

Metastable phases formation induced by mechanical alloying

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Elemental aluminium, titanium and iron powders with compositions of $\text{Al}_{90}\text{Ti}_{10}$, $\text{Al}_{55}\text{Ti}_{45}$, $\text{Al}_{65}\text{Ti}_{25}\text{Fe}_{10}$, respectively, were mechanically alloyed in a planetary ball mill. The sequence of phase formation was characterized by transmission electron microscopy (TEM), X-ray diffraction (XRD), and differential scanning calorimetry (DSC). Various metastable phases were experimentally observed: supersaturated solid solution Al(Ti) for $\text{Al}_{90}\text{Ti}_{10}$, amorphous phase and $\text{L}_{12}\text{-Al}_3\text{Ti}$ compound for $\text{Al}_{55}\text{Ti}_{45}$, amorphous phase and supersaturated solid solution Al(Ti,Fe) for $\text{Al}_{65}\text{Ti}_{25}\text{Fe}_{10}$, and an fcc crystalline phase was inevitably found in those alloys. The formation of the fcc crystalline phase has been critically assessed. The results suggest that the fcc crystalline phase seems to be metastable and it cannot be solely attributed to the contamination from the milling atmosphere under the present experimental conditions.

1. Introduction

Recently, high-energy ball milling has received considerable interest because it can be used as a non-equilibrium processing tool. It has been found that ball milling of intermetallic compounds (ball milling), or of elemental mixtures (mechanical alloying) can be employed to synthesize various metastable phases, such as amorphous phase [1, 2], supersaturated solid solution that is otherwise immiscible [3–5], nanostructured materials [6, 7], and quasicrystalline materials [8].

Mechanical alloying (MA) of aluminium and titanium has been the subject of recent investigations. Because aluminium–titanium intermetallics have high melting points and lower densities together with high strength, they can be used for structural applications. Also, by mechanically alloying aluminium and titanium elemental powders, the amorphization of Al–Ti alloys within a given composition range has been successfully carried out using different milling tools [9–16], but some arguments still remain concerning the sequence of phase transformation, the influence of contamination on the final products, especially on the formation of the fcc crystalline phase. Some authors have asserted that the fcc phase is due to the crystallization of the amorphous phase [10, 14]. Most of the studies, however, have pointed out that the fcc phase can be indexed to the TiN phase or (Ti,O) N phase, which was unexpectedly and almost inevitably introduced by contamination from the milling atmosphere [9, 12, 13]. Their experiments were based on the facts that there was large amounts of nitrogen introduced during ball milling and that the fcc phase exhibits excellent thermal stability. Suryanarayana and Froes [17], on the other hand, have rationalized that if the

hcp-structure titanium undergoes mechanical deformation, the phase transformation from hcp to fcc structure may occur due to the introduction of stacking faults.

In this work the formation of various metastable phases, e.g. supersaturated solid solution Al(Ti) or Al(Ti,Fe), amorphous phase, $\text{L}_{12}\text{-Al}_3\text{Ti}$ compound and fcc crystalline phase in mechanically alloyed Al–Ti alloys, was studied. The formation of the fcc crystalline phase was particularly addressed.

2. Experimental procedure

Elemental aluminium (200 mesh, 99.9%), titanium (360 mesh, 99.9%) and iron (250 mesh, 99%) were mixed to give the desired composition. Mechanical alloying was performed in a planetary ball mill in an argon atmosphere using hardened steel containers and balls with ball-to-powder weight ratio of 60:1. Because aluminium is a ductile component, there is a danger for it to adhere to the balls and containers and this makes the process of MA very inefficient. A small amount of hexane was added as a process control agent to avoid this tendency to stick at the beginning of 4 h. Then it was evacuated by a pump. However, a thick layer of powders still remained adhered to the balls and containers. This is the reason why low amounts of impurities from wear debris of the milling tools were detected.

X-ray diffraction (XRD) patterns were performed using a Rigaku X-ray powder diffractometer with a graphite monochromator CuK_α radiation ($\lambda = 0.15405 \text{ nm}$). Thermal analysis of the mechanically alloyed powders was performed by differential scanning calorimetry (Perkin-DSC-7) at a heating rate

of $20^\circ\text{C min}^{-1}$. Annealing treatment was carried out under a vacuum of 10^{-5} torr.

3. Results

Fig. 1 shows XRD patterns for $\text{Al}_{90}\text{Ti}_{10}$ alloy after various milling periods. The broadening of the XRD patterns indicates the introduction of the internal strain and the refinement of the grain size by the mechanical deformation. Concurrently, the aluminium Bragg peaks shift to a higher angle position with increasing milling time, accompanied by the disappearance of the Ti XRD lines, suggesting that the solubility for hcp-titanium in fcc-aluminium has been extended. In the equilibrium state, hcp-titanium in fcc-aluminium has a negligible solubility. Further evidence in Fig. 1 can be clearly observed that after 40 h ball milling: additional Bragg peaks, which correspond to an fcc crystalline phase, have developed. It has been reported that fcc-phase can be formed, especially at titanium-rich Ti–Al alloys [9, 12, 13]. Our experiment indicates that the fcc phase also appears in aluminium-rich Al–Ti alloys. For alloys with titanium contents ranging from 15%–36%, the single supersaturated solid solution has been successfully synthesized. When the titanium content is lower than 10%, an additional fcc phase, as in the above case, was inevitably formed [18].

Surprising changes occur for as-prepared $\text{Al}_{90}\text{Ti}_{10}$ alloy after being sealed at ambient temperature for 7 months. As can be seen from Fig. 1, the Bragg peaks indexed as an fcc crystalline phase, completely disappear, indicating that the fcc phase seems to be metastable and that the synthesis of the single solid solution is kinetically constrained during mechanical alloying.

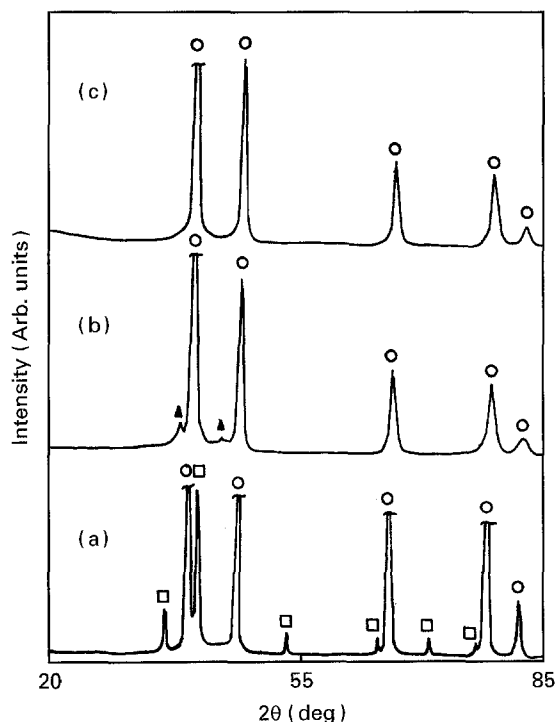


Figure 1 XRD patterns for $\text{Al}_{90}\text{Ti}_{10}$ alloy after (a) 10 h ball milling, (b) 40 h ball milling, and (c) sealed at ambient temperature for 7 months. (○) Al(Ti), (□) Ti, (▲) fcc.

Fig. 2 shows XRD patterns for $\text{Al}_{55}\text{Ti}_{45}$ alloy after various milling periods. After a 40 h ball mill, a broad halo representing the amorphous phase was observed, which is further confirmed by TEM observation, as shown in Fig. 3. After a 60 h ball mill, the amorphous phase crystallizes into a mixture of the metastable $\text{L}_{12}\text{-Al}_3\text{Ti}$ compound and the fcc phase. The positions of the Bragg peaks for the fcc phase are almost identical to the values in Fig. 1, suggesting that the fcc phase can be formed by different routes.

Other, more convincing, information concerning the formation of the fcc phase can be obtained from Fig. 4, which shows XRD patterns for $\text{Al}_{65}\text{Ti}_{25}\text{Fe}_{10}$ alloy after various milling times. Our primary attempt, by the addition of 10% Fe to Al–Ti alloy, was to study whether it was possible for iron atoms to stabilize the metastable $\text{L}_{12}\text{-Al}_3\text{Ti}$ compound, because the metastable $\text{L}_{12}\text{-Al}_3\text{Ti}$ compound may be transformed into the stable $\text{DO}_{22}\text{-Al}_3\text{Ti}$ compound at relative lower temperature. From Fig. 4, it can be seen that after a 56 h ball mill, the solid solution $\text{Al}(\text{Ti}, \text{Fe})$ and the amorphous phase which is buried in the spectrum background, are formed. When the as-prepared sample is annealed at 873 K for 24 h, the amorphous phase directly crystallizes into the fcc phase and the solid solution $\text{Al}(\text{Ti}, \text{Fe})$ transforms into the metastable $\text{L}_{12}\text{-(Al, Fe)}_3\text{Ti}$ compound. The results suggest that the addition of iron can, indeed, stabilize the L_{12} -type compound. The lattice parameter value for the fcc crystalline phase with $a = 0.423$ nm is in close agreement with the literature one, and is comparable with those in Figs 1 and 4 [9, 12, 13]. Because TiC phase is also observed in Fig. 4, it is believed that the formation of the TiC phase can be ascribed to the process control agent.

Fig. 5 shows DSC curves for mechanically alloyed powders. Two distinct exothermic peaks were clearly observed in Fig. 5a. By combining with XRD analysis, as shown in Fig. 6, the first peak corresponds to the structural relaxation and the partial ordering of the

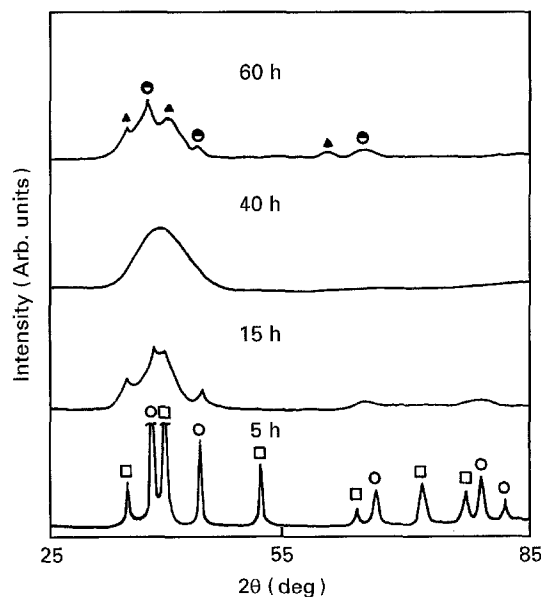


Figure 2 XRD patterns for $\text{Al}_{55}\text{Ti}_{45}$ alloy after various milling periods. (○) Al, (□) Ti, (●) $\text{L}_{12}\text{-Al}_3\text{Ti}$, (▲) fcc.

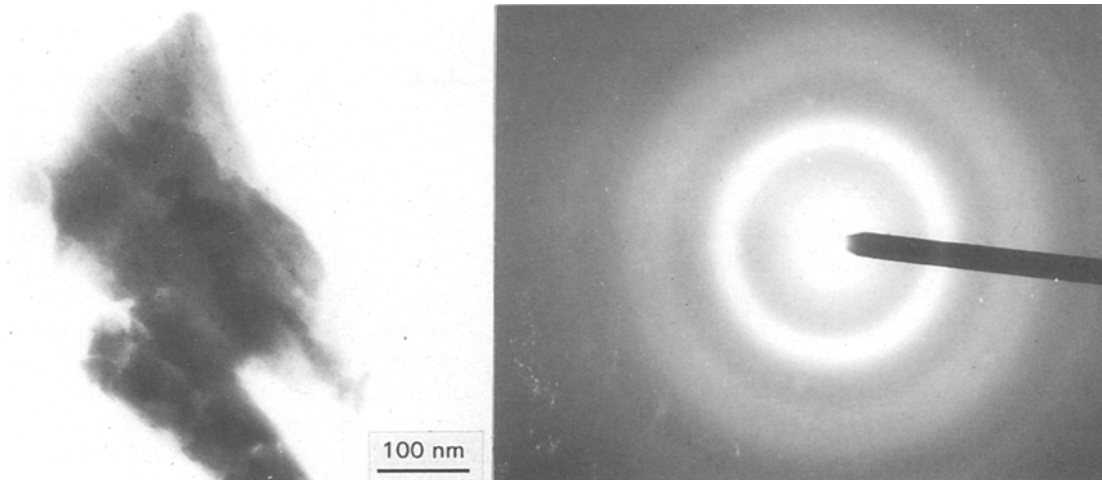


Figure 3 TEM image and SAD pattern for $\text{Al}_{55}\text{Ti}_{45}$ alloy after 40 h ball milling.

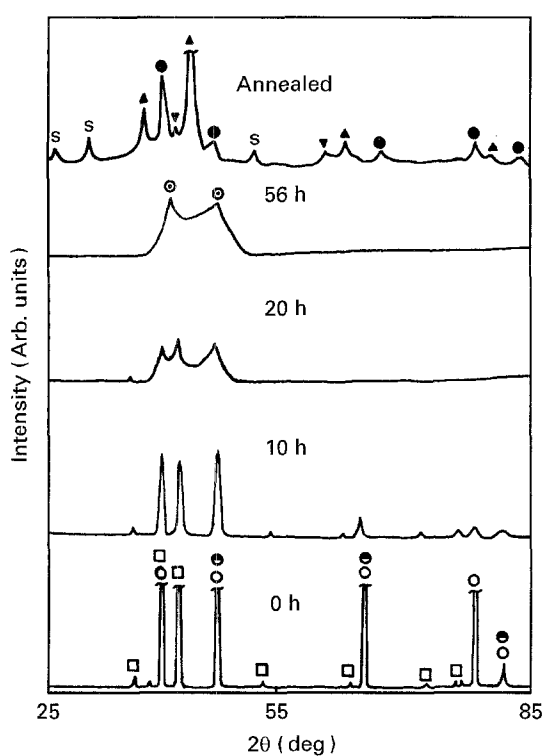


Figure 4 XRD patterns for $\text{Al}_{65}\text{Ti}_{25}\text{Fe}_{10}$ alloy after various milling periods. S, superlattice of L_{12} -(Al, Fe) $_3$ Ti compounds (○) Al, (□) Ti, (●) Fe, (▲) fcc, (●) L_{12} -(Al, Fe) $_3$ Ti, (▼) TiC, (⊙) Al(Ti, Fe).

solid solution, and the second peak to further structural relaxation, phase transformation from the solid solution Al(Ti) and the L_{12} - Al_3Ti compound into stable DO_{22} - Al_3Ti compounds. The exothermic peaks in Fig. 5b and c originate from the crystallization of amorphous phases. The crystallization temperature can be measured to be 686 K, 694 K, respectively.

4. Discussion

Four types of metastable phase were observed during mechanical alloying of Al-Ti and Al-Ti-Fe alloys, i.e. supersaturated solid solution Al(Ti) or Al(Ti, Fe), amorphous phase, L_{12} - Al_3Ti compound and an fcc

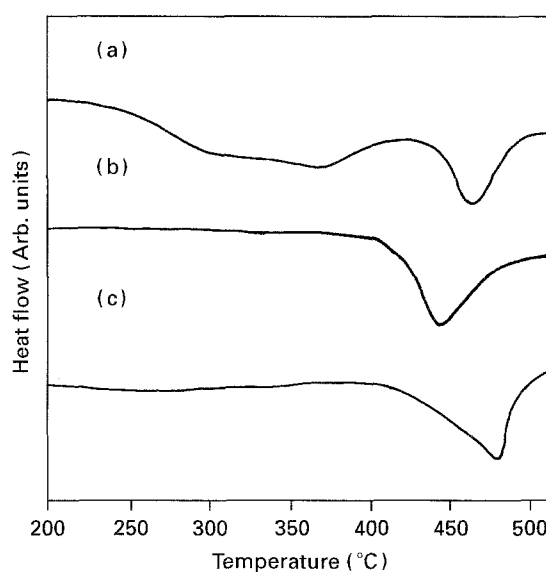


Figure 5 DSC curves for mechanically alloyed powders: (a) $\text{Al}_{90}\text{Ti}_{10}$ alloy after 40 h ball milling, (b) $\text{Al}_{55}\text{Ti}_{45}$ alloy after 40 h ball milling, and (c) $\text{Al}_{65}\text{Ti}_{25}\text{Fe}_{10}$ alloy after 56 h ball milling.

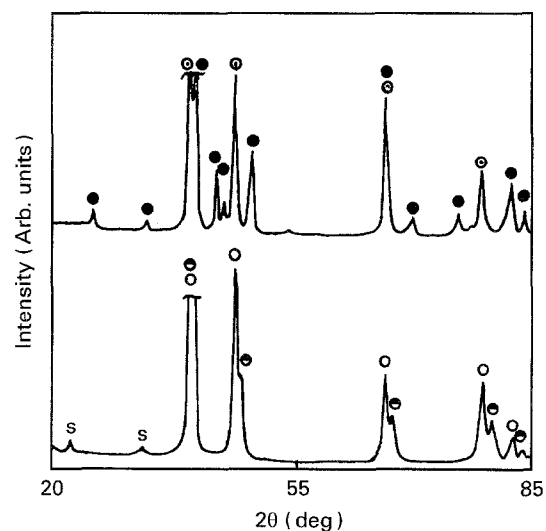


Figure 6 XRD patterns for $\text{Al}_{90}\text{Ti}_{10}$ alloy after (a) the first exothermic peak, and (b) the second exothermic peak in DSC. S, superlattice of L_{12} - Al_3Ti compound, (○) Al(Ti), (●) DO_{22} - Al_3Ti , (●) L_{12} - Al_3Ti , (⊙) Al.

crystalline phase. It was found that the fcc phase was inevitably formed during the last stage of ball milling.

The synthesis of supersaturated solid solution has been reported in various systems. The solubility can even be extended in some immiscible systems with positive heats of mixing, e.g. Fe–Cu [4], Cu–Co [5], and the thermodynamic aspect has not been well accounted for. Under equilibrium conditions, the hcp-titanium in fcc-aluminium has a negligible solubility. By MA, the solubility can be extended up to 36 at % [18]. The amorphous phase can be obtained with further increase in the titanium content. During MA, fine powders undergo mechanical impacts at the collision site within a short time range. Larger amounts of energy can be stored in the fine powders in the forms of lattice defects, nanocrystalline grain boundaries, and by forming metastable phases, e.g. the extension of solubility. The solid solution with extended solubility is far away from the equilibrium state energetically. If thermal activation is provided, the transition from the non-equilibrium state to the equilibrium state may occur. This behaviour is demonstrated in Figs 5 and 6. The structural relaxation (annihilation of lattice defects and the reduction of the volume of the grain boundaries) and the chemical ordering by the occurrence of a long-range chemical wave in the solid solution, may transfer the high-energy configuration to a relatively lower energy one in the temperature range 250–420°C (the first exothermal peak). In the temperature range 420–500°C a further structural relaxation and phase transformation into the fully equilibrium state, occurs (the second exothermal peak).

The formation of the fcc phase by mechanical alloying has actually been reported in Zr–Al [19] and Ti–Mg [17] systems. Fecht *et al.* [19] ascribed it to be crystallization of amorphous phase, and Suryanarayana *et al.* [17] on the other hand, attributed it to the formation of the metastable phase by the introduction of stacking faults in the hcp-titanium.

In the Al–Ti system, earlier studies have ascribed the formation to the crystallization of an amorphous phase because the fcc phase may appear at the expense of the amorphous phase during further ball milling. Recent investigations seem to support the idea that the formation of the fcc phase after prolonged ball milling may originate from the contamination of the milling atmosphere by, for example, nitrogen and oxygen, because high impurity levels of nitrogen and oxygen are detected by chemical analysis. The lattice parameter value of TiN (also with fcc structure) is very close to that observed for the fcc phase by ball milling the Al/Ti mixture. It is reported that the nitride can indeed be formed if the pure elemental titanium metal is milled under a nitrogen atmosphere [20]. A further supporting experiment indicates that the fcc phase is stable up to 900°C which is very closely related to the TiN phase [9, 13]. According to the reported experiments, the possibility of the contamination from the milling atmosphere, which results in the formation of the fcc phase if the milling condition is poor, cannot be ruled out. However, the above explanations cannot be generally accepted in the present condition.

The direct observation of the disappearance of the fcc crystalline phase, as shown in Fig. 3 is indeed interesting. It is almost improbable to expect the TiN phase to exhibit this behaviour at the ambient temperature, because it is stable up to the melting point. It has been reported that the nanocrystalline material may undergo grain growth through a diffusional process, even at ambient temperature. Bearing this in mind, it is not so surprising that the fcc phase may again be incorporated into the solid solution which has been constrained during ball milling. The gain of free energy resulting from the large negative heats of mixing, may act as the driving force for the reaction between the fcc phase and the solid solution. Our experimental evidence also indicates that the fcc phase may be crystallized from amorphous phases, not only by thermal activation but also by ball milling, as shown in Figs 2 and 4. Mizutani and Lee [21] have suggested that during ball milling, the outer atmosphere, e.g. oxygen, can accelerate the crystallization process from an amorphous phase. In this case, the crystallization of amorphous Al₅Ti_{4.5} alloy may be attributed to the impurities which cause the formation of an fcc phase. Nevertheless, it is inconceivable that the amorphous phase can also be directly crystallized into the fcc phase during heating in Al_{6.5}Ti_{2.5}Fe_{1.0} alloy. In the present case, the fcc phase is most probably related to a metastable phase, as has been suggested by Fecht *et al.* in the Zr–Al system [19].

The amorphous Al₅Ti_{4.5} alloy can be crystallized into the metastable L₁₂–Al₃Ti compound during ball milling. The stable DO₂₂–Al₃Ti compound was not observed, possibly due to its complex structure. Previous studies have revealed that the phase selection during ball milling is determined by the energetic and structural factors [11]. Phases with simple structure may be easily formed by ball milling. During heating, the metastable L₁₂–Al₃Ti compound may be restored into the stable state associated with the heat release.

5. Conclusion

By mechanically alloying Al₉₀Ti₁₀, Al₅₅Ti₄₅, Al₆₅Ti₂₅Fe₁₀ elemental powders, four kinds of metastable phase existing in these alloys, were observed. It was found that the fcc crystalline phase was almost inevitably formed during ball milling. The direct observation of the disappearance of the fcc phase at ambient temperature strongly supports the idea that the fcc phase cannot be the nitride which, in some cases, was introduced during ball milling in the Al–Ti system. The results indicated that the fcc phase seems to be metastable. Obviously, further experiments are necessary to understand this phenomena thoroughly.

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