Fabrication and characterization of amorphous-nanocrystalline Al$_{80}$Fe$_{10}$Ti$_5$M$_3$B$_2$ (M=Cr, Ni and Nb) alloys

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In this study, the formation and characterization of amorphous-nanocrystalline phases in Al$_{80}$Fe$_{10}$Ti$_5$M$_3$B$_2$ (M=Cr, Ni and Nb) powder mixtures by the means of mechanical alloying (MA) have been investigated. The milled samples are characterized using X-ray diffraction (XRD), differential scanning calorimetry (DSC) and transmission electron microscopy (TEM). Mechanical alloying of these alloying systems shows that amorphous phase can be formed only in Al$_{80}$Fe$_{10}$Ti$_5$Ni$_3$B$_2$ powder mixture and the final products in other systems are combination of amorphous and nanocrystalline phases. The produced amorphous phase in different alloying systems, exhibits one-stage crystallization on on heating (at a temperature up than temperature higher than 800°C) and the crystallization’s activation energy is more than 240±20 kJ/mol. The crystallization products (Al$_{13}$Fe$_4$) and mechanism (polymorphism) of amorphous phase in these three systems are the same.

Keywords: Amorphous-nanocrystalline phase, Al-base alloys, Mechanical alloying, Crystallization kinetic

Structural materials with high-specific strength are consistently of considerable interest to the transportation and aviation industries$^1$. Thus, the development of Al-based alloys is eagerly awaited in these industries due to its perceived benefits$^2$. Among various Al alloys, Al-Fe system is attractive because of the two practically used metals. A new class of Al-base alloys, which has received a great deal of attention over the last few years, as nanocrystalline ones, is amorphous as well as nanocrystalline ones$^3$,$^6$. It is predicted that the strength of the lightweight aluminium alloys can be significantly enhanced from approximately 450-600 MPa in age hardened conditions to over 1500 MPa in amorphous or amorphous-nanocrystalline structures$^7$,$^8$.

It has been shown that, this type of structureless can be prepared by different methods including rapid quenching of liquid, vapor deposition and solid state processes. Among the different methods in producing non-equilibrium and quasi-equilibrium structures, mechanical alloying overweighs the other methods. This process not only has shown higher glass amorphous forming ability in wider ranges of composition in comparison to rapid solidification processes, but also it takes place at room temperature which is far below the crystallization temperature$^3$,$^7$,$^9$. Although, Al-Fe alloying system is of technological interest because of their advantageous properties, the ability of this alloying system to formation of amorphous phase is low and preparation of this phase is so difficult. For instance, there are many reports about the formation of amorphous phase in Al-Fe alloying system during mechanical alloying. All of these reports were illustrated that the time required achieving amorphous phase during this process is so long$^{10}$,$^{13}$. Howbeit the ability of Al-Fe alloys in formation of amorphous phase is so low, the researches were shown that by addition of one or more alloying elements to this binary system, the amorphous forming ability and the thermal stability of amorphous phase can be improved$^8$,$^{10}$. In our previous study, the effect of different alloying elements on formation of amorphous phase in Al$_{80}$Fe$_{10}$M$_{10}$ (M= Ti, Ni, V and TiNi) alloys were investigated$^{11}$,$^{15}$. In this study, the formation and characterization of amorphous-nanocrystalline phases in Al$_{80}$Fe$_{10}$Ti$_5$M$_3$B$_2$ (M=Cr, Ni and Nb) alloying systems are investigated. The structural evolution and thermal behavior of produced samples are monitored investigated using X-ray diffraction, transmission electron
microscopy and differential scanning calorimetry. The crystallization kinetics of produced amorphous phase have also been analyzed.

**Theory**

Crystallization kinetics of amorphous materials can be described by three kinetic parameters, namely, the activation energy for crystallization, the Avrami exponent, which reflects the mechanism of the nucleation and growth process, and the frequency factor. In calorimetric measurements, non-isothermal methods can be used to calculate these parameters. In these methods, the sample is heated at a constant heating rate ($\beta$), and the heat produced is recorded as a function of temperature or time. The theoretical basis for interpreting thermal analysis data for crystallization is provided by the classical Johnson-Mehl-Avrami (JMA) model\(^{18-20}\). In this model, the crystallized volume fraction ($\alpha$) can be expressed as a function of time according to the following relation:

$$\alpha(t) = 1 - \exp\left\{-Kt^n\right\} \quad \text{... (1)}$$

where $K$ is defined as the effective overall reaction rate constant and $n$ is the Avrami exponent. The constant $K$ usually has Arrhenius temperature dependence as follows:

$$K = K_0 \exp\left(-\frac{E}{RT}\right) \quad \text{... (2)}$$

where $K_0$ is the frequency factor, $T$ is temperature, and $E$ is the activation energy describing the overall crystallization process.

In this study, Kissinger equation\(^{21}\) is considered to evaluate the crystallization kinetics of the amorphous phases using the non-isothermal DSC measurements:

$$\ln\left(\frac{\beta}{T^3}\right) = \frac{E}{RT} + \text{constant} \quad \text{... (3)}$$

where $T$ stands for the peak temperature of the exothermic peak, $\beta$ is the heating rate, $R$ is the gas constant, and $E$ is the effective activation energy of crystallization. The Kissinger plot $\ln(\beta / T^3)$ versus $1/T$ consists of approximately straight lines with slope equal to the $E/R$.

**Experimental Procedure**

The powders of Al (99%), Fe (99.9%), Ti (99%), Cr (99.8%), Ni (99.3%), Nb (99%) and B (99.5%) were used as raw materials. The elemental powders with composition of 80%Al-10%Fe-5%Ti-3%Cr-2%B, 80%Al-10%Fe-5%Ni-2%B and 80%Al-10%Fe-5%Ti-3%Nb-2%B (in atomic percentage) were mechanically alloyed in a planetary ball mill under inert argon atmosphere. The MA process was carried out in a steel container at room temperature. The rotation speed of 250 rpm and ball to powder ratio of 10:1 was employed. Stearic acid powder (1wt%), was used as the process control agent (PCA).

X-ray diffractometry was used to observe the structural changes of powders during the milling and the subsequence annealing process. A Philips diffractometer (40 kV) with Cu $K_\alpha$ radiation ($\lambda=0.15406$ nm) was used for XRD measurements. The XRD patterns were recorded in the 20 range of 20-100° (step size: 0.025°; time per step: 1 s). Besides, transmission electron microscope (Jeol.JSM.6330) was used to analyze the produced amorphous phases.

Differential thermal analysis was also conducted to study the thermal stability of produced amorphous samples using the NETZSCH STA 409 PC/PG differential thermal analyzer. The samples were placed in Al$_2$O$_3$ pans and heated in dynamic argon atmosphere up to 1200°C at different heating rates of 10, 20 and 30°C/min.
**Results and Discussion**

The XRD patterns of the Al\textsubscript{80}Fe\textsubscript{10}Ti\textsubscript{5}B\textsubscript{2}Ni\textsubscript{3} powder mixtures after various MA processing periods are shown in Fig. 1. The XRD results demonstrate that, increasing in the milling time, leads to the declining of the intensity diffraction peaks’ intensities of the alloying elements while the Al peaks shifted to higher angles declines progressively. These changes suggest that these elements dissolved in an the Al matrix and Al supersaturated solid solution forms. Another feature that can be seen in these XRD patterns is the broadening of the Al diffraction peaks due to the reduction of grain size and increase in lattice strain. In the XRD pattern obtained after 10 h of milling, one can see broad Al based solid solution peaks and a small broad halo due to an amorphous component seeming to overlap the most intense peak. After 40 h of MA, the Al peaks vanish completely and only an amorphous halo is visible (this is in agreement with the TEM result which is presented in Fig. 2). Therefore, according to these results, the structural changes during mechanical alloying in this alloying system (until 40 h) can be written as:

\[
\text{Al}_{80}\text{Fe}_{10}\text{Ti}_{5}\text{B}_{2}\text{Ni}_{3} \rightarrow \text{Supersaturated solid solution (SS)} \rightarrow \text{Amorphous Phase}
\]

Similar to Al\textsubscript{80}Fe\textsubscript{10}Ti\textsubscript{5}B\textsubscript{2}Ni\textsubscript{3}, the XRD patterns of Al\textsubscript{80}Fe\textsubscript{10}Ti\textsubscript{5}B\textsubscript{2}Cr\textsubscript{3} and Al\textsubscript{80}Fe\textsubscript{10}Ti\textsubscript{5}B\textsubscript{2}Nb\textsubscript{3} powder mixtures after different milling times are presented in Figs 3 and 4, respectively. According to these figures, the structural changes during mechanical alloying in different alloying systems are different and these changes (until 40 h) can be written as:

\[
\text{Al}_{80}\text{Fe}_{10}\text{Ti}_{5}\text{B}_{2}\text{Cr}_{3} \rightarrow \text{SS+ Cr rich phase} \rightarrow \text{amorphous phase + Cr rich phase}
\]

\[
\text{Al}_{80}\text{Fe}_{10}\text{Ti}_{5}\text{B}_{2}\text{Nb}_{3} \rightarrow \text{SS+ Al}_{3}\text{Nb} \rightarrow \text{Amorphous + Al}_{3}\text{Nb}
\]

By attention to these results, the final structures after mechanical alloying (until 40 h) in these three systems are different. Unlike the Al\textsubscript{80}Fe\textsubscript{10}Ti\textsubscript{5}B\textsubscript{2}Cr\textsubscript{3} and Al\textsubscript{80}Fe\textsubscript{10}Ti\textsubscript{5}B\textsubscript{2}Nb\textsubscript{3} alloying systems, performed mechanical alloying in Al\textsubscript{80}Fe\textsubscript{10}Ti\textsubscript{5}B\textsubscript{2}Ni\textsubscript{3} alloy lead to the formation of amorphous phase. This is opposite of...
the theoretical calculations (base on Miedema theory\textsuperscript{25}) about that. According to the theoretical calculations, the activation energy of Nb-containing alloy is higher than Ni and Cr-containing alloys, indicating higher ability to formation of amorphous phase and thermal stability of this alloy. In fact, our previous studies\textsuperscript{11-15} showed that, the theoretical calculations cannot be a benefit tools for determination of the amorphous forming ability of one alloy by means of mechanical alloying. According to those studies, formation of stable phases (such as Al\textsubscript{3}Nb or Cr rich phase) in early state of milling, lead to the reduction of the rate of amorphization process\textsuperscript{13-15}. In fact, the amorphization of the stable phases is harder than non-stable phases such as supersaturated solid solution. It is clear that, increasing the milling time can be due to the full amorphization of Al\textsubscript{80}Fe\textsubscript{10}Ti\textsubscript{5}B\textsubscript{2}Cr\textsubscript{3} and Al\textsubscript{80}Fe\textsubscript{10}Ti\textsubscript{5}B\textsubscript{2}Nb\textsubscript{3} alloys which was neglected in this study.

In order to study the thermal stability of the produced amorphous phases in Al\textsubscript{80}Fe\textsubscript{10}Ti\textsubscript{5}B\textsubscript{2}Ni\textsubscript{3}, Al\textsubscript{80}Fe\textsubscript{10}Ti\textsubscript{5}B\textsubscript{2}Cr\textsubscript{3} and Al\textsubscript{80}Fe\textsubscript{10}Ti\textsubscript{5}B\textsubscript{2}Nb\textsubscript{3} alloying systems, the samples were examined using DSC under continuous heating conditions. The results showed that the DSC heating behavior of these three systems are similar (each system showed one-stage crystallization on heating). For example, the DSC heating trace of the Al\textsubscript{80}Fe\textsubscript{10}Ti\textsubscript{5}B\textsubscript{2}Ni\textsubscript{3} amorphous phase at a constant heating rate of 20°C/min is presented in Fig. 5. As seen, only one exothermic peak (crystallization temperature ($T_c$)) appeared in this DSC curve and there is not each evidence about glass transition evolution ($T_g$). According to above, the amorphous forming ability of produced alloys is low and the glass transition evolution occurs in the temperature near to the crystallization transformation\textsuperscript{14-20} (the $T_g$ and $T_c$ of produced amorphous phases are presented at Table 1).

To analyze the crystallization process related to the exothermic peak, the produced amorphous sample was annealed in argon atmosphere at 1000°C for 20 min. The XRD pattern of this sample is shown in Fig. 6. As seen, this sample is composed of Al\textsubscript{13}Fe\textsubscript{4} intermetallic phase. Therefore, the exothermic peak in Fig. 5 should be attributed to the precipitation of the Al\textsubscript{13}Fe\textsubscript{4} phase from the amorphous phase (the polymorphism mechanism in crystallization in crystallization). Meanwhile, the endothermic peak in this figure is related to the melting of the alloy.

The similar analysis was also performed for Al\textsubscript{80}Fe\textsubscript{10}Ti\textsubscript{5}B\textsubscript{2}Cr\textsubscript{3} and Al\textsubscript{80}Fe\textsubscript{10}Ti\textsubscript{5}B\textsubscript{2}Nb\textsubscript{3} alloys and the results are shown in Figs 7 and 8, respectively. According to these figures, the total crystallization sequence (one-stage crystallization process), crystallization product (Al\textsubscript{13}Fe\textsubscript{4} intermetallic phase) and mechanism (polymorphism) of amorphous phase in Al\textsubscript{80}Fe\textsubscript{10}Ti\textsubscript{5}B\textsubscript{2}Cr\textsubscript{3} and Al\textsubscript{80}Fe\textsubscript{10}Ti\textsubscript{5}B\textsubscript{2}Nb\textsubscript{3} alloys are similar to Al\textsubscript{80}Fe\textsubscript{10}Ti\textsubscript{5}B\textsubscript{2}Ni\textsubscript{3}. Moreover, the crystallization’s temperature of amorphous phase in Al\textsubscript{80}Fe\textsubscript{10}Ti\textsubscript{5}B\textsubscript{2}Ni\textsubscript{3}, Al\textsubscript{80}Fe\textsubscript{10}Ti\textsubscript{5}B\textsubscript{2}Cr\textsubscript{3} and Al\textsubscript{80}Fe\textsubscript{10}Ti\textsubscript{5}B\textsubscript{2}Nb\textsubscript{3} alloys (regarding the DSC curves at heating rate of 20°C/min) are 840, 845, and 840°C, respectively. This illustrates that the thermal stability of the amorphous phase in these three systems is the same.

![Fig. 5–The DSC curve of produced amorphous Al\textsubscript{80}Fe\textsubscript{10}Ti\textsubscript{5}B\textsubscript{2}Ni\textsubscript{3} phase at heating rate of 20°C/min (The DSC curves of this alloy at different heating rate is also presented in this figure)](image)

![Fig. 6–The XRD pattern of produced amorphous Al\textsubscript{80}Fe\textsubscript{10}Ti\textsubscript{5}B\textsubscript{2}Ni\textsubscript{3} phase annealed at 1000°C for 20 min)](image)

### Table 1—Different crystallization parameters in Al\textsubscript{80}Fe\textsubscript{10}Ti\textsubscript{5}B\textsubscript{2}Ni\textsubscript{3}, Al\textsubscript{80}Fe\textsubscript{10}Ti\textsubscript{5}B\textsubscript{2}Cr\textsubscript{3} and Al\textsubscript{80}Fe\textsubscript{10}Ti\textsubscript{5}B\textsubscript{2}Nb\textsubscript{3} amorphous phases

<table>
<thead>
<tr>
<th>Alloy</th>
<th>$T_g$ (°C)</th>
<th>$T_c$ (°C)</th>
<th>Activation energy (kJ/mol)</th>
<th>Avrami exponent (n)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al\textsubscript{80}Fe\textsubscript{10}Ti\textsubscript{5}B\textsubscript{2}Ni\textsubscript{3}</td>
<td>800</td>
<td>840</td>
<td>250±15</td>
<td>3– 3.8</td>
</tr>
<tr>
<td>Al\textsubscript{80}Fe\textsubscript{10}Ti\textsubscript{5}B\textsubscript{2}Cr\textsubscript{3}</td>
<td>797</td>
<td>845</td>
<td>240±20</td>
<td>2.8– 3.5</td>
</tr>
<tr>
<td>Al\textsubscript{80}Fe\textsubscript{10}Ti\textsubscript{5}B\textsubscript{2}Nb\textsubscript{3}</td>
<td>807</td>
<td>840</td>
<td>260±20</td>
<td>3– 3.9</td>
</tr>
</tbody>
</table>
The crystallization kinetic analysis for amorphous phase in $\text{Al}_{80}\text{Fe}_{10}\text{Ti}_{3}\text{B}_{2}\text{Ni}_3$, $\text{Al}_{80}\text{Fe}_{10}\text{Ti}_{3}\text{B}_{2}\text{Cr}_3$ and $\text{Al}_{80}\text{Fe}_{10}\text{Ti}_{3}\text{B}_{2}\text{Nb}_3$ alloys were performed using Eqs (3)-(6) and the results are shown in Table 1. As seen, the crystallization activation energy of amorphous phase in different alloying systems has nearly magnitudes.

As explained above, the Avrami exponent, $n$, can directly reflect explain the crystallization process mode. According to Table 2, the Avrami exponent for different alloying systems in this work is equal (in the range $2.8 < n < 3.9$). In order to determine the nucleation and growth parameters, the achieved calculated Avrami exponent in different alloying systems were analyzed by Ranganathan and Heimendahl equation$^{24}$ (different parameters are presented in Table 2). According to this analysis, the nucleation ($0 < a < 1$), i.e., they are decreasing nucleation rate and growth mechanism ($c = 1$), i.e., interface control growth) in these three amorphous phases is similar. This effect can be as a result of the same crystallization mechanism in these three systems. In fact, the crystallization mechanism of amorphous phases in these alloying systems is polymorphism. In this mechanism, an amorphous phase crystallizes into a single crystalline phase without any change in composition (no need of long range diffusion). It is obvious that the growth mechanism in this crystallization process is interface control.

**Conclusions**

The performed mechanical alloying in in $\text{Al}_{80}\text{Fe}_{10}\text{Ti}_{3}\text{B}_{2}\text{Ni}_3$, $\text{Al}_{80}\text{Fe}_{10}\text{Ti}_{3}\text{B}_{2}\text{Cr}_3$ and $\text{Al}_{80}\text{Fe}_{10}\text{Ti}_{3}\text{B}_{2}\text{Nb}_3$ alloying systems showed that, only in $\text{Al}_{80}\text{Fe}_{10}\text{Ti}_{3}\text{B}_{2}\text{Ni}_3$ alloy system amorphous phase can be formed and the milling products in other systems are combination of amorphous and nanocrystalline phases. The produced amorphous phases in these alloying systems exhibit one-stage crystallization on during heating and the activation energy for crystallization is more than $240\pm20$ kJ/mol. The crystallization product ($\text{Al}_{13}\text{Fe}_{4}$) and mechanism (polymorphism) of amorphous phase in these three systems are similar.

**References**