide selection of suitable compositions of materials, lower preparation cost, easier process control, material savings and mass production [21]. Accordingly, mechanical alloying allows for the alloying of powder in the solid state, avoiding melting and solidification. MA is a ball-milling process where a powder mixture placed in the ball mill is subjected to a high-energy collision from the balls. The most important events involved in mechanical alloying are the repeated cold welding, fracturing and rewelding of the powder mixture; it is critical to establish a balance between the
processes in order to alloy successfully. MA is now recognized as a unique method for synthesizing a range of equilibrium and non-equilibrium alloy phases beginning with a mixture of elemental or pre-alloyed powders. Supersaturated solid solutions, metastable crystalline and quasi-crystalline phases, nanostructures and amorphous alloys are among the non-equilibrium phases prepared [22–26]. As intermediate phases generated in mechanically alloyed powders can be magnetic or nonmagnetic, their total magnetic characteristics rely on their phase compositions and microstructures. Nanocrystalline soft magnetic materials’ coercive forces rely on their crystallite sizes. Various milling intensities and times yield alloy powders with different coercive forces. Studying the saturation magnetization of alloys is also important, as reducing the grain size to the single magnetic domain size eliminates magnetic barriers [27].

Al-based metallic glasses, such as Al-Fe-La, Al-Fe-Ni-La and Al-V-Fe-Cu, typically have a minor positive heat of mixing. For these alloys, this leads to a long milling time to reach a fully or partially amorphous structure by mechanical alloying. Meanwhile, the enthalpy of mixing values of binary pairs Fe-La and Fe-Cu are 5 and 13 kJ/mole, respectively [28]. Choi et al. took 350 h to obtain a fully amorphous Al₈₂Fe₁₄Ni₄La₁₈ structure by mechanical alloying using a planetary ball mill [29]. Bo Zhu et al. observed that the glass-forming ability (GFA) of Al₇V₁₂Fe₂₂₅₄Cu₂ alloys, prepared by mechanical alloying, decreased with an increase of copper content [30]. In order to improve the GFA of Al-Fe based systems, it is necessary to select the elemental metals with negative mixing enthalpy among atomic pairs of elements, such as Al-Fe-Y, Al-Fe-Ti and Al-Fe-Ni [28,31,32]. In Al-Fe-Ni systems, enthalpies of mixing between binary elements Al-Fe, Al-Ni and Fe-Ni are −11, −22 and −2 kJ/mole [28], respectively, which are favorable for GFA.

There are several compaction techniques to produce bulk amorphous alloys from amorphous powders samples, such as static hot-pressing, warm extrusion, hot pressing and spark plasma sintering [19]. The analysis of the literature in [33] shows that spark plasma sintering (SPS) has many significant advantages over the conventional consolidation technique, such as a lower sintering temperature, faster heating rates and a shorter holding time [33–38]. In SPS, the spark discharges appear in the gap between the particles of a material, and a local high temperature occurs at the contact zones of the powder particles. There is a mass transport from the surface with a high temperature and the internal parts of the powder particles. Together with heating the sample, external pressure is applied to make full-density bulk samples. Nowadays, SPS is widely used to consolidate nanostructured/amorphous bulk samples. Until now, few works investigated the effect of milling speed on the amorphization and the thermal stability of Al-based amorphous alloys. Nowadays, SPS is widely used to consolidate nanostructured/amorphous bulk samples. There is an effort to produce a bulk amorphous alloy sample using spark plasma sintering to obtain full density and high strength.

In this article, the fully amorphous Al₈₂Fe₁₄Ni₄ alloys were synthesized by mechanical alloying, and the influence of ball milling intensities on the microstructural evolution, thermal stability and magnetic properties was investigated. The as-milled amorphous powders were consolidated by SPS to produce bulk samples. The densification behavior and compression tests followed by a failure analysis of the sintered samples were also investigated.

2. Materials and Methods

Elemental powders of Al (−200, +325 mesh) and >99.5% purity, Fe (−325 mesh) and >97% purity and Ni (−325 mesh) and >99.5% purity were used as the raw materials. An alloy with a nominal composition of Al₈₂Fe₁₄Ni₄ (as given in Table 1) was milled by using an AGO-2 planetary ball mill. A total of 10 g of the mixture powder and 200 g of WC hexagonal balls (3–5 mm in diameter) was put into hardened steel vials. Additionally, 50 mL of n-hexane was added as a process control agent into the vial before milling to reduce the sticking phenomena between the powder and the milling tools. The milling process
was conducted at rotation speeds of 250 and 350 rpm and under an argon atmosphere to prevent oxidation.

**Table 1.** The composition of the elemental powder mixture.

| Atom | Atomic Weight, g/mol | at.% | wt.% |
|------|----------------------|------|------|
| Al   | 26.98                | 82   | 68.52|
| Fe   | 55.84                | 14   | 24.21|
| Ni   | 58.69                | 4    | 7.27 |

The X-ray patterns of the as-milled powders and bulk samples were measured using Panalytical X’pert Pro diffractometer (Malvern Panalytical, Almelo, The Netherlands) equipped with Cu Kα radiation. The MDI Jade version 6.5 (associated with the ICDD PDF2 database, 2007) was used to find the peaks matching the reference sample. The microstructures of the samples were analyzed by scanning electron microscopy HITACHI TM4000 PLUS (Hitachi High-Tech Corporation, Tokyo, Japan). The particle size distributions of the alloyed powders were determined by a Horiba LA-960 laser diffraction particle size analyzer (Horiba Ltd., Kyoto, Japan) in distilled water. The differential scanning calorimeter (DSC) curves were measured for the milled powders using DSC-1150B with a heating rate equal to 20 K/min in a protective purity N2 atmosphere. The magnetic properties were examined by vibrating system magnetometers (VSM, MicroSense, EV9, Lowell, MA, USA), in which each sample was measured five to ten times and an average value was obtained.

After being milled at 350 rpm for 60 h, the amorphous Al82Fe14Ni4 powders were compacted under a high-vacuum state at sintering temperatures of 450, 500 and 600 °C for 180 s, with a heating rate of 10 K/min and applied pressures of 300 MPa using LABOX-210 (Spark Plasma Sintering System). The relative densities of the bulk samples were obtained by Olympus PMG3 optical microscope (Olympus Corporation, Tokyo, Japan) with computerized image analysis with a magnification of 100x. The compression tests of the sintered samples were performed with a normal displacement rate of 0.1 mm/min in an Instron 4469 Advanced Tensile Tester (Instron®, Norwood, CO, USA).

### 3. Results and Discussion

In the MA technique, the impact of the ball collision on the mixture of powder particles results in cold welding and fracturing phenomena. The change in particle powder size can be observed in the SEM micrographs (Figures 1 and 2). After milling for 5 h (Figure 1a), the powders milled at 250 rpm become agglomerated to form the irregular-feature microstructures because of the cold-welding phenomenon. Powder particles were formed reaching a size of 20–40 μm. At the higher milling speed of 350 rpm, the size of the agglomerates was about 5–30 μm (Figure 2a). At a higher milling time of 10 h, the morphology of agglomerates milled at 250 rpm changed from irregular microstructures to sub-spherical shapes (Figure 1b). At this stage, the strong collisions between balls or balls and vials during milling led to larger deformations of powders, and the fracture was dominant. For powders milled at 350 rpm, the grain sizes reduced only slightly. Continuing to a longer milling time from 20 h to 60 h, the as-milled powder tended to be finer for the 350 rpm, while at 250 rpm, the powder tended to fragment after 10 to 20 h of milling, and the powder had a tendency of agglomeration (due to cold-welding), returning to the grain size of powder milled for 40 h, and further refinement of milled powder up to 60 h (see Figure 3 and Table 2). The particle sizes continued to decrease and tended to be stable for both alloys at a milling time of 60 h. The fracturing of the particles must have occurred, resulting in reduced particle sizes at a longer milling time. After milling for 60 h, the morphology of both alloy powders tended to be a more spherical in shape (Figures 1e and 2e).

Figure 3 displays a typical particle size distribution (a–b) of Al82Fe14Ni4 powders after milling at 250 and 350 rpm for 60 h and the cumulative distribution of the alloy powders milled at (c) 250 rpm and (d) 350 rpm for different milling times. The median particle sizes
(D50) of the Al₈₂Fe₁₄Ni₄ powders after milling at 250 and 350 rpm for 5 h are 26.6 μm and 23.3 μm, respectively (Table 2). At the same milling time, the particle sizes of powders milled at 250 rpm were smaller than those of powders milled at 350 rpm. This is in agreement with the particle size in SEM (Figures 1a and 2a). When the milling time was prolonged from 10 to 20 h, the powder particle sizes drastically decreased. The median particle diameters (D50) of powders milled for 20 h at 250 and 350 rpm were about 11.8 and 22.8 μm, respectively. After milling for 60 h, the powders tended to become more uniformed. The median particle diameter (D50) of powder particles milled at 250 and 350 rpm reduced to 11.1 and 9.5 μm, respectively. This is because of the dominance of fracturing over the cold welding that was taking place. Figure 3a,b compares the cumulative size distribution curve of powders milled for different times and speeds. The cumulative size distribution curve shifted leftwards, indicating that particle size shifted to a smaller micron range (<19.4 μm and 14.6 at 90% volume fraction for powders milled at 250 and 350 rpm, respectively).
Figure 1. SEM images of Al₈₂Fe₁₄Ni₄ alloy powders milled at 250 rpm for (a) 5 h, (b) 10 h, (c) 20 h, (d) 40 h and (e) 60 h.
Figure 2. SEM images of Al₈₂Fe₁₄Ni₄ alloy powders milled at 350 rpm for (a) 5 h, (b) 10 h, (c) 20 h, (d) 40 h and (e) 60 h.

Figure 3. The typical particles size distribution of Al₈₂Fe₁₄Ni₄ alloy powders milled at (a) 250 rpm for 60 h and (b) 350 rpm for 60 h; cumulative distribution of the alloy powders milled at (c) 250 rpm and (d) 350 rpm.
The XRD profiles of the as-milled Al82Fe14Ni4 powders after different milling times are given in Figure 4. The XRD patterns obtained for both powders milled after 5 h show all of the characteristic peaks corresponding to the constituent elements of Al (PDF#04-0787), Fe (PDF#06-0696) and Ni (PDF#04-0850). For the powders milled at 350 rpm, the diffraction peaks were broadened compared with those of powders milled at 250 rpm. Moreover, a broad halo peak corresponding to an amorphous phase could be detected in the 2θ range of 40–50° for powders milled at 350 and 250 rpm after 10 and 20 h milling, respectively. The amorphization started seeming to be earlier in powders milled at 350 rpm. Powders milled at 250 rpm have lower impact energy than those of 350 rpm, leading to slower amorphization in the earlier milling state (up to 20 h). After a milling time of 60 h, the width of the diffraction pattern was further increased, and all crystals disappeared for both alloy powders. Only a broad diffuse halo remained to indicate the XRD amorphous phase in both cases, the same as in Choi’s observation of a hollow peak found for full amorphous Al82La10Fe4Ni4 alloy after 350 h of milling [29]. The alloying process in this system was due to the relatively high negative heats of the mixing of the Al-Fe, Al-Ni and Fe-Ni pairs being −11, −22 and −2 kJ/mol, respectively [28].

![Figure 4. XRD patterns of Al82Fe14Ni4 powders under different milling times at (a) 250 rpm and (b) 350 rpm.](image)

The hysteresis loops of Al82Fe14Ni4 alloys milled at 250 and 350 rpm after different milling times are presented in Figure 5a,b. All curves present the sigmoidal shape and do not reach the completely saturated state at applied fields as high as 15,000 Oe. The small hysteresis losses are the properties generally desired in soft magnetic materials [39]. The values of the saturation magnetization (Ms) and coercivity (Hc) of Al82Fe14Ni4 alloys with the increase of milling time are given in Table 3. For Al82Fe14Ni4 alloys, the Ms values of powders milled at 250 rpm and 350 rpm are decreased from the maximum 35.27 emu/g and 20.76 emu/g (5 h of milling) to the minimum 4.75 emu/g and 0.37 emu/g (60 h of milling), respectively. It is reported that the saturation magnetization of Al82Fe14Ni5Y amorphous alloys prepared by MA [40] were about 0.8 emu/g. Yongbo Xu et al. [41] also

| Milling Time (h) | MA at Speed of 250 rpm | MA at Speed of 350 rpm |
|-----------------|-----------------------|-----------------------|
|                 | D0 (μm) | D50 (μm) | D90 (μm) | D0 (μm) | D50 (μm) | D90 (μm) |
| 5               | 15.4    | 26.6     | 37.8     | 11.4    | 23.3     | 47.8     |
| 10              | 11.1    | 21.8     | 37.0     | 11.0    | 21.2     | 39.3     |
| 20              | 6.4     | 11.8     | 21.4     | 11.4    | 22.8     | 37.0     |
| 40              | 8.7     | 18.0     | 41.8     | 7.9     | 13.6     | 22.2     |
| 60              | 6.2     | 11.1     | 19.4     | 5.8     | 9.5      | 14.6     |

Table 2. Characteristics of particle size distributions for powders after MA.
reported that the decrease of $M_s$ is due to chemical composition, the local environment of the magnetic atoms and the electronic structures of the materials. Phong et al. revealed that the $M_s$ and $H_c$ of a micro-sized particle are significantly influenced by its structure [42]. For Al$_8$Fe$_{14}$Ni$_4$ alloys, the addition of the ferromagnetic element Ni decreases the content of the ferromagnetic element Fe, as the electronic interaction between Fe-Ni is weaker than Fe-Fe. Therefore, the $M_s$ of the Al$_8$Fe$_{14}$Ni$_4$ alloy is lower. In addition, the dissolution of the ferromagnetic atoms Fe into the paramagnetic Al-rich phase to produce amorphous phases (40–60 h) lead to a reduction of $M_s$ (Figure 5). The tendency could similarly be observed for amorphous Ti$_3$Fe$_6$Si alloys prepared by MA [41]. The highest $H_c$ values (Table 3) of the powders milled at 250 and 350 rpm were approximately 384 and 366.38 Oe after 10 and 5 h of milling, respectively. The increase of coercivity can be found in the Co$_{60}$Fe$_{22}$Ta$_8$B$_{30}$ alloy produced by MA [43]. It can be explained that the increase of the coercivity was derived from the existence of a high dislocation density and residual stresses in the powders during milling [43–46]. Two alloy powders were milled at the different speeds had different values of macrostrain, which increased with the milling time. Upon further milling, amorphization started and progressed slowly. As in the Al$_8$Fe$_{14}$Ni$_4$ alloy, this transformation was delayed, and it could be expected that the changes in the coercive force would occur in powders milled at 250 rpm more slowly than in the alloy powder milled at 350 rpm. After milling for 60 h, the coercive force values for powders milled at 250 and 350 rpm were 258.05, and 173.10 Oe, respectively. In this work, Al$_8$Fe$_{14}$Ni$_4$ alloys demonstrated soft magnetic behavior. However, Guihua Li et al. found that the amorphous alloys Al$_8$Ni$_4$La$_5$, Al$_8$Ni$_4$(La$_{0.5}$Ce$_{0.5}$)$_3$ and Al$_8$Ni$_4$(Ni$_{0.5}$Co$_{0.5}$)$_8$(La$_{0.5}$Ce$_{0.5}$)$_3$ have diamagnetic properties by using the arc-melting method [47].

![Figure 5. Hysteresis curves of the powders milled for 5, 10, 20, 40 and 60 h (a) at 250 rpm and (b) at 350 rpm.](image)

Table 3. $M_s$ and $H_c$ values obtained from VSM analyses of Al$_8$Fe$_{14}$Ni$_4$ alloys milled for different times at 250 and 350 rpm.

| MA Speed (rpm) | Milling Time, h | $H_c$ (Oe) | $M_s$ (emu/g) | $H_c$ (Oe) | $M_s$ (emu/g) | $H_c$ (Oe) | $M_s$ (emu/g) | $H_c$ (Oe) | $M_s$ (emu/g) | $H_c$ (Oe) | $M_s$ (emu/g) |
|---------------|-----------------|------------|--------------|------------|--------------|------------|--------------|------------|--------------|------------|--------------|
| 250           | 05              | 204.00     | 35.27        | 384.64     | 25.28        | 372.97     | 16.30        | 246.05     | 8.20         | 258.05     | 4.75         |
|                | 10              | 366.38     | 20.76        | 270.00     | 9.59         | 259.80     | 6.42         | 221.44     | 1.49         | 173.10     | 0.37         |
| 350           | 20              |            |              |            |              |            |              |            |              |            |              |
| 350           | 40              |            |              |            |              |            |              |            |              |            |              |
| 350           | 60              |            |              |            |              |            |              |            |              |            |              |

In order to study the thermal stability of amorphous Al$_8$Fe$_{14}$Ni$_4$ alloys, the powders were crystallized in the DSC measurements by continuous heating at a rate of 20 K/min. There are two exothermic crystallization peaks observable for the amorphous alloy
powders milled at 250 and 350 rpm (Figure 6) for 60 h. Each exothermic crystallization peak can be characterized by its onset (T_p) and peak (T_x) temperatures. Amorphous alloy powders milled at the speed of 350 rpm have higher T_x than that at 250 rpm. For the first exothermic peak, the T_x of the alloy powders milled at 250 and 350 rpm were 341 and 377 °C, respectively. The second peak corresponds to the transformation of the residual amorphous alloy to intermetallic compounds, with T_x and T_p temperatures of 537 °C and 570 °C (milled at 250 rpm) and 531 °C and 581 °C (milled at 350 rpm), respectively.

![DSC curves of AlFeNi powders milled at 250 and 350 rpm for 60 h using a heating rate of 20 K/min.](image)

To investigate the structural changes of the as-milled powders (60 h MA) under the crystallization temperature as observed on the DSC curves, the alloys were annealed at 480, 600 and 700 °C. The XRD patterns of the annealed powders are presented in Figure 7. The onset crystallization temperature is considered to be the nucleation stage for crystallization, while the peak temperature corresponds to the growth of nuclei [48,49]. The alloys are heated beyond the peak temperature where the presumed phases at this stage are those crystallized. After annealing the amorphous alloy powders to 480 °C, the diffraction peaks corresponded to cubic Al together with the residual amorphous phase. For an amorphous alloy prepared at 250 rpm (as seen in Figure 7a), a peak of the AlFe3 phase was also detected after annealing at 480 °C. Further increasing the annealing temperature beyond the secondary peak crystallization temperature resulted in the disappearance of the residual amorphous peak. The formation of an Al13Ni7Fe15 (PDF#42-1042) metastable phase besides the AlNi and AlFe phases was also observed in both alloys after annealing at 600 °C. The Al13Ni10Fe5’s formation is remarkable as a quasicrystal phase that decomposes into intermetallics when the annealing temperature is raised to 700 °C for both the 250 and 350 rpm milling modes. As a metastable phase, it can be decomposed into the AlNi phase in the Ni-rich regions and the AlFe phase in the Fe-rich regions when the temperature is raised and energy is provided beyond the enthalpies of mixing ΔH values [50]. The phases produced during the annealing of two amorphous alloy powders (milling at 250 and 350 rpm) at 700 °C include Al (PDF#04-0787), AlFe (PDF#29-0042) and AlNi (PDF#20-0019). The analysis of the crystallization of AlFeNi amorphous alloys powders after heat treatment indicates that the phases precipitated from the amorphous phase may be correlated with the milling speed: primary crystallization in amorphous alloys milled at 350 rpm and eutectic crystallization in amorphous alloys milled at 250 rpm. The strong chemical interactions of higher milling speeds can change the short-range order to more stable configurations. At the same composition of
Al$_82$Fe$_{14}$Ni$_4$ amorphous alloys milled at 250 rpm seem to be an easier arrangement of the atoms to become crystalline in structure compared with those of amorphous alloys milled at 350 rpm.

Figure 7. XRD patterns of Al$_82$Fe$_{14}$Ni$_4$ amorphous alloys after heat treatment at (a,d) 480, (b,e) 600 and (c,f) 700 °C.

Amorphous Al$_82$Fe$_{14}$Ni$_4$ powders milled at 350 rpm were selected for SPS consolidation due to their higher thermal stability compared with that of 250 rpm. Based on the DSC curve shown in Figure 6, the sintering temperatures chosen were within the exothermal peaks. Consolidation of mechanically alloyed powders was performed on a spark plasma sintering to produce bulk samples. The sintering temperature was selected based on the results of the DSC thermal analysis and the shrinkage behavior of the sample during sintering [33]. Figure 8 exhibits the change in shrinkage (obtained by Z-displacement) of amorphous Al$_82$Fe$_{14}$Ni$_4$ powder during sintering at 600 °C under a pressure of 300 MPa. The degree of shrinkage increased as the sintering temperature increased. The shrinkage went up to 400 °C and held steady up to 570 °C. The shrinkage increased to 600 °C throughout the holding time. During the holding time, the viscosity of the sample decreased and the mobility of the atoms increased, resulting in an increase in sample shrinkage. Scudino, S et al. mentioned that the mechanical properties of Al-based bulk amorphous alloys can be enhanced in cases where nanometer-sized face-centered cubic Al (fcc-Al) precipitates homogeneously in the amorphous matrix [11]. Therefore, as-milled powders were sintered at different temperature of 450, 500 and 600 °C. Figure 9 shows the fracture surface of the Al$_82$Fe$_{14}$Ni$_4$ sintered samples after the compression test. The fracture surfaces of the samples sintered at 450 and 500 °C exhibited a clean surface with average grain sizes of about ~10 μm. The specimen broke along the compression direction, and the fracture surface displayed a decohesive-like rupture [19] and inter-granular crack propagation. However, the trans-particle fracture mechanism observed in Figure 9b indicates the efficiency of the sintering condition. The density and compressive strength values of the compacted samples increased with the increasing sintering temperature, as seen in Table 4. The highest compressive strength obtained for sample sintered at 600 °C was about 710 MPa. This strength value is higher than the strengths of the Al–145Si–2.5Cu–0.5Mg alloy (654 MPa) and Al$_{82}$La$_{10}$Fe$_{14}$Ni$_4$ alloy (650 MPa) fabricated by SPS [51,52].
The highest relative density of about 97.4% was obtained for the sample sintered at 600 °C. Porosity still existed in the sintered sample, which was the main reason behind the failure, as can be observed in Figure 9.

Table 4. Relative densities and compression strengths of the sintered samples.

| Alloys              | Compression Strength (MPa) | Relative Density (%) |
|---------------------|-----------------------------|----------------------|
| Al82Fe14Ni4 (450 °C)| 600                         | 88.4%                |
| Al82Fe14Ni4 (500 °C)| 650                         | 92.6%                |
| Al82Fe14Ni4 (600 °C)| 710                         | 97.1%                |

The XRD patterns of the sintered samples are presented in Figure 10. There is a peak shift to the higher diffraction angle of about 44° of the sintered samples. This indicates that aside from the amorphous phase, there is another nanocrystals’ precipitation phase. For the sample sintered at 450 °C, diffraction peaks of fcc-Al can be detected (Figure 10b). The halo peak, which is characterized by the amorphous phase (Figure 10b) in the range of 43°–45°, becomes narrow compared with a fully amorphous alloy (Figure 10a). This is consistent with the XRD of as-milled powders annealing at 450 °C, as is displayed in Figure 7d. At higher sintering temperatures of 500 and 600 °C, only the diffraction peaks of the nanocrystal β-bcc phase can be seen from the XRD patterns in Figure 10c,d. At these sintering temperatures, the crystallization and recovery of the crystal lattice occur, causing the characteristic peaks to sharpen and shift to the standard position.
Figure 9. SEM images of the fracture surfaces of Al$_{82}$Fe$_{14}$Ni$_{4}$ samples sintered at (a,b) 450, (c,d) 500 and (e,f) 600 °C at different magnifications of 200× and 3000×.

Figure 10. XRD patterns of amorphous Al$_{82}$Fe$_{14}$Ni$_{4}$ samples (a) after milling for 60 h, (b) sintered at 450, (c) 500 and (d) 600 °C.

4. Conclusions

This work investigated the influence of high-energy mechanical milling on the microstructures and magnetic properties of Al$_{82}$Fe$_{14}$Ni$_{4}$ amorphous alloys prepared by mechanical alloying. During the milling process, Al, Ni and Fe atoms in Al$_{82}$Fe$_{14}$Ni$_{4}$ alloy powder can interact with each other to form a supersaturated solid solution Fe(Al,Ni) before the formation of a completely amorphous structure. The amorphization of alloy powders milled at 350 rpm takes place earlier than that of powders milled at 250 rpm. After 60 h of milling, both alloys have a fully amorphous structure.

The saturation magnetization of powders milled at both 250 and 350 rpm is decreased with an increase in the milling time, which supports the results of the phase analysis. The
coercivity force values also decrease after 5 h of milling due to the reduction of the crystallite size of the alloy and the formation of the amorphous phase. This reveals that the samples exhibit a paramagnetic behavior.

The crystallization of two alloys corresponds to the devitrification of the amorphous phase mainly into cubic fcc-Al beyond the primary crystallization peak and followed by transformation into intermetallic phases. The crystallization onset temperature of amorphous powders milled at 250 rpm is 341 °C, which is lower than that of powders milled at 350 rpm (377 °C). This indicates that the amorphous powders milled at higher speeds possess higher thermal stability. Milling speed possesses a significant influencing performance on the ball-milling process in terms of the energy impact, microstructural evolution, thermal stability and magnetic properties of as-milled powder alloys. Following the sintering of amorphous alloy powders milled at 350 rpm at 600 °C under a pressure of 300 MPa, a highest density of 97.4% and a compressive strength value of 710 MPa was obtained. The morphology of the failure surface of the bulk amorphous Al8Fe4Ni4 alloy shows the transparticle fracture mechanism, indicating the efficiency of the sintering condition.

**Author Contributions:** Conceptualization, N.H.V. and N.T.H.O.; methodology and investigation, D.N.B. and N.H.V.; software, D.N.B.; validation, N.H.V. and N.T.H.O.; writing—original draft preparation, D.N.B.; writing—review and editing, N.H.V. and N.T.H.O.; visualization, N.H.V. and D.N.B.; supervision, N.H.V.; project administration, N.T.H.O.; funding acquisition, N.T.H.O. All authors have read and agreed to the published version of the manuscript.

**Funding:** This research is funded by the Ministry of Industry and Trade of the Socialist Republic of Vietnam under grant number: DT.BO.107/21 (Contract number: 107.2021.DT.BO.HDKHCN).

**Institutional Review Board Statement:** Not applicable.

**Informed Consent Statement:** Not applicable.

**Data Availability Statement:** Not applicable.

**Conflicts of Interest:** The authors declared no potential conflict of interest with respect to the research, authorship, and publication of this article.

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