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Synthesis of nanocrystallite by mechanical alloying and in situ observation of their combustion phase transformation in Al_3Ti

C. E. WEN
Department of Materials Science and Engineering, Beijing University of Aeronautics and Astronautics, Beijing, 100083, People's Republic of China

Advanced Processing Laboratory, Materials Processing Department, National Industrial Research Institute of Nagoya, 1-1 Hirate-cho, Kita-ku, Nagoya 462, Japan

K. KOBAYASHI, A. SUGIYAMA, T. NISHIO, A. MATSUMOTO
Advanced Processing Laboratory, Materials Processing Department, National Industrial Research Institute of Nagoya, 1-1 Hirate-cho, Kita-ku, Nagoya 462, Japan

Elemental powders of stoichiometric Al_3Ti were mechanically alloyed (MA) in order to investigate the phase formation during the milling process. Furthermore the stability of MA powders were studied under transmission electron microscopy (TEM). The results indicate that a supersaturated Al(Ti) solid solution with nanocrystalline size has been formed after mechanical alloying for 360 ks in consuming the elemental powders of Al and Ti and no further phase transformation can be detected upon longer milling. The MA powders are unstable being irradiated by electron beams under the TEM observation, exothermically forming various intermetallic compounds. The combustion phase transformation processes and products are depending on the time of mechanical alloying. The structural changes and phase transformations during both mechanical alloying process and annealing process were also characterized by using X-ray diffraction measuring. © *2000 Kluwer Academic Publishers*

1. Introduction

Due to their attractive properties, such as high melting temperature, extremely low density, and excellent oxidation resistance, the Al_3Ti intermetallics are being considered as potential high temperature structural materials for aerospace applications [1–4]. However, Al_3Ti alloys have found only limited applications as high temperature structural materials because of the extremely high reactivity of the constituent elements in the melt [5], and more importantly, their brittleness at room temperature.

Since the works of Benjamin [6], metallurgists have realized that the mechanical alloying (MA) technique is a versatile powder metallurgical tool for increasing the performance capabilities of light metals such as titanium and aluminium intermetallics. Recently this technique has been extensively exploited to produce a variety of stable or metastable crystallines, nanocrystallines, and amorphous structures. As the grain size decreases continuously with milling time, consequently, the MA powders may have nanometer-sized grains [7–8]. This provided further avenues for possible improvement in the ductility/fabricability of the intermetallics because of the increased tendency of the materials to deform plastically.

There are a number of investigations concerning to the phase transformation of Ti-Al system during mechanical alloying process. However, results from different investigators have long been in contradiction and remain so at this time [9–15]. There are various reasons for the disagreement of the data obtained by different investigators such as milling conditions, contamination, process control agents etc. Moreover, there are few papers talking about the *in situ* transformation under the transmission electron microscopy of the mechanically alloyed powders which may be an important factor related to the thermal stability of the obtained powders so far. In this paper we combined the results from the transmission electron microscopy (TEM) observations and the X-ray diffraction analyses attempting to have a clear understanding of the mechanical alloying process. The thermal stability of the mechanically alloyed powders of Al_3Ti were investigated by observing the *in situ* phase transformations of the Al_3Ti under the irradiation of electron beams in TEM.

2. Experimental procedure

2.1. Starting materials and milling procedure

Elemental titanium (99.9% purity, $\leqq 50\,\mu$m)and aluminum (99.5% purity, $\leqq 150\,\mu$m) powders were used as starting materials. These powders were blended together to yield a stoichiometrical composition of Al_3Ti.

The MA processes were performed in a planetary ball milling by using a hardened high Cr steel vials (500 ml) and balls (Φ 10 mm) under 66 kPa argon gas atmosphere. For each run, 40 grams of the powders were loaded. The weight ratio of ball to powder is 10 : 1. About 1 mass% of stearic acid ($CH_3(CH_2)_{16}COOH$) was used as a process control agent. The ball milling was carried out at the rotation rate of 170 r.p.m. and cooled by air conditioner.

2.2. Characterization

The mechanically alloyed powders were characterized by means of X-ray diffraction with Cu K_α radiation at 30 kV and 40 mA. The crystal size was calculated by using the Scherrer Formula [9]: $t = 0.9\lambda/B_c \cos\theta$. Where t is the crystal size estimated by a (hkl) line; λ is the X-ray wavelength; B_c is the angular width at half of the maximum intensity; θ is the diffraction angle.

Transmission electron microscopy (TEM) observation was performed by using a voltage of 160 kV. TEM specimens were prepared by mixing the powders in a small amount of ethanol and mounted on a copper microgrid to observe their shapes, sizes, and structures, as well as the combustion synthesis processes.

3. Results and discussion

3.1. Structural changes with the mechanical alloying times

The X-ray diffraction (XRD) patterns of powder mixtures after different milling time are shown in Fig. 1. After milling for 180 ks, Fig. 1a shows that there are still diffraction peaks of hcp-Ti and fcc-Al. After milling 360 ks, Fig. 1b shows obviously a new fcc phase has been synthesized. The fcc phase has the lattice parameter: $a = 0.3980 \pm 0.0005$ nm as determined from XRD patterns which may correspond to Al(Ti) supersaturated solid solution, as pure aluminum has very close lattice parameter: 0.405 nm. The average crystalline size of the fcc phase is 3.940 nm as determined by Scherrer formula. There are no traces of diffraction of (100) and (110) superlattice lines of the ordered phase of $L1_2$ as reported by Ref. [12–15], and also amorphous-like state reported by Ref. [11]. The appearance of reflection peaks which can be ascribed to fcc-Al(Ti) crystalline structure suggests that mechanical alloying may promote the formation of a supersaturated solid solution of Al(Ti) over a wide range of compositions. Hence we can deduce that a phase transformation was induced by mechanical alloying, and the synthesized nanocrystalline phase might be considered as Al(Ti)-supersaturated solid solution. Upon further milling, the amount of the synthesized nanocrystallite fcc-Al(Ti) increased as shown from Fig. 1c to d. No other phase transformation can be detected during the mechanical alloying process.

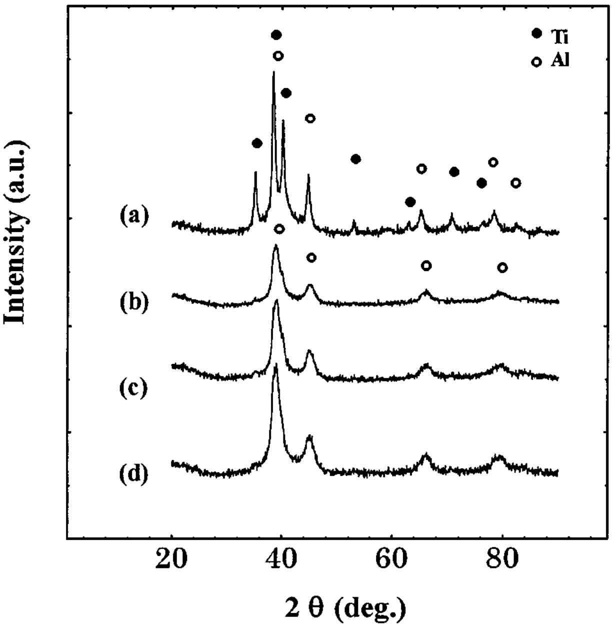

Figure 1 XRD patterns of stoichiometric Al_3Ti powders mechanically alloyed for various times (a) MA, 180 ks (b) MA, 360 ks (c) MA, 540 ks (d) MA, 720 ks.

3.2. In situ observation of the combustion phase transformation

3.2.1. Elemental Al_3Ti powders mechanically alloyed for 180 ks

TEM analyses were performed in order to understand and recognize the microstructure changes and the combustion phase transformation processes of the powders after mechanically alloyed for different times. Before the combustion transformation, Fig. 2a presents the bright field image (BF) and Fig. 2b the related selected area diffraction pattern (SADP) of the Al_3Ti powders after mechanically alloyed for 180 ks. As shown in the SADP, near smooth rings of the hcp-Ti and fcc-Al solid solution coexisted indicating small crystal size as well as the absence of preferred orientation. For the same mechanically alloyed stoichiometric Al_3Ti powders, as the combustion transformation processing, the avalanche-like reaction occurred after being irradiated for around 40 seconds under an energy density of 20 PA/cm^2. The edge of powder particles quickly collapsed and the phase transformation process completed in twinkling much like avalanche, forming a number of fine particles. And further phase transformation has not been observed under the large range of energy density during an understandable period. Fig. 3a displays the BF micrograph of the combustion phase transformation process and Fig. 3b shows the dark field (DF) micrograph of the reacted products particles, as well as the related SADP in Fig. 3c indicating a mixture of a new tetragonal phase of Al_5Ti_2 and the fcc-Al(Ti) phases. These Al_5Ti_2 particles are very fine and homogeneous grains with several nanometers in diameter as shown in the dark field micrograph.

3.2.2. Elemental Al_3Ti powders mechanically alloyed for longer than 360 ks

For the Al_3Ti powders mechanically alloyed for over than 360 ks, *in situ* combustion phase transformation happened in two steps separately. At first, the combustion phase transformation quickly happened after

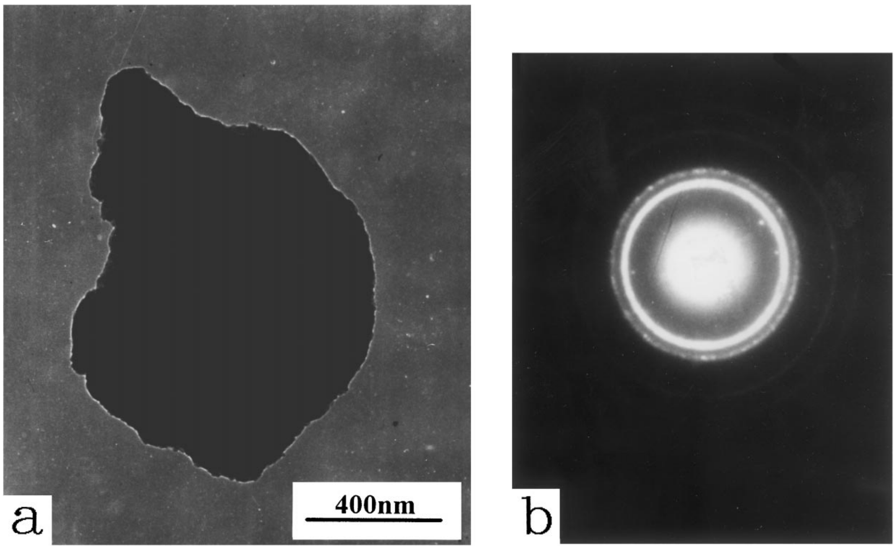

Figure 2 TEM bright-field image (BF) with related selected-area diffraction pattern (SADP) of a stoichiometric Al_3Ti specimen mechanically alloyed for 180 ks (a) BF (b) SADP.

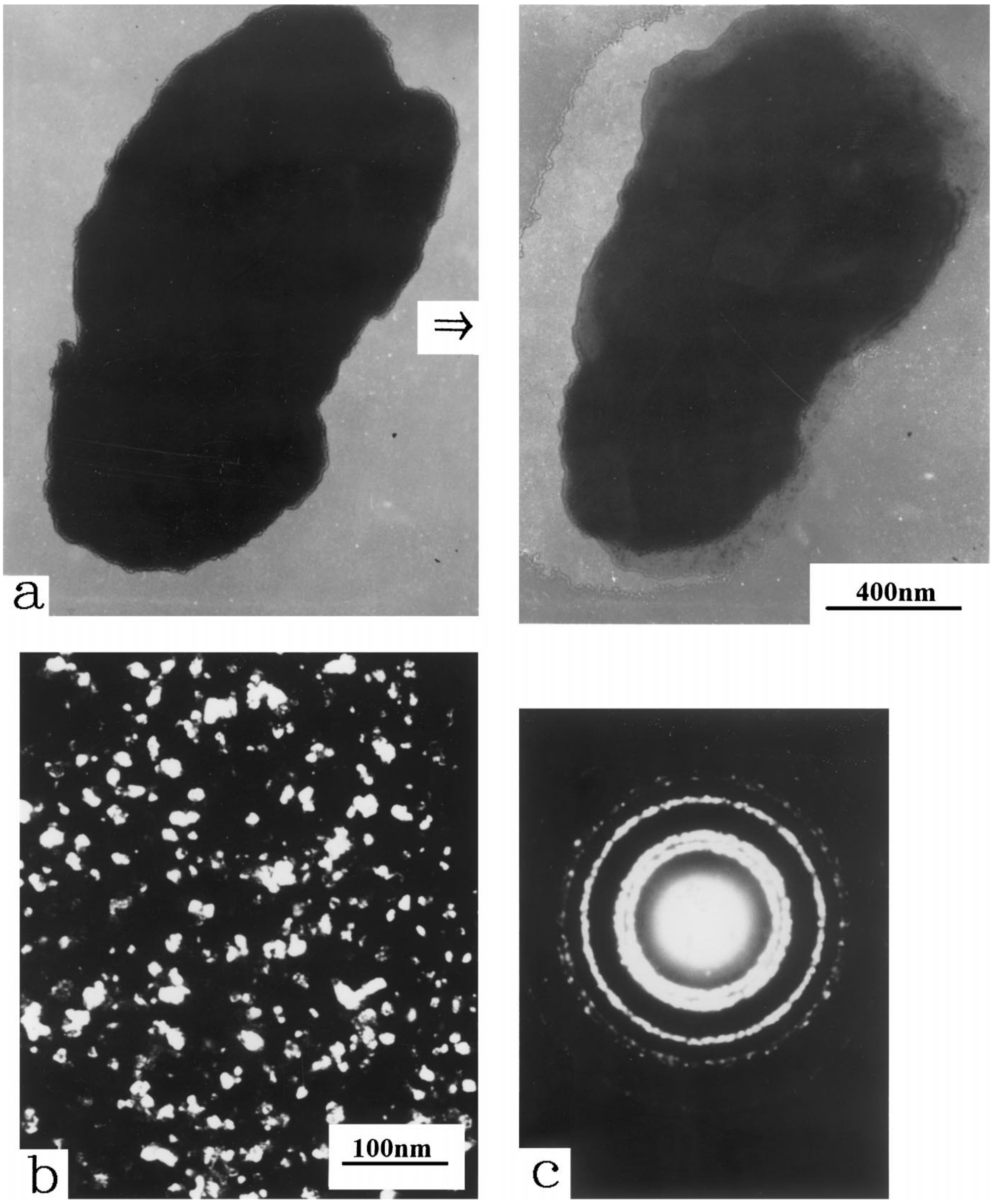

Figure 3 TEM micrographs with related selected-area diffraction pattern of a stoichiometric Al_3Ti specimen mechanically alloyed for 180 ks showing the combustion phase transformation (a) BF (b) DF (c) SADP.

being irradiated for around one second under an energy density 20 PA/cm^2, while the reaction process was too rapidly to record the image of the original particles, so that the only record of the original particles was the diffraction pattern using very weak beam intensity. Fig. 4 shows the SADP of the Al_3Ti powders mechanically alloyed for 360 ks before combustion phase transformation. Obviously, the SADPs have completely sharp Debye-Scherrer rings corresponding to fcc-Al(Ti) supersaturated solid solution with very fine crystallite size. The lattice parameters which can be amounted to be 0.3982 nm are in good agreement with the results of the XRD analysis. These results suggest that a nanocrystalline phase of fcc-Al(Ti) solid solution has been synthesized during this stage of MA process. For those powders upon further milling until 720 ks, no other synthesized phase can be observed.

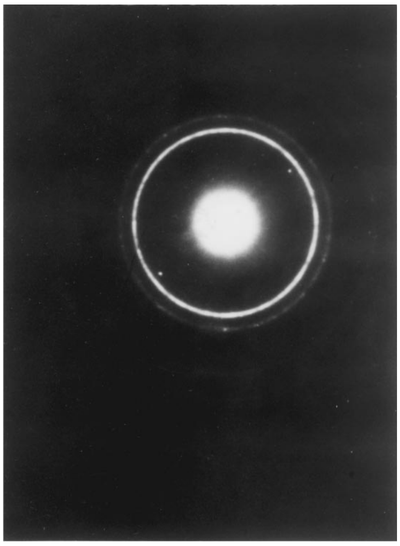

Figure 4 Selected-area diffraction pattern of a stoichiometric Al_3Ti specimen mechanically alloyed for 360 ks before combustion phase transformation.

The product of the first-step combustion phase transformation showed the same structure with those in mechanically alloyed for 180 ks which can be identified

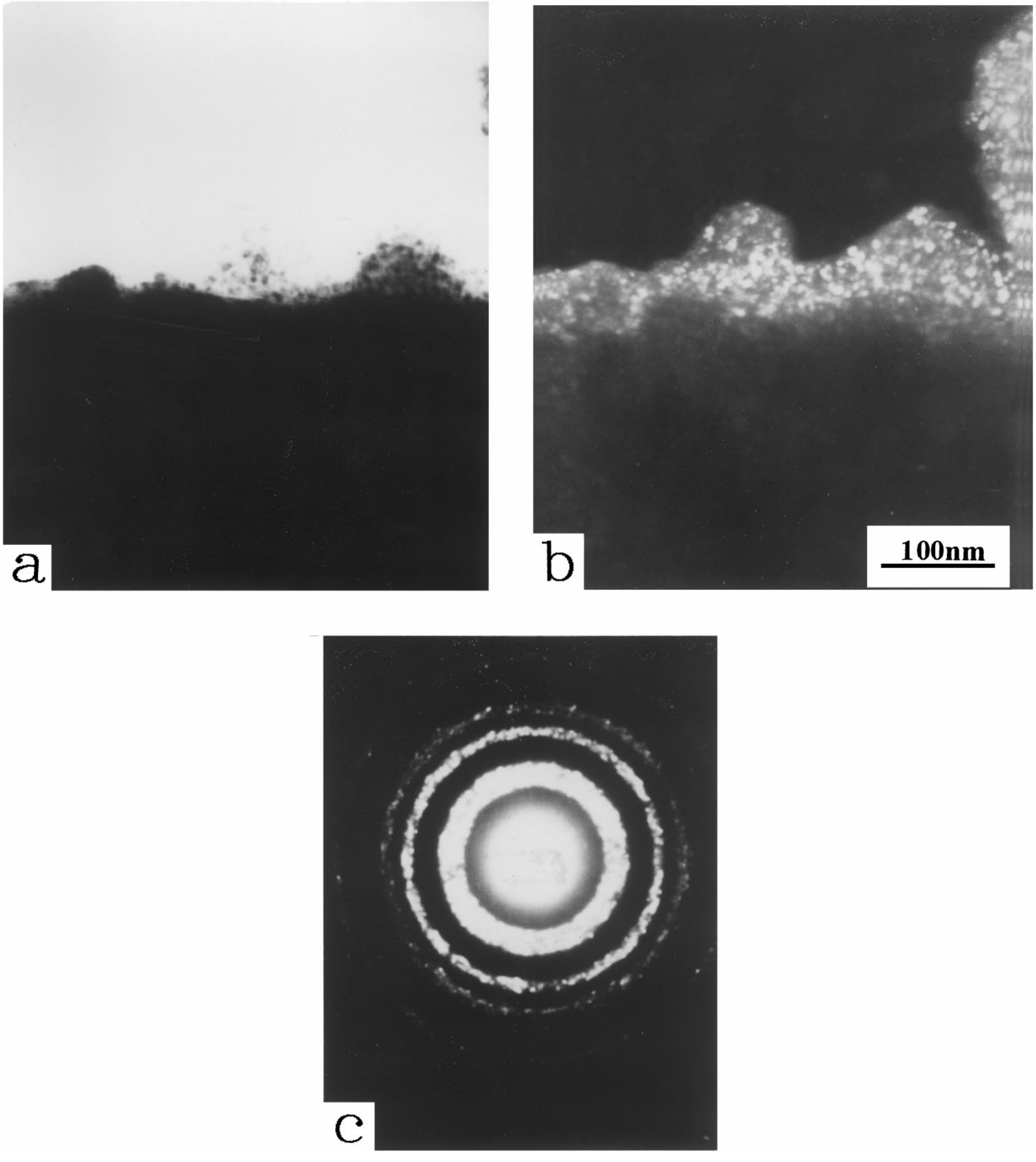

Figure 5 TEM micrographs with related selected-area diffraction pattern of a stoichiometric Al_3Ti specimen mechanically alloyed for 360 ks showing the first step of combustion phase transformation (a) BF (b) DF (c) SADP.

as a mixture of Al_5Ti_2 phase and the un-reacted fcc-Al(Ti) phase. Fig. 5a displays the BF micrograph of the transformed product and Fig. 5b shows the DF micrograph indicating very small size of a few nanometers, while Fig. 5c shows the SADP with near Debye-Scherrer rings corresponding to a mixture of a tetragonal phase of Al_5Ti_2 and fcc-Al(Ti) phase.

For being irradiated over 70 seconds under the same energy intensity, these fine particles disappeared and relatively larger particles formed *in situ* twinklingly. The products of this second-step combustion transformation were very stable under the large range of energy intensity during an understandable period. Fig. 6 present the process of this second-step combustion transformation. The DF image in Fig. 6b shows the size of these products are about 50 nm as well as the related SADP shows the sharp spot patterns of products can be indexed as DO_{22}-Al_3Ti, ordered superstructure of $Al_{24}Ti_8$, and Al_2Ti phases. There are no diffraction rings in this SADP.

Meanwhile, heat treatments were performed on the mechanically alloyed powders at 873 K and 1073 K respectively. After annealing at the temperature of 873 K, Al_5Ti_2 phase was obtained from the powders both mechanically alloyed for 180 ks and 360 ks, the XRD patterns were shown in Fig. 7b and Fig. 8b. It is coincide with the results of the combustion phase transformation that happened during the TEM observation for the powders milled for 180 ks and the first-step combustion transformation for the powders milled for 360 ks. Also, three phases of DO_{22}-Al_3Ti, ordered superstructure of $Al_{24}Ti_8$ and Al_2Ti were obtained from the powders milled for longer than 360 ks as annealed at the temperature of 1073 K, which is in agreement with the results of the second-step combustion phase transformation under the TEM observation from the

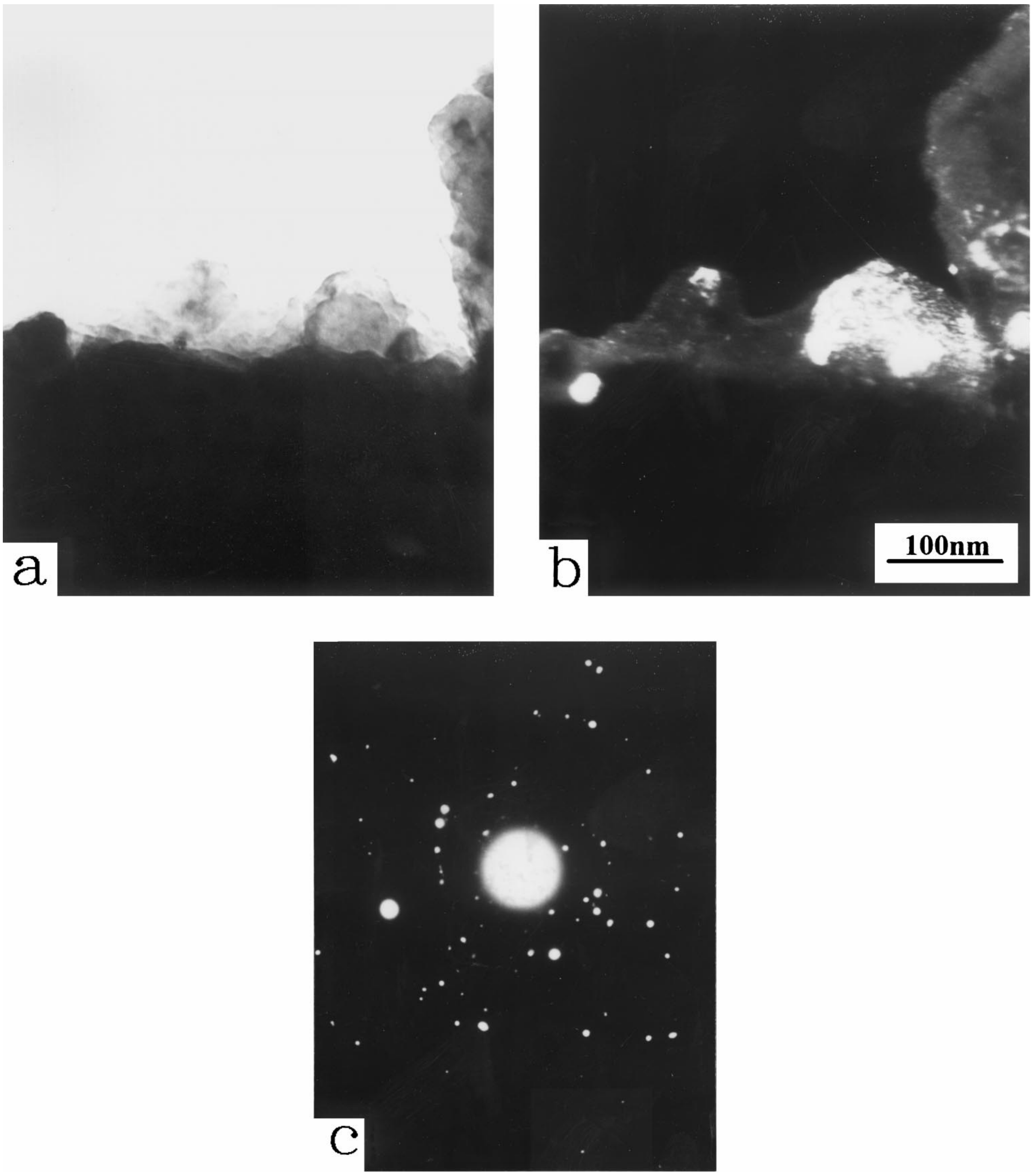

Figure 6 TEM micrographs with related selected-area diffraction pattern of a stoichiometric Al_3Ti specimen mechanically alloyed for 360 ks showing the second-step of combustion phase transformation (a) BF (b) DF (c) SADP.

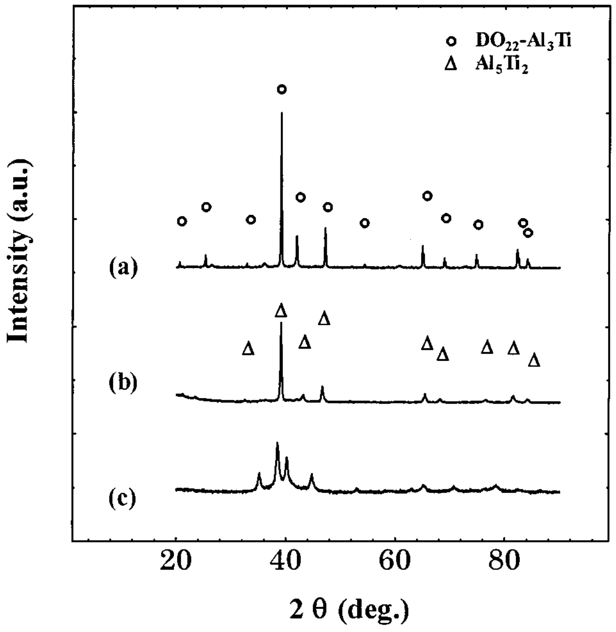

Figure 7 XRD patterns of stoichiometric Al_3Ti samples after mechanically alloyed for 180 ks and annealed at various temperatures (a) annealed at 1073 K (b) annealed at 873 K (c) as-milled powders.

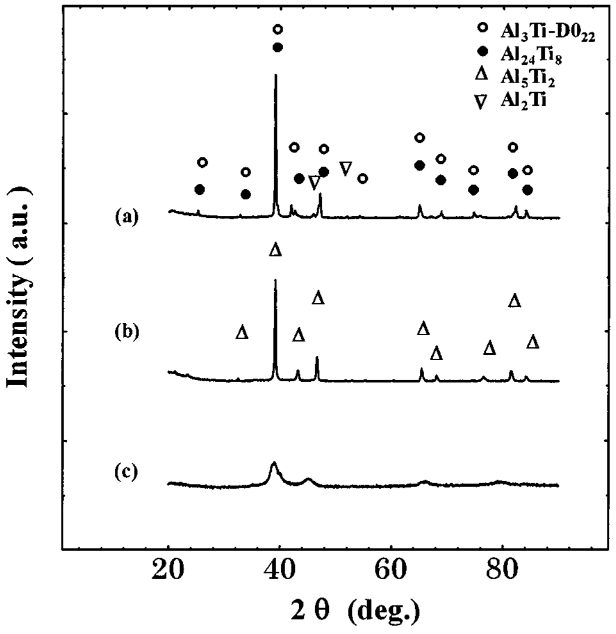

Figure 8 XRD patterns of stoichiometric Al_3Ti samples mechanically alloyed for 360 ks and annealed at various temperatures (a) annealed at 1073 K (b) annealed at 873 K (c) as-milled powders.

powders milled for longer than 360 ks. The XRD patterns are shown in Fig. 8a. However, only DO_{22}-Al_3Ti phase was obtained from the powders milled for 180 ks as annealed at the temperature of 1073 K. The XRD patterns are shown in Fig. 7a. This step of combustion phase transformation can not be detected under the TEM observation. It means that the irradiation energy of the electron beam is not enough for the phase transformation of $Al(Ti) \rightarrow DO_{22}$-$Al_3Ti$. In another words, the accumulated energy of the powders mechanically alloyed for 180 ks is not enough to improve this step of transformation.

It is well known that a metastable phase is a non-equilibrium phase of matter for which the evolution toward the equilibrium phase is suppressed by a kinetic barrier. This barrier must be overcome by thermodynamic fluctuations. Mechanical deformation, irradiation, chemical interdiffusion, pressure variation, as well as other externally driven processes can thus be used to produce metastable phases, and further equilibrium phases. In this study, the elemental stoichiometric Al_3Ti becomes very fine titanium and aluminium particles with severe mechanical deformations after milling for 180 ks which have a non-equilibrium concentration of defects such as dislocations, partial dislocations, anti-phase boundaries and so on. These mechanically alloyed powders can transform into a metastable phase of Al_5Ti_2 under the electron irradiation in TEM. Because of the stored energy is limited by milling of 180 ks, no further transformation can be detected during a understandable irradiation period. For the milling time longer than 360 ks, we got a metastable nanocrystalline phase of supersaturated Al(Ti), which have the higher amount of stored energy of defects. These stored energy of defects can be used to drive the system to transform into a more stable but still metastable phase of Al_5Ti_2 as irradiated for about one second and transform to a equilibrium state as irradiated for longer time of 70 seconds. In this irradiation process, the excess energy of defects provides the driving force to form equilibrium phases as DO_{22}-Al_3Ti, ordered superstructure of $Al_{24}Ti_8$ and Al_2Ti.

4. Conclusions

In this research, we reported the synthesis of a nanocrystalline phase of Al(Ti) supersaturated solid solution through mechanical alloying stoichiometric Al_3Ti blends. Furthermore, the *in situ* combustion phase transformation process under TEM observation are also investigated in detail. The main results are as follows:

1. Mechanical alloying of the elemental powders of stoichiometric Al_3Ti blends under an argon atmosphere initially produces the alloying of the elements Ti and Al, followed by the synthesis of a nanocrystalline phase of fcc-Al(Ti) supersaturated solid solution. Upon further milling, there are no further structure forming.
2. The mechanically alloyed powders are unstable under the irradiation of electron beam in TEM, exothermically transforming into various intermetallic compounds. For those powders milled for longer than 360 ks, there are two steps combustion phase transformations occurred. In the first-step, Al_5Ti_2 was obtained immediately under the irradiation of the electron beam, and DO_{22}-Al_3Ti, ordered superstructure of $Al_{24}Ti_8$, and Al_2Ti were obtained as the products of the second-step combustion phase transformation under about 70 seconds of irradiation with an energy intensity of 20 PA/cm^2.
3. On the contrast, for the powders that milled for 180 ks, only one step combustion phase transformation can be detected with the transformation product being Al_5Ti_2 phase under about 40 seconds of irradiation with an energy intensity of 20 PA/cm^2. Further phase transformation has not been observed under large range of energy density during an understandable period.

4. Heat treatment were carried out at different temperature. Those as milled powders will transform to Al_5Ti_2 phase annealed at 873 K for all the milling time. As annealed at 1073 K, three equilibrium phases were obtained as DO_{22}-Al_3Ti, ordered superstructure of $Al_{24}Ti_8$, and Al_2Ti for the powders milled for 360 ks and only DO_{22}-Al_3Ti phase was obtained from the powders milled for 180 ks which did not form under the irradiation of electron beam in TEM.

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