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Preparation of nitrides dispersed Al–Ti alloy by reactive ball milling in N_2 gas

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Abstract

The nitride dispersed Al–Ti alloys have been prepared by reactive ball milling (RBM) of elemental powders of Al and Ti in nitrogen gas. XRD and TEM analyses showed that when Al-10, 20 wt. % Ti elemental powder mixtures were ball milled in nitrogen gas, no nitrides could be observed in Al–Ti alloy powders. In order to accelerate the formation of Ti nitrides, when only Ti powder was milled in nitrogen gas at the first stage and then a second stage milling was carried out with as-milled Ti powder and elemental Al powder in the two-step RBM, TiN readily formed and dispersed in the Al matrix. The particle size and grain size were effectively reduced by the hard and brittle TiN and dissolved nitrogen atoms. High resolution TEM analysis showed that the TiN, having the grain size of 5 nm, existed between the Al matrix. The hardness of Al–Ti alloys milled in nitrogen gas was higher than that of Al–Ti alloys milled in Ar gas. It seems that the TiN is an effective dispersion strengthener in Al–Ti alloys. After annealing treatment at 500°C, the hardness of Al–Ti alloys hardly decreased with annealing time and they exhibited a good thermal stability.

Keywords: Reactive ball milling; Ti nitride; Nitride dispersed Al–Ti alloy; Thermal stability

1. Introduction

Al–Ti alloys have been developed for aircraft structural applications because of their low density, ambient and high temperature strength, good corrosion resistance and low cost compared with Ti alloys [1,2]. In the preparation of Al–Ti alloys, mechanical alloying (MA) process has been considered as an effective method [3,4]. MA process has been exploited mainly for dispersing a second phase such as intermetallic compound Al_3Ti oxide and carbide within a matrix [3,4]. Generally, MA process is performed in an inert gas to avoid excessive oxidation of the elemental powder during the process. However, reactive ball milling (RBM) is carried out under a reactive gas such as H_2, N_2 and NH_3 [5,6]. It has been reported by several authors that the solid-gas reaction between the elemental powder and charging gas by RBM at room temperature could produce metal hydrides or even metal nitrides which have been known to be usually synthesized by reaction of metal with nitrogen at very high temperature and pressure [5–9].

In the present work, we have introduced a RBM process for the preparation of nitrides dispersed Al–Ti alloy. RBM of Al and Ti elemental powders in N_2 gas could promote the reaction between these powders and nitrogen to form nitrides. In addition to this, unreacted nitrogen atoms could dissolve in Al–Ti composite powder during RBM and these atoms could produce additional Al or Ti nitrides during the consolidation process of the composite powder. These nitrides are expected to play roles as effective dispersoids which resist grain growth and particle coarsening of dispersion strengthened Al–Ti alloys at high temperature.

2. Experimental procedures

Reactive ball milling was carried out using a high energy ball mill, attritor with SUS 304 stainless steel container and balls. Elemental Ti powder (99.9% in purity, -325# in mean size) and Al powder (99.5% in purity, -325# in mean size) were used as the starting materials and the ball to powder weight ratio was 100:1, the mill was rotated at 250 rpm. In order to prevent excessive welding of powders, 2 wt. % stearic acid was added to the powder.

Before milling, the attritor was charged with as-mixed Al-10, 20 wt. % Ti powders and then evacuated with a

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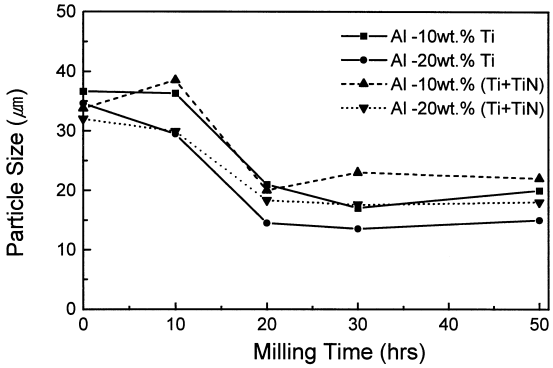

Fig. 1. Particle size variations of as-milled powders with milling time.

rotary pump (about 10^{-3} Torr) and 1.4 atm N_2 gas flowed into it during milling. In addition to this one-step RBM, in order to accelerate the formation of Ti nitrides, we used two-step reactive ball milling. In the two-step RBM, only Ti powder was milled in a flow of N_2 gas first and then an additional milling was carried out with as-milled Ti powder and elemental Al powder in a flow of N_2 gas. The as-milled Ti powder was composed of Ti and TiN.

The structure of the as-milled powder was characterized by X-ray diffraction (XRD) with Cu Kα radiation and transmission electron microscopy (TEM). High resolution TEM (HRTEM) analysis was performed to study the structure in detail. The size variation analysis of the as-milled powder was carried out by particle size analyzer with the monochromatic laser. The powder was consolidated by cold pressing (300 MPa) and vacuum hot pressing (VHP) at 450°C under a pressure of 22 MPa. The micro-Vickers hardness test was performed to each bulk specimen. A 200 g load and a load duration of 15 s were used for each specimen and ten measurements were made. To investigate the thermal stability, these consolidated specimens were annealed at 500°C for 50, 100 h and hardness tests and TEM analysis were carried out.

3. Results and discussions

3.1. Analysis of alloy powder

In Fig. 1 the variation of the particle size with milling time is shown. As the milling time increased, the initial particle size of 35 μm decreased to 20 μm for Al-10 wt. % Ti and 15 μm for Al-20 wt. % Ti after 50 h milling and the particle size was constant with further milling. For the Al-10, 20 wt. % (Ti+TiN) formed by two-step RBM, the particle sizes decreased to about 22 μm and 18 μm, respectively, after 50 h milling. The particle sizes decreased more with increasing Ti content and milling time. In a previous experiment performed in Ar atmosphere, the particle size of ball milled Al-8 wt. % Ti powder was 40 μm for 300 rpm [10]. The results showed that the particle size of the Al–Ti alloys ball milled in N_2 gas was smaller than that of the Al–Ti alloys ball milled in Ar. There is little difference in particle size of the same composition between one-step and two-step RBM processes. But the effect of nitrides for the decrease in particle size was not clear in this experiment.

However, contrary to the insignificant contribution of the TiN to the decrease in particle size decrease, the TiN showed a prominent effect on the grain size refinement as shown in Fig. 2. In Fig. 2 TEM micrographs of Al-20 wt. % Ti powder milled for 50 h are shown. The bright field and dark field images show that the grain size is about 10–15 nm. From the analysis of TEM images of Al-20 wt. % (Ti+TiN) powder milled by two-step RBM shown in Fig. 3, the grain size was about 5–10 nm. It was very clearly shown that the grain size of Al-20 wt. % (Ti+TiN)

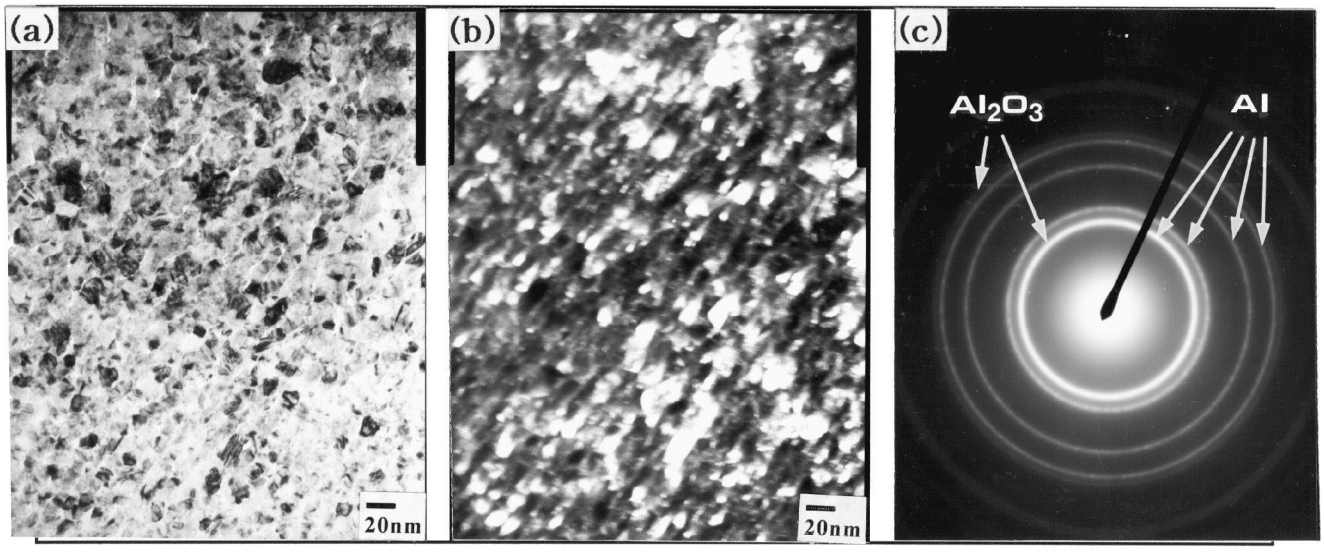

Fig. 2. TEM micrographs of Al-20 wt. % Ti powder milled by one-step RBM (a) Bright field image; (b) Dark field image; (c) SAD pattern.

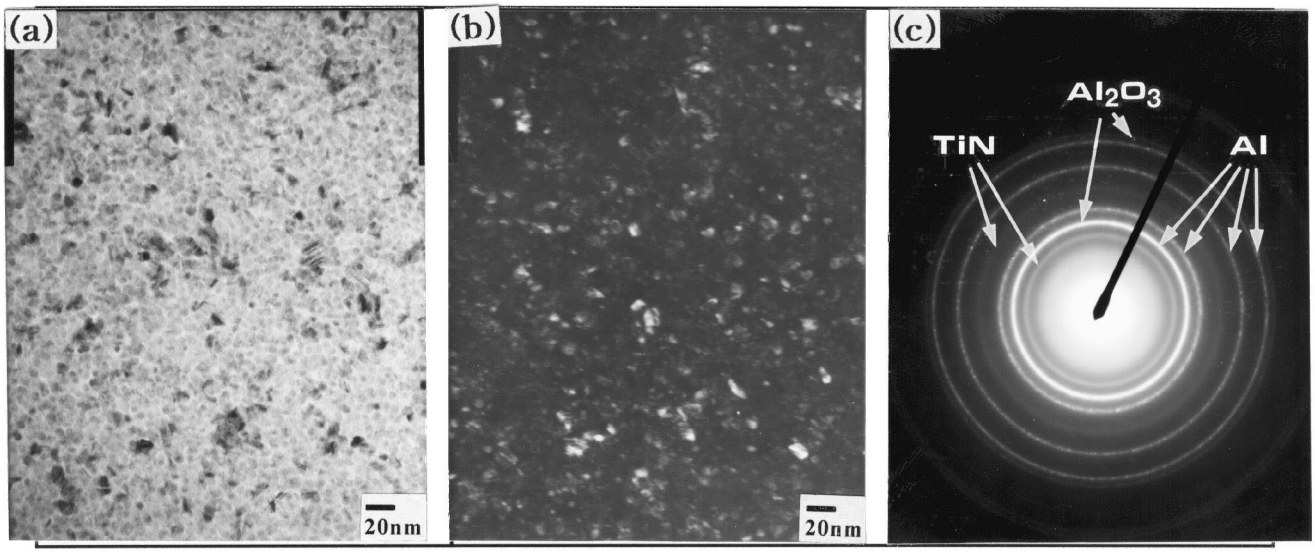

Fig. 3. TEM micrographs of Al-20 wt. % (Ti+TiN) powder milled by two-step RBM (a) Bright field image; (b) Dark field image; (c) SAD pattern.

was smaller than that of Al-20 wt. % Ti powder. During the two-step RBM process the grain refinement was accelerated by brittle and hard Ti nitrides. Also, as mentioned by Wang [11], nitrogen atoms could be segregated in grain boundaries in Al–Ti alloys and these atoms could act as a strain accumulator by preventing the defect mobilities and thus work hardening promoted by these segregated N_2 atoms. As a result, the fracture of powder was promoted and therefore the grain size became smaller than that milled in Ar atmosphere.

In Fig. 4 the X-ray diffraction patterns of the as-milled Al–Ti powders with milling times are shown. The intensities of Al and Ti peaks were weakened and their peaks became broader indicating the grain refinement as the milling time increased. In XRD analysis of one-step ball milled powders, no nitride peak could be observed. The reason why AlN was not formed is presumably because the oxygen from stearic acid ($CH_3(CH_2)_{16}COOH$) and N_2 gas react with Al powder to form Al_2O_3 scale on the surface of Al powders. The heat of formation of Al_2O_3 (-400 kcal mole^{-1}) has a much higher negative value than that of AlN (-76 kcal mole^{-1}). Thus, Al_2O_3 could easily form prior to AlN formation. The nitrogen absorption on the surfaces of the Al powders was prevented by the Al_2O_3 scale. As a result, the diffusion of the nitrogen into the Al matrix and formation of nitride might be also difficult. This fact corresponds with the results of the Al–Ti alloy RBM study by Miki [12], who reported that there was no nitride in Al-10 wt. % Ti RBM in N_2 atmosphere and a very small amount of nitride in Al-20 wt. % Ti. The amount of the Al_2O_3 scale must be very small compared to the total amount of Al powders. Thus, Al_2O_3 was not identified by the XRD, but detected by high resolutive analyses such as TEM and HREM as shown in Figs. 2, 3 and 9. The formation of TiN seemed to be prevented because Ti powders were surrounded by soft Al powders and Ti dissolved in the Al matrix without reacting with the nitrogen. In Fig. 5 the SEM and EDS images of Al-20 wt. % Ti alloy powder milled for 30 h are shown. This

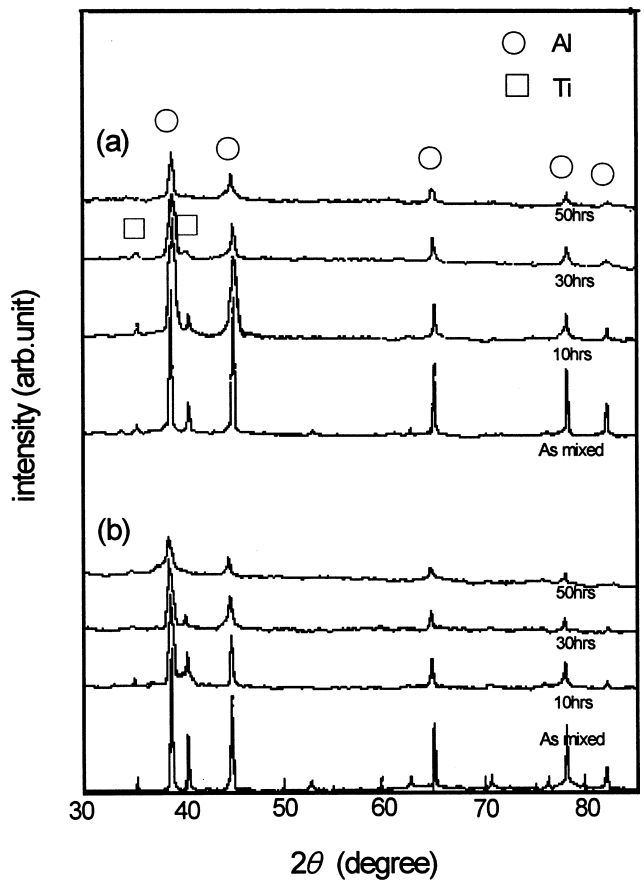

Fig. 4. XRD patterns of one-step ball milled powders (a) Al-10 wt. % Ti; (b) Al-20 wt. % Ti.

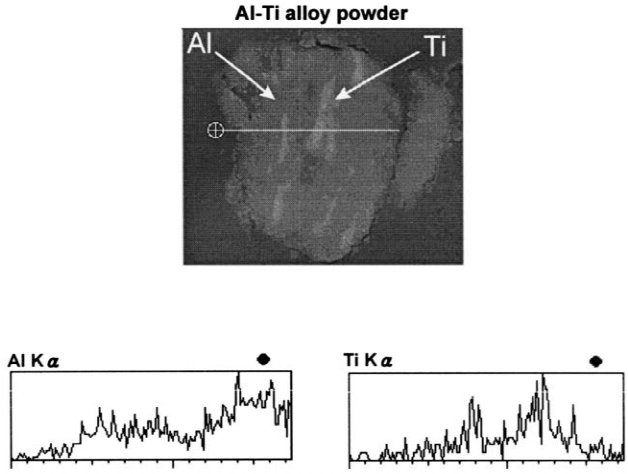

Fig. 5. SEM image and line scanning of Al-20 wt. % Ti ball milled for 30 h in N_2.

image and line scanning analysis of Al and Ti elements in powder shows that the Ti elements were surrounded with the Al matrix. When only Ti powder was milled in N_2 gas at the first stage in the two-step milling, TiN was readily formed as shown in Fig. 6. The comparison of the ratio of the XRD intensities of Ti and TiN shown in Fig. 6 and that of the pure Ti and TiN revealed that the Ti:TiN weight ratio in the milled Ti powder was 35:65. In Fig. 7 the Al-10, 20 wt. % (Ti+TiN) powders, which was a two-step ball mill, show that the TiN peaks were clear in the initial milling. The peaks were getting smaller as the milling time increased. This decrease of intensity of TiN is attributed to the dispersion of TiN into the Al matrix without decomposition of TiN to Ti and N because the milling was carried out in N_2 gas at 1.4 atm.

To investigate the phase transformation and the formation of nitrides during heat treatment, the X-ray diffraction patterns from the powder which were annealed for 1 h at temperatures between 350–500°C are shown in Fig. 8. In the patterns of Al-20 wt. % Ti, Fig. 8(a), at 450°C and 500°C, a peak of nitride was shown and it was presumed to be formed by reaction between Ti and nitrogen dissolved

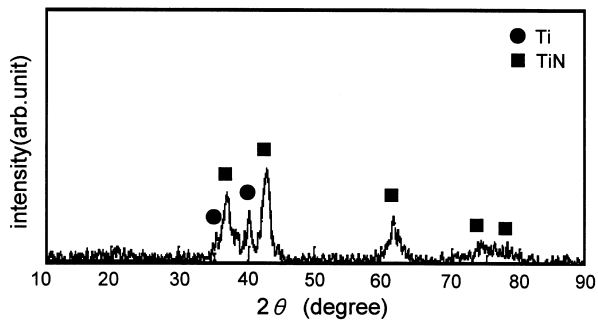

Fig. 6. XRD patterns of TiN powder ball milled for 25 h in N_2.

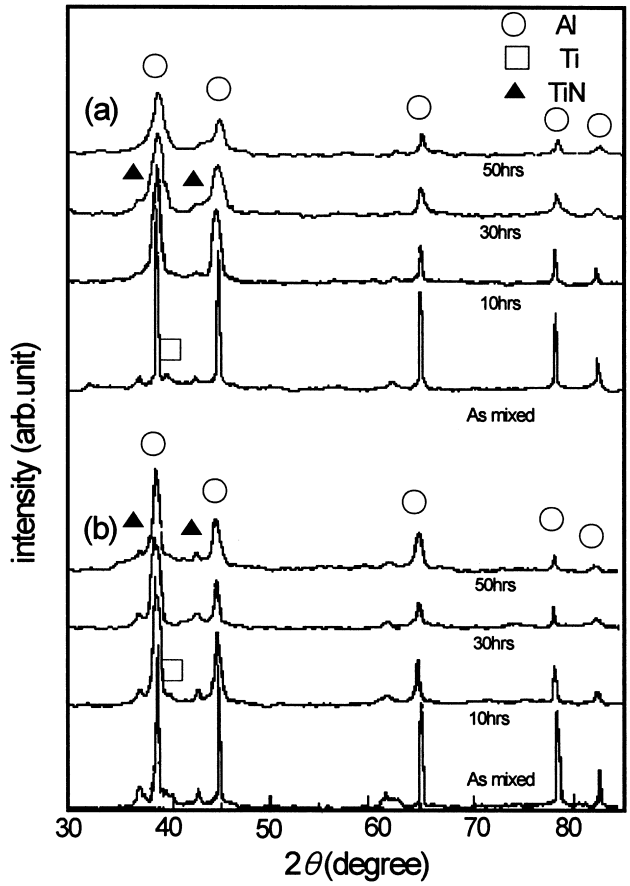

Fig. 7. XRD patterns of two-step ball milled powders (a) Al-10 wt. % (Ti+TiN); (b) Al-20 wt. % (Ti+TiN).

in Al–Ti alloy powder. However, the amount was very small and the AlN was not formed at any temperature. In the Al-20 wt. % (Ti+TiN) the nitrides peaks were shown in the as-milled powder and the peak intensities increased gradually and the shapes were sharper with increasing annealing temperature. It was considered that the small amount of nitrides were formed during the heating process in addition to the existing TiN. In Fig. 8(a) and (b), the shapes of Al peaks were getting sharper indicating the grain growth. The Al_3Ti peak was shown after 350°C annealing treatment in the patterns of Al-20 wt. % Ti powder and at 400°C in the Al-20 wt. % (Ti+TiN) powder. The intensity of Al_3Ti peak in the Al-20 wt. % (Ti+TiN) was weaker than that of Al-20 wt. % Ti powder because the initial Ti content was small. Generally, these Al_3Ti dispersoids are formed when the Al–Ti alloy powder is consolidated for the bulk and shows the main dispersion strengthening effect in Al–Ti alloys. However, these dispersoids have a problem of grain growth owing to Ostwald ripening when the alloy was used in high temperature for long time [13]. In the Al-20 wt. % (Ti+TiN), the dispersoids were composed of TiN and Al_3Ti and anticipated to resist grain growth during annealing treat-

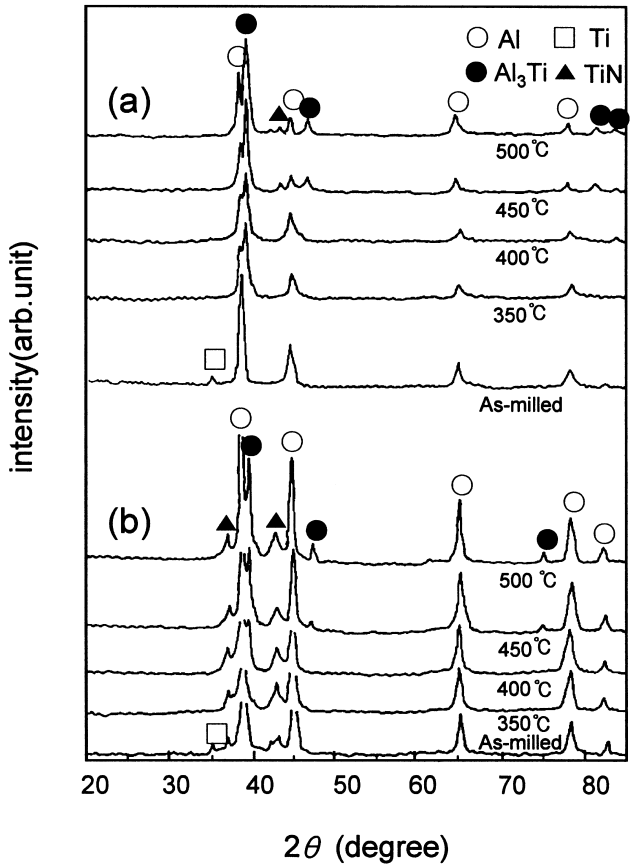

Fig. 8. XRD patterns of 50 h ball milled powder by annealing treatment at various temperatures (a) Al-20 wt. % Ti milled by one-step RBM; (b) Al-20 wt. % (Ti+TiN) milled by two-step RBM.

ment and consequently to improve the grain refinement of the Al matrix.

From the selected area diffraction (SAD) pattern analysis in Fig. 2(c) the nitrides were not detected in one-step ball milled powders, but the TiN was detected in the SAD pattern of the two-step RBMed powder as shown in Fig. 3(c). In Fig. 9 the HRTEM structures and diffraction pattern of the powder obtained by two-step RBM of the Al-20 wt. % (Ti+TiN) powder mixture for 50 h are represented. As shown in Fig. 9 the powder obtained by two-step RBM could be divided into seven distinctive regions which were indicated by A to G and a SAD pattern showing that the area examined consisted of five different phases such as Al, TiN, Ti, Al_2O_3 and TiO. Based on the SAD pattern analysis of this area, each crystalline region was characterized by investigating the lattice spacing. Region A consists of Al having lattice spacing of 2.34 Å with a grain size of about 10–30 nm and regions B and C consist of TiN having a lattice spacing of 2.43 Å(B) and 2.12 Å(C) with a grain size of about 5 nm. Regions D and E consist of unreacted Ti and regions F and G consist of TiO and Al_2O_3, respectively. Although the TiN phases were not identified by the TEM analysis in Fig. 2(a) and Fig. 3(a), HRTEM analysis showed that TiN, having a grain size of 5 nm, existed between the Al matrix and TiO, Al_2O_3 and unreacted Ti could be detected.

3.2. Thermal stability of the bulk specimens of alloy powder

In Fig. 10 the results of the micro-Vickers hardness (HV) of the specimens which were consolidated by vacuum hot pressing (VHP) are shown. The micro-hardnesses of Al-10 wt. % (Ti+TiN) specimens were 195–210 $kg\,mm^{-2}$ and that of Al-20 wt. % (Ti+TiN) specimens were 224–230 $kg\,mm^{-2}$. The hardness increased with milling time and TiN content. For example, the hardness of Al-10, 20 wt. % (Ti+TiN) specimens was higher by about 2.6 and 10.3%, respectively than that of Al-10, 20 wt. % Ti specimens. As shown in Fig. 10 the hardness of the hot pressed compacts made from powders milled in N_2 was much higher than that of the results of previous experiment in Ar(10). On the assumption that the unreacted Ti was converted fully to Al_3Ti, the theoretical volume fraction of Al_3Ti and TiN was calculated as follows. The moles of Al_3Ti and TiN, which were theoretically formed, were calculated from the mole of Ti corresponding to the charged mass of Ti, and then the mass of Al used for formation of Al_3Ti was computed by using mole ratio of Al and Ti in Al_3Ti and atomic weight of Al. The remaining mass of Al which was not used to form Al_3Ti was considered to become the Al matrix. The volume of each phase was obtained by dividing the mass of each phase by its density. The total volume was summed by either adding the volumes of Al and Al_3Ti for one step ball milling or adding the volume of Al, Al_3Ti and TiN for two step ball milling. The volume fraction of each phase was computed by dividing the volume of each phase by total volume and the results are represented in Table 1. Though the exact volume fraction of Al_3Ti and TiN was not measured, it is anticipated that in Al-20 wt. % (Ti+TiN), two-step RBM could substitute TiN for a large amount of Al_3Ti as shown in Table 1. Estimating the results of the hardness test in Fig. 10, it was considered that a smaller amount of TiN exhibited a role of effective dispersoid strengthening compared with Al_3Ti.

In Fig. 11 results of the hardness variation of VHPed specimens which were annealed at 500°C with annealing time are shown. The Al-10, 20 wt. % (Ti+TiN) specimens experienced only little losses in hardness after 100 h at 500°C and thus we can conclude that these two-step RBM alloys have good thermal stability at high temperature. It seems that this stability was due to the presence of TiN and Al_3Ti dispersoids, resisting the grain growth and coalescence at high temperature and thus stabilizing the fine grained structure. TEM micrographs of the specimen before and after annealing are shown in Fig. 12. The micrographs show that the grain size of the VHPed specimen is about less than 100 nm and after annealing at

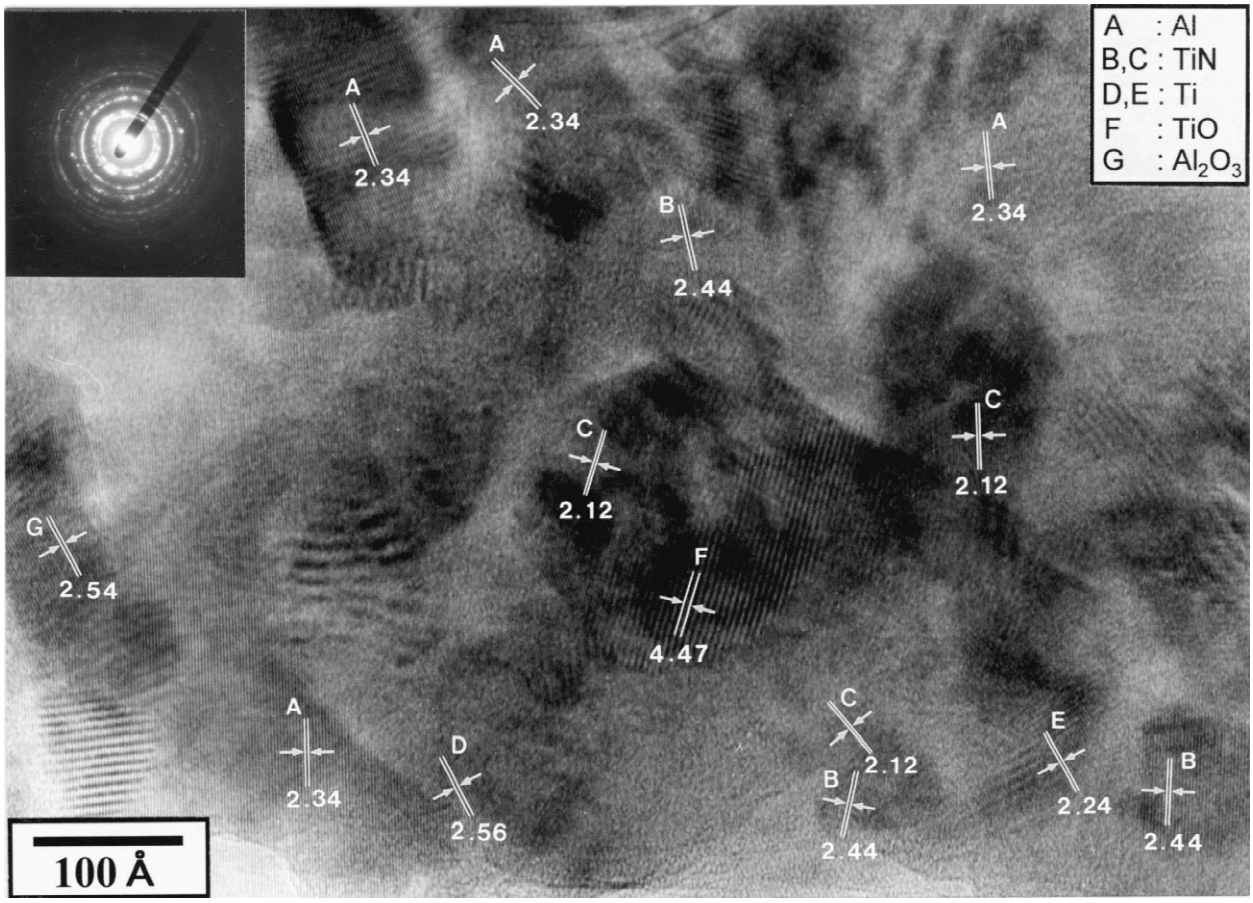

Fig. 9. HRTEM image of Al-20 wt. % (Ti+TiN) powder milled by two-step RBM.

500°C for 100 h, the grain size is about 150–200 nm. In the previous experiment, the grain size of as-extruded Al–Ti alloy was 300–400 nm [14]. Taking into consideration the annealing treatment at 500°C for 100 h in this experiment, the grain size was very small compared to that of the bulk specimen of the powder milled in Ar. A number of fine TiN and Al_3Ti particles, smaller than 10 nm, are well distributed throughout the Al matrix before and after annealing and these fine dispersoids affect the stabilization of the fine structure and the maintenance of

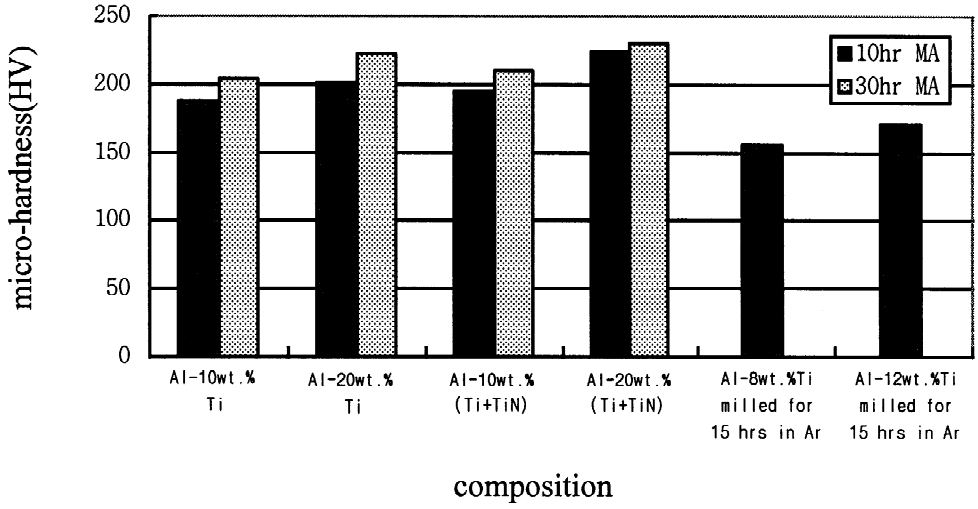

Fig. 10. The results of the micro-hardness (HV) test.

Table 1
Volume fractions of Al_3Ti, TiN in Al–Ti alloy powder

	Volume fraction Content of alloy	Al_3Ti (%)	TiN (%)	Total (%)
One-step ball milling	Al-10 wt. % Ti	23.1	0	23.1
	Al-20 wt. % Ti	48.8	0	48.8
Two-step ball milling	Al-10 wt. % (Ti+TiN)	8.1	3.4	11.5
	Al-20 wt. % (Ti+TiN)	17.1	7.2	24.3

the hardness. However, the grain size of the as-milled powder was 10–15 nm and the grain size increase after consolidation was ten times that of the as-milled powder. Therefore, a more effective consolidation method that maintains the nano-grain size is needed in future work.

4. Conclusions

In this experiment reactive ball milling of Al and Ti elemental powders in N_2 gas was carried out and the structure of the nitride dispersed Al–Ti alloy and its hardness was investigated. The conclusions obtained are summarized as follows:

(1) When Al-10, 20 wt. % Ti powder was ball milled in N_2, the formation of nitrides was not detected. However, by the two-step reactive ball milling of Al-10, 20 wt. % (Ti+TiN), TiN is formed and distributed finely in the Al matrix.

(2) The grain size of RBMed Al–Ti alloy was about 10 nm by TEM analysis and the reactive ball milling in N_2 is considered an effective method for grain refining of Al–Ti alloys. The grain size of TiN was measured to be 5 nm by HRTEM analysis.

(3) The hardness of Al–Ti alloys milled in N_2 was higher than that of Al–Ti alloys milled in Ar. It seems that the Ti-nitrides are effective dispersion strengtheners in Al–Ti alloys. When the consolidated specimens were annealed at 500°C, the hardness of the specimens scarcely decreased and they exhibited a good thermal stability.

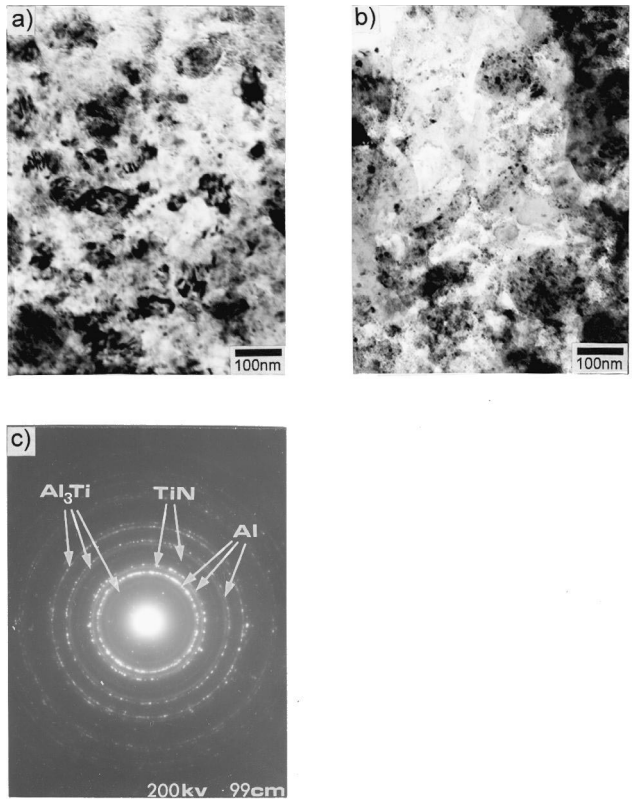

Fig. 12. TEM micrographs of VHPed Al-20 wt. % (Ti+TiN) specimens (a) before; (b) after annealing treatment; (c) is a SAD pattern of (a).

Acknowledgements

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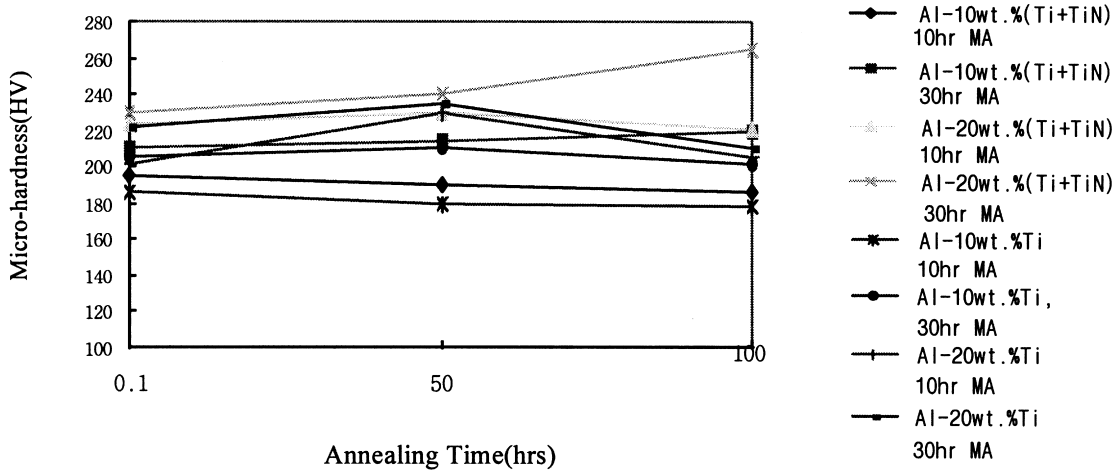

Fig. 11. The results of hardness variations of VHPed specimens with annealing time at 500°C.

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