THERMAL STABILITY OF THE MECHANICALLY ALLOYED Al-10Ti NANOCRYSTALLINE ALLOY DURING CONSOLIDATION PROCESS①

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ABSTRACT Nanocrystalline Al-10Ti alloy powder was prepared by mechanical alloying. The processed powder was then consolidated by hot pressing and hydrostatic extrusion. The grain size of milled powders and consolidated materials was determined by analyzing the broadening of the X-ray diffraction peaks and by TEM observation. The results showed that vacuum hot pressing led to larger grain size than simple annealing of the powders, and that hot hydrostatic extrusion led to more serious grain growth than hot pressing at the same temperature.

Key words nanocrystalline Al-10Ti alloy consolidation process thermal stability

1 INTRODUCTION

Nanocrystalline materials, namely the polycrystals with nanometer-sized crystallites (less than 100 nm), are the subject of intense research, motivated by their unusual physical and mechanical properties[1-3]. Initially, nanocrystalline powders were made by a vapour condensation method, and attempts were made to consolidate such powders at low temperature to give bulk materials[4, 5]. Recently, mechanical alloying has been used to synthesize nanocrystalline metals and alloys. However, the thermal stability and consolidation of mechanically alloyed nanocrystalline alloys have not yet clearly studied. The present paper reported the difference in grain growth behavior of mechanically alloyed Al-10Ti nanocrystalline alloy during simple annealing, hot pressing and hot hydrostatic extrusion.

2 EXPERIMENTAL PROCEDURE

Elemental Al and Ti powders (99.5% purity) with particle sizes of $\leqslant 80\ \mu m$ were mixed in the composition of Al-10Ti(%), and mechanically alloyed in a high energy attritor under an argon atmosphere using hardened chrome steel balls. The ball to powder weight ratio was 10 : 1, and the rotational velocity was kept at 400 r/min.

The mechanically alloyed powders were annealed and hot pressed under 500 MPa in a vacuum of better than 4×10^{-2} Pa; the heating and cooling rate was 0.5 ℃/s. The hot pressed billet was then hot hydrostatically extruded at various temperatures with an extrusion ratio of 14:1; the preheating time before extrusion was 10 min.

The mechanically alloyed powders and consolidated materials were characterized by X-ray diffraction using RIGAKUD/max-rB diffractometer with CuK_α radiation. The microstructures were analysed by transmission electron microscope (Philips EM420). Thin foils for TEM observation were prepared by a conventional dual jet electropolishing technique. The electrolyte consisted of 25%(in

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volume) nitric acid and 75%(in volume) methanol.

Thermal analysis was performed in a Perkin-Elmer DSC7 differential scanning calorimeter under flowing nitrogen.

3 RESULTS AND DISCUSSION

3.1 *Mechanical Alloying*

The X-ray diffraction patterns of powders mechanically alloyed for various times are shown in Fig. 1. Evidently, the diffraction peaks broaden and decrease in their heights with increasing milling time, indicating a continuous decrease in crystal size and an increase of microstrain. Indeed measurements made from the width at half-maxium of peaks[6] show that the grain size decreases with increasing milling time as indicated in Fig. 2, which has been confirmed by TEM observation of the milled powders cold consolidated, and that the microstrain increases with milling time to a maxium value of 0.7%, and then decreases with grain size to less than 30nm. After 43h milling, the grain size decreases to 28 nm.

3.2 *Simple Annealing*

Fig. 3 shows the DSC curves (scanning rate was 20K/min) of powders milled for various times, in which two exothermic peaks can be observed. With increasing milling time the peak positions shift to lower temperature. To get more insight into the nature of the two exothermic events we performed annealing experiments for powders milled for different times. The samples were heated at 20 K/min in the DSC to the peak temperature of the exothermic reaction and then rapidly cooled to room temperature. The XRD analyses confirmed that the second exothermic peak at higher temperature resulted from the formation of Al_3Ti intermetallic compound. After

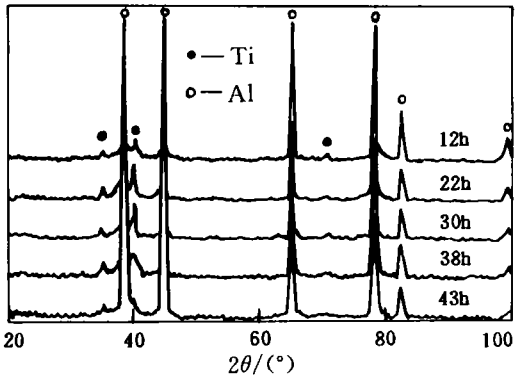

Fig. 1 XRD patterns of Al-10Ti powders milled for various times

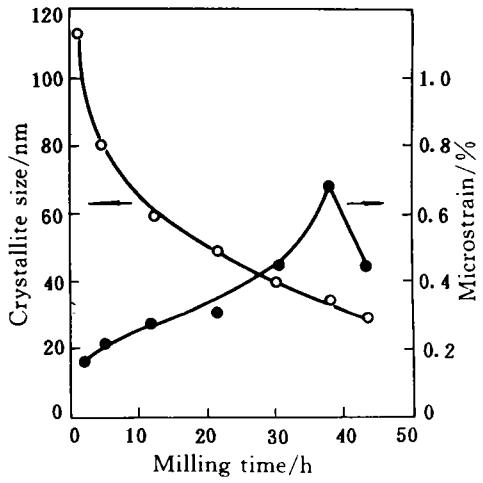

Fig. 2 Grain size and microstrain of milled powders as a function of milling time

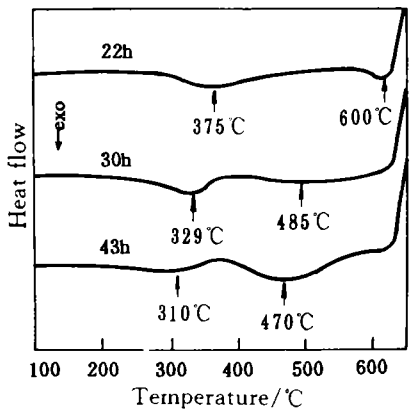

Fig. 3 DSC curves of powders milled for various times at a scanning rate of 20K/min

lower temperature heat treatment, no new phases were formed except the sharpening of the diffraction peaks, which suggested that the first exothermic peak resulted from the grain growth and the release of microstrain. The activation energies of the first and second exothermic reactions were determined by Kissinger's[7] peak shift method using the following equation:

$$\ln(\frac{C}{T_p^2}) = -\frac{E_c}{RT_p} + A \quad (1)$$

where C is the heating rate (10, 20, 40 K/min); T_p is the peak temperature; E_c is the activation energy; R and A are constants, E_{c_1} = 50.7, 46.8 and 45.2 kJ/mol respectively at lower temperature and E_{c_2} = 154.5, 151.7 and 148 kJ/mol at higher temperature for powders milled 22, 30 and 43 h.

In order to simulate the influence of the consolidation temperature, the powders mechanically alloyed for 43 h were annealed for various time from 0.5 to 10 h in vacuum. The grain size values are shown in Fig. 4. Evidently, the grain size coarsens slowly at 200 ℃ and increases rapidly at high temperature. The microstrain decreases rapidly with extending annealing time at 500 ℃, but there is no obvious change in it after annealing at 200 ℃ for 10 h as shown in Fig. 4(b). Generally, the grain growth data must be fit empirically to the following relationship[8]:

$$d^n - d_0^n = Kt \quad (2)$$

where n is the grain growth exponent and $K = K_0\exp(-\frac{Q}{RT})$, with Q denoting the activation energy for grain growth. For normal grain growth, the grain growth exponent n = 2 can be predicated[8], but the grain growth exponent depends on many factors which hinder the movement of grain boundary, such as solute drag, particle pinner. Grain growth exponent much larger than 2 are frequently reported[9]. Generally, the grain growth exponent decreases with decreasing annealing temperature. Here, by linear regression of the experimental data, we obtain n = 4 for 300 and 400 ℃ annealing, and n = 10 and 22 for 200 and 500 ℃ annealing respectively. It can be inferred that at higher temperature (500 ℃), more volume fraction of Al_3Ti particles would precipitate, which as grain boundary pinners, hinders the grain growth. While at lower temperature (200 ℃), the diffusion of atoms is very difficult. These results mean that the grain growth behavior is greatly influenced by the microstructure of the original nanocrystalline powders and precipitation of the second phase. The activation energy for grain growth of 43 h milled powders at 300~400 ℃ is decided to be 54.4 kJ/mol by analysing experimental K value. The activation energy is approxi-p mately equal to the results (45.2 kJ/mol) de-

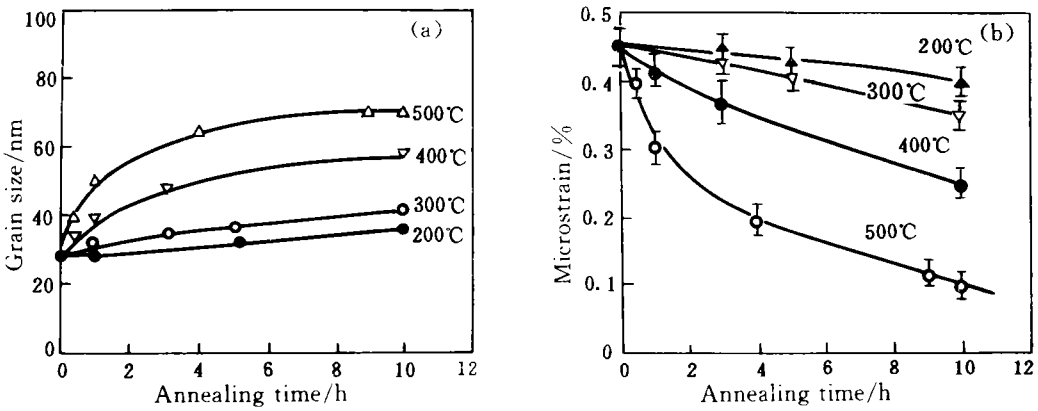

Fig. 4 Grain sizes (a) and microstrain (b) of mechanically alloyed 43 h powders isothermally annealed from 0.5 to 10 h at various temperatures

termined by DSC analysis. This value is a little less than the activation energy (60 kJ/mol) for grain boundary self-diffusion of aluminium[10].

3.3 *Consolidation*

Fig. 5 shows the average grain size of the consolidated materials measured by TEM method. From Fig. 5(a) one can see that the grain size of materials consolidated at the same condition decrease with increasing milling time and have much larger grain size after hydrostatic extrusion than after vacuum hot pressing. Fig. 5(b) shows the grain sizes for 43 h milled powders after vacuum annealing, vacuum hot pressing and hydrostatic extrusion at various temperatures. Evidently, the grain size values increase faster with temperature during vacuum hot pressing than during simple vacuum annealing of the powders, and the grain size coarsens more drastically after hydrostatically extruded at the same temperature than after vacuum hot pressing. These results indicate that nanocrystalline Al-10Ti exhibits deformation-enhanced grain growth; the hydrostatic pressure in hot pressing and shear strain in hot hydrostatic extrusion intensify the grain coarsening.

Fig. 6 shows the bright and dark field transmission electron micrographs of some consolidated alloy, from which we can see that grain sizes are not very uniform. The larger grain may be formed by the realignment of small grains with less difference in orientation.

Fig. 7 shows the relative density of compacts vacuum hot pressed at different temperatures. We observe that powders milled for 22 h are easy to be densified than that milled for 43 h under the same hot pressing condition. The cold pressed billets have relative densities of 77% and 75% for 22 and 43 h milled powders respectively. When hot pressed at 350 ℃ for 10 min, the relative densities are 96.5 and 85% respectively. Compared with Fig. 5, we can see that the grain size is less than 100 nm when powders are consolidated to almost fully dense.

The above results indicate that nanocrystalline powders can be densified by hot pressing at relative low temperature or hot hydrostatically extruded at much lower temperature without significant attendant grain growth.

4 CONCLUSION

Al-10Ti alloy with nanometer-sized grains can be synthesized by mechanical alloying starting from elemental aluminium and titanium powders. The mechanically alloyed

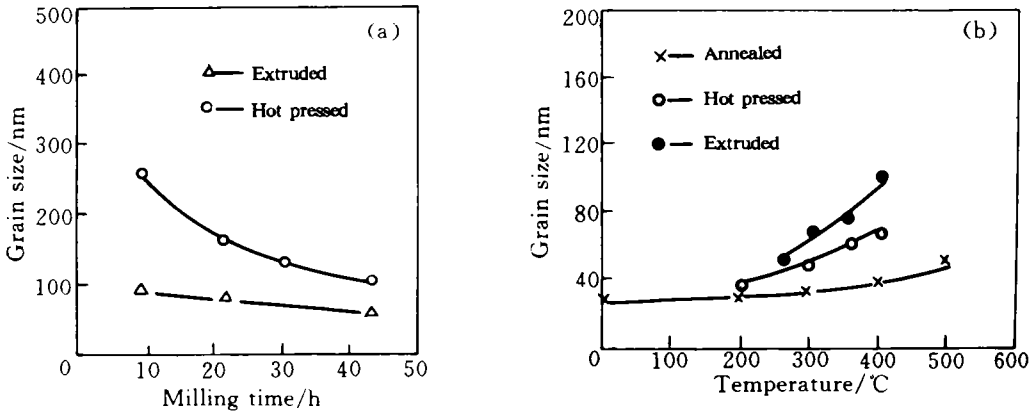

Fig. 5 Grain sizes of consolidated materials as a function of milling time (a) and temperature (b)

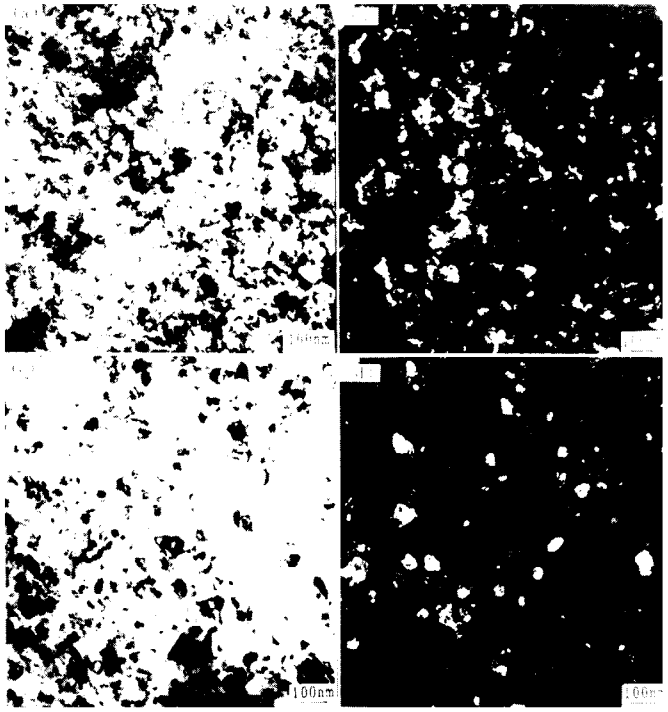

Fig. 6 Transmission electron micrographs of some consolidated materials
(a), (b)—cold consolidated;
(c), (d)—hot pressed at 350 ℃ for 0.5 h and hot extruded at 350 ℃

nanocrystalline powders can be consolidated to full density without serious grain coarsening by vacuum hot pressing and hydrostatic extrusion. The grain growth has been investigated, and the following conclusions can be drawn:

(1) The data in grain growth of simple annealing were found to fit a power law equation of the form $d^n - d_0^n = Kt$. The grain growth exponent was $n = 10$ at 100 ℃, $n = 4$ at 300～400 ℃ and $n = 22$ at 500 ℃. An apparent activation energy for grain growth at 300～400 ℃ was determined to be 54.2 kJ/mol, which was a little less than the activation energy of grain boundary diffusion for aluminium.

(2) Vacuum hot pressing and hot hydrostatic extrusion of nanocrystalline powders resulted in more serious coarsening of grain size

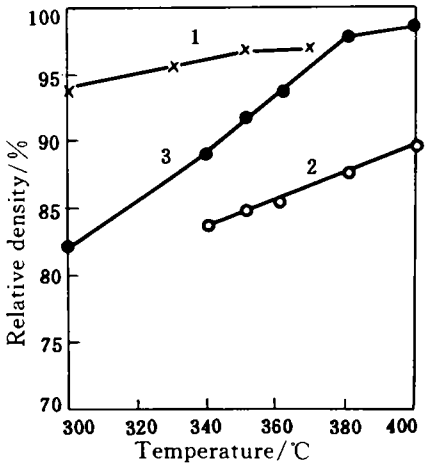

Fig. 7 Relative density of hot pressed compacts as a function of temperature
1—22 h milled powders, hot pressed for 10 min;
2—43 h milled powders, hot pressed for 10 min;
3—43 h milled powders, hot pressed for 30 min

than simple annealing, exhibiting deformation enhanced grain growth behavior. In addition, the grain growth was more sensitive to temperature in hot hydrostatic extrusion than in hot pressing.

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(*From page 88*) novel alloy is tiny hard phases dispersing in soft matrix. This kind of microstructure may not only upgrade the mechanical properties of the alloy, but also fit well into the requirement of tribology.

4 CONCLUSIONS

(1) The novel zinc-alloy (ZMJ) contains new phases of Cu_9Al_4, Al_5MnZn, $Al_9(MnZn)_2$, and $Al_{65}Mn(R.E)_6Ti_4Zn_{36}$ besides α (Al), β (Zn) and ε phases.

(2) The lattice parameters of α, β and Cu_9Al_4 are changed due to the solute elements. ε is solid solution of intermetallic compound $CuZn_3$.

(3) Phases containing Mn, such as Al_5MnZn, $Al_9(MnZn)_2$, and $Al_{65}Mn(R.E)_6Ti_4Zn_{36}$ are much harder than α phase and distribute uniformly in the matrix in forms of block or rod. The content of such hard particles in the sandy casting ZMJ alloy is about 15%.

(4) Some tiny hard phases with certain forms dispersing in the soft matrix is the main characteristic of this novel alloy.

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