Mechanical Alloying of Fe$_{25}$Al$_{75}$–$_x$Ti$_x$ Mixed Powders

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Elemental aluminum, titanium and iron powders with compositions of Fe$_{25}$Al$_{75}$–$_x$Ti$_x$ ($x = 0, 3.75, 7.5, 11.25$ and $15$) were mechanical alloyed in a planetary ball mill. The transformations and thermal stabilities of milled powders were characterized by X-ray diffraction (XRD) and differential scanning calorimetry (DSC). Supersaturated solid solutions were found in low Ti concentration ($x = 0–7.5$). The addition of Ti shortened the milling time for the formation of solid solution. The amorphous phases were obtained with high Ti concentration ($x = 11.25$ and $15$). The activation enthalpies of crystallization for amorphous phases increased with Ti. The crystallization temperatures of amorphous alloys were calculated, which are in good agreement with the experimental values.

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1. Introduction

Mechanical alloying (MA) is one of the most promising and rapidly developing present-day methods for new materials. It has been extensively used in the synthesis and processing of nano-structural materials, supersaturated solid solutions, amorphous alloys, quasicrystallites and intermetallics in recent years.1)

There have been a number of investigations in the literature on the mechanical alloying of binary Fe-Al alloys.2–9) For the mixed elemental powders with iron content of about 25 at%, the final productions by mechanical alloying largely depend on the type of mills and other instrumental facilities. Most of the phases obtained by mechanical alloying are the amorphous phase.3–10) The intermetallic Al$_5$Fe$_2$ is developed after annealing the amorphous powders. However, Cardellini et al.10,11) and Mukhopadhyay et al.12) directly obtained Al$_5$Fe$_2$ intermetallic after mechanical alloying without annealing. Morris and Morris15) also reported the direct formation of intermetallic Al$_5$Fe by mechanical alloying. It is indicated that the milling of compositions containing about 25 at% Fe in high energy agitation leads to the formation of intermetallic phases of the Al$_5$Fe$_2$ or Al$_5$Fe types, while the low-energy milling over longer period produces amorphous phase.

The addition of the third element can also influence the microstructure of Fe-Al system. Zhu et al.14) studied the effect of Ti-substitution for Fe in the Fe$_5$Al system on the mechanical alloying process. They concluded that the addition of Ti shortened the milling time for the solid solution formation and the grain size of the solid solutions decreased with increasing Ti concentration. Krasnowski et al.15,16) studied the structure and the transformation of ternary Al$_{50}$Fe$_{25}$Ti$_{25}$ alloy by mechanical alloying. The final microstructure and phase of milled powders are affected by the addition of ethanol. Leonov et al.17) obtained single nanocrystalline alloys after milling the Al$_{50}$Ti$_{50}$–Fe$_x$ powder. For Al-rich ternary alloys, Fan et al.18) obtained solid solution Al(Fe,Ti) and amorphous phase by milling the Al$_{50}$Ti$_{25}$Fe$_{15}$. The results of mechanical alloying for Al$_{58}$–Ti$_{12}$Fe$_x$ ($x = 0–7$)19) indicate that the content of Fe can affect the structure of milled mixture.

In this paper, the effects of Ti-substitution of Al in Al$_3$Fe system during the mechanical alloying have been investigated by means of X-ray diffraction and differential scanning calorimeter.

2. Experimental Procedures

Elemental aluminum (particle size, about 100 μm; purity 99.0%), titanium (particle size, 50–100 μm; purity 99.9%) and iron (particle size, about 100 μm; purity 99.8%) were blended. Mechanical alloying was performed in a high energy planetary ball mill in argon atmosphere using stainless steel vial and balls with diameter of 9.8 mm. The ball-to-powder weight ratio is 20:1. The milling was interrupted at milling times and a small amount of powder was taken out of the vial. The structures of samples were determined by a Rigaku X-ray powder diffractometer with Zr monochromator MoK$_\alpha$ radiation ($\lambda = 0.707370 \text{ nm}$). Thermal analysis up to 973 K was performed by differential scanning calorimetry (Netzsch STA409PC). The crystallization temperature was evaluated at a heating rate of 20 K min$^{-1}$. The activation energy of crystallization was measured with different heating rates of 5, 10, 15 and 20 K min$^{-1}$.

3. Results and Discussion

X-ray diffraction pattern of Al-25 at%Fe powder mixtures after MA for different times are shown in Fig. 1. The patterns show that peaks of aluminum shift to higher diffraction angle and were broadened after mechanical alloying after 20 h, which indicates that iron dissolves into the aluminum and the crystalline size refines. The peaks of iron shift to low angle and are also broadened after 20 h and longer. The atomic radius of aluminum is bigger than that of iron. So this indicates that aluminum dissolves into iron. Only a broad peak exists after 100 h. The two exothermic peaks in DSC curve for the sample indicate amorphous phase and solid solution Fe(Al) co-exist. The prolonged milling time results in the formation of intermetallic Al$_3$Fe$_2$ phase.

Figure 2 shows the XRD patterns of Al-25 at%-7.5 at%Ti mixed powders after milling. The Bragg peaks of Ti
disappear after 10 h, and those of aluminum shift to higher angle. It indicates that the formation of supersaturated solid solution Al(Fe, Ti) during the early stage of MA. Fan et al.\textsuperscript{18} obtained the same result for mechanical alloyed \( \text{Al}_{65}\text{Ti}_{25}\text{Fe}_{10} \). The diffraction peaks of Fe shift to low angle and the peaks of Al disappear after 20 h. The refined aluminum dissolves into iron and the supersaturated solid solution Fe(Al) is formed. No amorphous phase is formed as prolonging the milling time. It is indicated that Ti-substitution can shorten the time to form the supersaturated solid solution by mechanical alloying. The present results are similar to that of Zhu et al.\textsuperscript{14} for Ti-substitution to Fe in the Fe\textsubscript{3}Al system. The XRD patterns of Al-25 at\%Fe-3.75 at\%Ti are similar to those of Al-25 at\%Fe-7.5 at\%Ti and are not given here for simplicity.

Figure 3 shows the XRD patterns of Al-25 at\%Fe-15 at\%Ti mixed powders after milling. It can be seen that the peak of aluminum becomes weaker and broad quickly, while those of Fe and Ti do not change so fast and the diffraction peak of iron shits to low angle. This indicates that the size of aluminum decrease and aluminum dissolves into iron. From the comparison of two samples milled for 10 h of Ti-content of 7.5 at\% and 15 at\%. The Bragg peaks of Ti exist in the latter and the height of Fe diffraction peaks are weaker and broad. A complete amorphous phase is formed after 50 h. The XRD patterns of Al-25 at\%Fe-11.25 at\%Ti have the same tendency. The XRD patterns of different Ti-content samples are given in Fig. 4. It is indicated that the increase of Ti concentration results in easy amorphization of Al\textsubscript{3}Fe alloy.

The DSC traces of milled samples are shown in Fig. 5. Two overlapped exothermic peaks are observed from 631 to
708 K for milled powder without titanium. This implies that two thermal effects of different natures may be involved. The exothermic reaction at 663 K corresponds to the crystallization of amorphous phase. A similar exothermic effect (at 660 K) was observed for the mechanical alloying of Al-30 at%Fe.21) The peak at temperature 663 K is the results of solid solution transformed to Al11Fe2. The DSC traces for two samples of Al-25 at%Fe-3.75 at%Ti and Al-25 at%Fe-7.5 at%Ti are similar. There is only one exothermic peak at temperature 660–710 K and a small heat release during heating, which implies that the thermal effects correspond to a little amount of aluminum and iron forms intermetallic compound Al3Fe2. There are substantial exothermic peaks for Al-25 at%Fe-11.25 at%Ti and Al-25 at%Fe-15 at%Ti at 747.8 K and 752.2 K respectively. This is similar to the results of Al-25 at%Fe-25 at%Ti. The exothermic reaction is the crystallization of amorphous phase. It is noted that the crystallization temperature of amorphous phase is different with and without Ti.

The DSC traces of samples of amorphous powders were examined with different heating rate 5, 10, 15 and 20 K/min. The crystallization temperatures of Al-25 at%Fe-11.25 at%Ti and Al-25 at%Fe-15 at%Ti are 747.8 K and 752.2 K respectively at heat rate 20 K/min. The activation energies for crystallization are estimated using Kissinger’s method,20) as shown in Fig. 6. The activation energies of Al-25 at%Fe-11.25 at%Ti and Al-25 at%Fe-15 at%Ti are 747.8 K and 752.2 K respectively. This is similar to the experimental values by DSC with the heating rate of 20 K/min. The calculated results are in good agreement with the experimental data (747.8 K and 756.9 K respectively. The calculated values for Al-25 at%Fe-11.25 at%Ti and Al-25 at%Fe-15 at%Ti are 746.9 K and 756.9 K respectively. The calculated results are in good agreement with the experimental data (747.8 K and 752.2 K respectively at heating rate 20 K/min).

Shindo et al.21) predicted the crystallization temperature of amorphous alloys obtained by rapid quenching. The crystallization temperature of ternary amorphous alloys can be related with the formation enthalpies of monovacancy. The formation enthalpy of a monovacancy of the constituent of the smallest atom in ternary alloys can be defined as follows,

\[ \Delta H_V(A \text{ vacancy}) = f_B^A \left( \frac{V_A}{V_B} \right)^{\frac{1}{6}} \Delta H_V(B) + f_A^C \Delta H_V(C) + f_A^C \Delta H_V(A) \]

where \( \Delta H_V(A) \), \( \Delta H_V(B) \) and \( \Delta H_V(C) \) are the formation enthalpies of monovacancy in pure constituents A, B and C, respectively. \( f_B^A \) and \( f_A^C \) represents the short range order (ORD) in the binary amorphous phase A-B and A-C respectively and can be written as:

\[ f_B^A = C_B^A (1 + 5 C_B^A C_A^C)^2 \]  
\[ f_A^C = C_B^A (1 + 5 C_B^A C_A^C)^2 \]  
\[ f_A^C = 1 - f_B^A - f_A^C \]  
\[ C_i = \frac{x_i V_i^{2/3}}{\sum_j x_j V_j^{2/3}} \]

where \( i \) and \( j \) represents one of the constituents of ternary alloys. \( x_i \) is the composition of constituent \( i \). \( V_i \) is the mole volume of pure constituent \( i \). \( C_i \) is the composition of surface of constituent \( i \). The crystallization temperature can be estimated with the empirical relation between experimentally determined \( T_x \) and the \( \Delta H_V \) proposed by Weeber et al.22)

\[ T_x = 5 \Delta H_V + 275 \]

The crystallization temperature of amorphous phase obtained by mechanical alloying was estimated with the method mentioned above. The parameters used in the calculation come from reference.23) The estimated values for Al-25 at%Fe-11.25 at%Ti and Al-25 at%Fe-15 at%Ti are 746.9 K and 756.9 K respectively. The calculated results are in good agreement with the experimental data (747.8 K and 752.2 K respectively at heating rate 20 K/min). The crystallization temperature increases with the increment of Ti-concentration.

4. Conclusions

The effects of Ti-substitution to Al in Fe25Al75-xTi_x system during the process of mechanical alloying have been investigated.

(1) The addition of Ti can shorten the time for the formation of solid solution and amorphous phase by mechanical alloying. For low Ti-concentration (Fe25Al75-xTi_x (x = 0, 3.75, 7.5)), the supersaturated solid solution Al(Fe) or Al(Ti, Fe) are formed at the early stage of MA. The final products of them were supersaturated solid solution Fe(Al) or Fe(Al, Ti) and amorphous phase.

(2) The high Ti-concentration (Fe25Al75-xTi_x (x = 11.25, 15)) results in formation of amorphous phase.

(3) The activation enthalpies of amorphous phase increases with Ti.

(4) The calculated crystallization temperatures of Fe25Al75-xTi_x (x = 11.25, 15) are in good agreement with the experimental values by DSC with the heating rate of 20 K/min.

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