

Nitrogen-doped TiAl alloys

Part I *Microstructure control*

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Effects of nitrogen addition on the microstructure control of two-phase TiAl intermetallic compounds were investigated. 1.0 at.% nitrogen addition leads to remarkable grain refinement in the fully lamellar microstructure but had little effect on the duplex microstructure. Only Ti_3AlN precipitate was formed in 0.3 at.% nitrogen-doped alloy and both Ti_2AlN and Ti_3AlN precipitates were formed in 1.0 at.% nitrogen-doped alloy. Since the formation of the gamma phase is retarded by nitrogen addition, long-term heat treatment is needed for the duplex microstructure in the 1.0 at.% nitrogen-doped alloy. Though 0.3 at.% nitrogen-doped alloy had much lower elongation than the mother alloy, 1.0 at.% nitrogen addition had little effect on room temperature elongation and increased room temperature yield strength by two times in the fully lamellar microstructure. © 2000 Kluwer Academic Publishers

1. Introduction

Gamma-based TiAl alloy has been known to be one of the most promising candidates for high-temperature structural applications [1, 2]. However, two typical microstructures of the TiAl alloy, such as the duplex microstructure and the fully lamellar microstructure, have shown a so-called inverse relationship between room-temperature ductility and fracture toughness/creep resistance. The fully lamellar TiAl alloys have excellent creep resistance and fracture toughness, even though poor room temperature ductility. In contrast, the duplex TiAl alloys have considerable room temperature ductility but low levels of creep properties. Therefore, it is necessary to develop a TiAl alloy system with balanced mechanical properties.

We considered two ways to achieve balanced mechanical properties. One is improving the room temperature ductility of fully lamellar TiAl alloy, and the other is enhancing the high temperature strength and creep resistance of the duplex alloy. To improve room temperature ductility of fully lamellar TiAl alloys, recent research progress toward lamellar grain size refinement using a methods such as the thermomechanical process and the addition of interstitial elements like boron [3], carbon [4] and nitrogen [4, 5]. Moreover, one of the methods to enhance the high temperature strength and creep resistance of duplex alloy is formation of sta-

ble precipitates such as carbide and nitride during high temperature heat treatment. Thus the addition of carbon and nitrogen may reveal one of the solutions for balanced mechanical properties of TiAl alloys.

In the present work, the microstructures of nitrogen-doped TiAl+Mo alloys have been investigated. Especially, the effects of nitrogen on fully lamellar and duplex microstructure control have been studied. The tensile properties have also been examined at room temperature. The high temperature strength and creep properties will be explained in a separate paper (Part II).

2. Experimental

The alloys used in this study were prepared from starting materials of 99.99 wt.% Ti and Al, 99.9 wt.% Mo, and 99.9 wt.% TiN powder by vacuum arc melting under an argon atmosphere. The alloys were named by the content of nitrogen, such as 1.5Mo (Ti-48.5Al-1.5Mo(at.%)) and 1.0N (Ti-48.5Al-1.5Mo-1.0N) alloys. In the present study, two types of heat treatment schemes were performed. One is for only microstructure control: (1200–1390)°C/(2–48) hr/FC. The other is adding an aging treatment for 12 hours at 900°C after the above-mentioned schemes to enhance the precipitate formation. Microstructure observations were performed using an optical microscope, a scanning

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electron microscope and a transmission electron microscope. The samples for transmission electron microscopy (TEM) observations were prepared by electropolishing in a 60% methyl alcohol +35% n-butyl alcohol +5% perchloric acid solution using a twin-jet polishing method. Tensile specimens were manufactured into plates with the gauge length of 5 mm and the effective cross section area of $2 \times 1 \text{ mm}^2$ using a spark cutting machine. The specimens were polished first mechanically and then electrically. Yield stress in this paper is 0.2% offset stress and the yield strength indicates the fracture stress in the case of elongation below 0.2%.

3. Results and discussion

3.1. Effects of nitrogen on fully lamellar microstructure

Fig. 1 is the optical micrograph of the 1.5Mo alloy, 0.3N alloy and 1.0N alloy heat-treated for 2 hours at 1390°C in order to obtain the fully lamellar microstructure. As seen in the figure, the grain size of the 1.5Mo alloy with over $1700 \mu\text{m}$ decreased to $1300 \mu\text{m}$ by the addition of 0.3 at.% N, and to $100 \mu\text{m}$ by the addition of 1.0 at.% N, approximately. Though not shown in this figure, the microstructure of the 2.0N alloy is similar to that of the 1.0N alloy. In consequence, the addition of 1.0 at.% N led to a remarkable grain refinement.

Fig. 2 is the scanning electron microscopy (SEM) investigation of the precipitate morphology in the 0.3N alloy and the 1.0N alloy. It was observed that two types of precipitate morphology exist. One is fine precipitate, which is located primarily on the lamellar boundaries, and the other is large blocky precipitate, which is formed randomly. The former is seen in all alloys with nitrogen additions, but the latter is found only in alloys with more than a 1.0 at.% N addition. Through the investigation using TEM in Fig. 3, which is a TEM micrograph of fully lamellar 1.0N alloy, it is confirmed that the small precipitate is Ti_3AlN phase and the large blocky precipitate is Ti_2AlN phase. In the case of Ti_2AlN precipitates, they formed preferentially inside the equiaxed gamma grains, which were located among the lamellar grains (marked 1 in Fig. 3a), and had no orientation relationship with the TiAl matrix.

On the other hand, Ti_3AlN precipitates were observed to form mainly inside gamma grains (marked 2 in Fig. 3a) and along the dislocations (marked 3 in Fig. 3c). In these cases, precipitate-free-zones (PFZ) formed around Ti_3AlN [6, 7]. In addition, Ti_3AlN precipitates, which formed both at the lamellar/lamellar interfaces (marked 4 in Fig. 3b) and inside the gamma lamellae (marked 5 in Fig. 3b), were also observed in the area of lamellar grains. Such precipitation behavior was also observed in the duplex microstructure. In the case of the 0.3N alloy, we investigated that only Ti_3AlN precipitate was found by the same behavior. It is known that the nitrogen solubility limit is about 0.15% [8]. Thus the 0.3N alloy might contain the nitrogen atoms mostly during solidification, and then formed Ti_3Al precipitate after aging.

Remarkable grain refinement of the 1.0N alloy could be explained by the solidification sequence of each

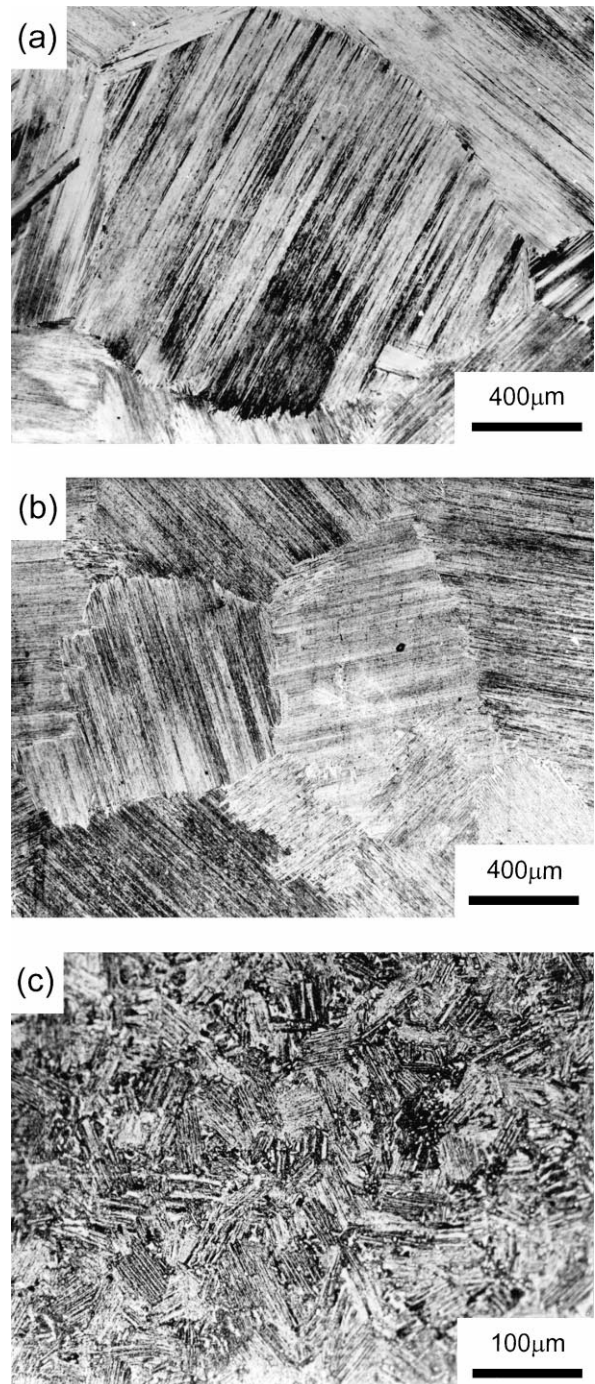


Figure 1 Optical micrographs of (a) Ti-48.5Al-1.5Mo alloys, (b) Ti-48.5Al-1.5Mo-0.3N alloys and (c) Ti-48.5Al-1.5Mo-1.0N alloys with the fully lamellar microstructure.

phase. Thus the primary solidification phase from liquid may be TiN or Ti_2AlN [9], though the alpha phase in the case of the general TiAl alloys. It might be that TiN or Ti_2AlN precipitate acts as the nucleation site during formation of the alpha phase. Thus, the grain size of the alpha phase of the 1.0N alloy is smaller than that of 1.5Mo alloy and 0.3N alloy, for the 1.5Mo alloys do not have a precipitate and the 0.3N alloys do not have large precipitates to act as nucleation sites.

3.2. Effects of nitrogen on duplex microstructure

In the general case of the TiAl alloy, the heat treatment time for the duplex microstructure was a few

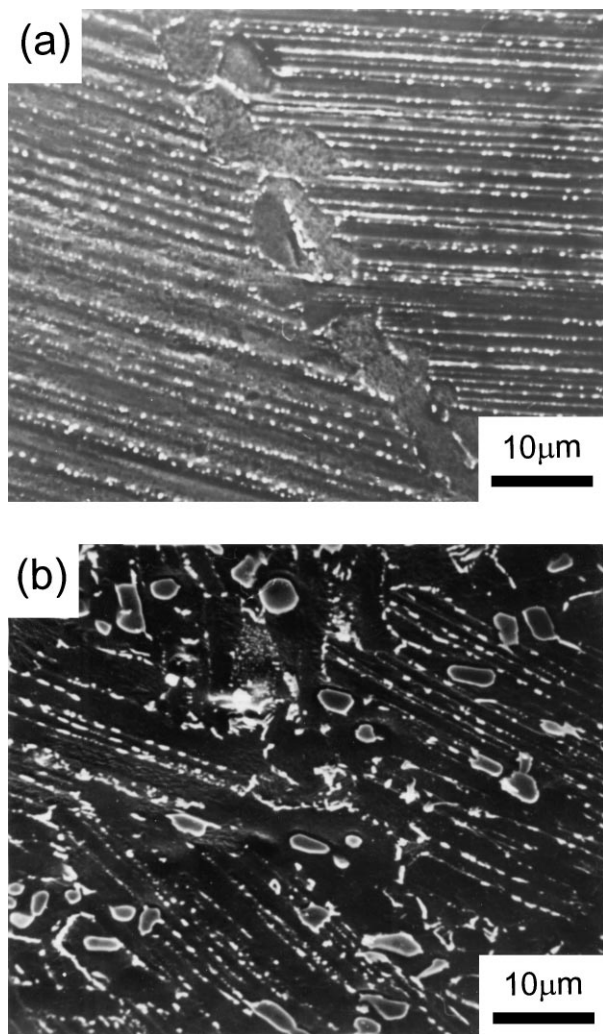


Figure 2 Scanning electron micrographs of (a) Ti-48.5Al-1.5Mo-0.3N alloys and (b) Ti-48.5Al-1.5Mo-1.0N alloys with the fully lamellar microstructure.

hours below 1300°C. In the present work, the duplex microstructure of the 1.5Mo alloy was also obtained after heat treatment at 1300°C for 2 hours. However, the 1.0N alloy could not be obtained in the same condition. Fig. 4 shows the microstructural change of the 1.0N alloy after the various heat treatments to obtain the duplex microstructure. As can be seen in Fig. 4a–d, the duplex microstructure of the 1.0N alloy could be obtained after a much longer heat treatment time than 24 hours at 1300°C. This suggests that the growth of the gamma phase delayed by the addition of 1.0 at.% N. Fig. 4e and f show the duplex microstructure control at 1250°C for 24 hours and 48 hours, respectively. This result shows that the heat treatment for duplex microstructure at lower temperature than 1300°C require a longer heat treatment time than 48 hours. Though not shown in these figures, in the case of 0.3N alloy, it took relatively shorter heat treatment time.

Therefore, from these results, it was concluded that the duplex microstructure control of nitrogen-doped alloy concerned to the kinetic term such as diffusivity of the matrix atoms. It could be supposed that the nitrogen addition decreased the diffusion rate of Ti and Al atoms. In other words, the interstitial nitrogen atoms may cause “the locking effect” on Ti and Al atoms. “The locking effect” means that interstitial nitrogen atoms distort the lattice and the movement of Ti and Al may be disturbed. In consequence, long-term heat treatment is required for the sound duplex microstructure because the diffusion of Ti and Al atoms is retarded by the locking effect.

3.3. Effects of microstructure on room temperature tensile properties

Fig. 5 shows the stress-strain curves and the room temperature tensile properties of fully lamellar TiAl

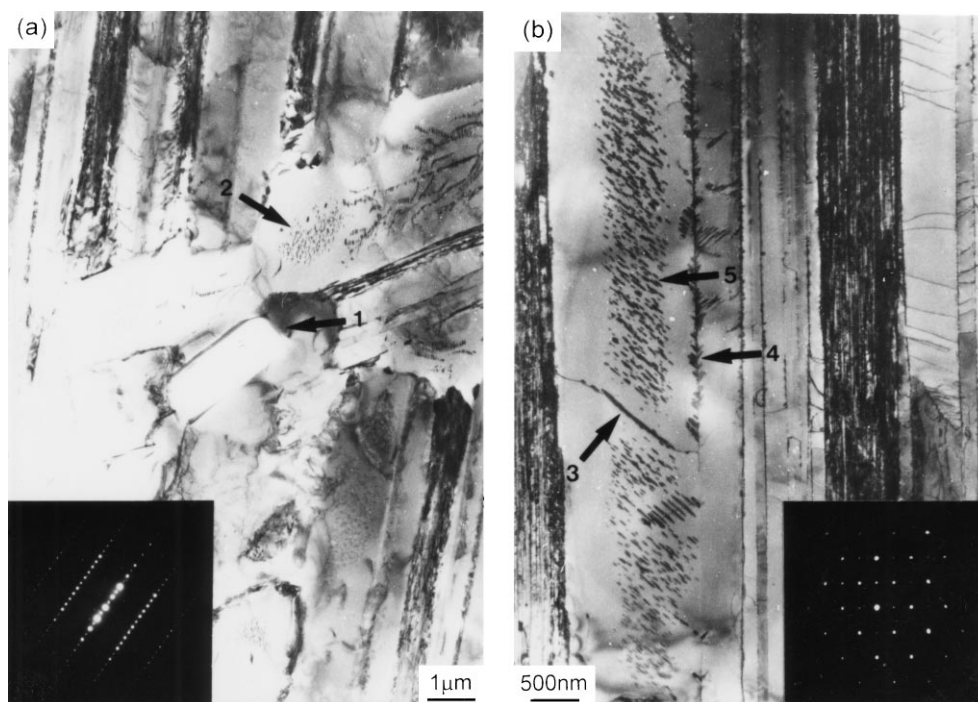


Figure 3 Transmission electron micrographs (TEM) and corresponding selected area electron diffraction (SAED) patterns of Ti_2AlN (marked 1) and Ti_3AlN (marked 2–5) precipitates observed in Ti-48.5Al-1.5Mo-1.0N alloys with fully lamellar microstructure.

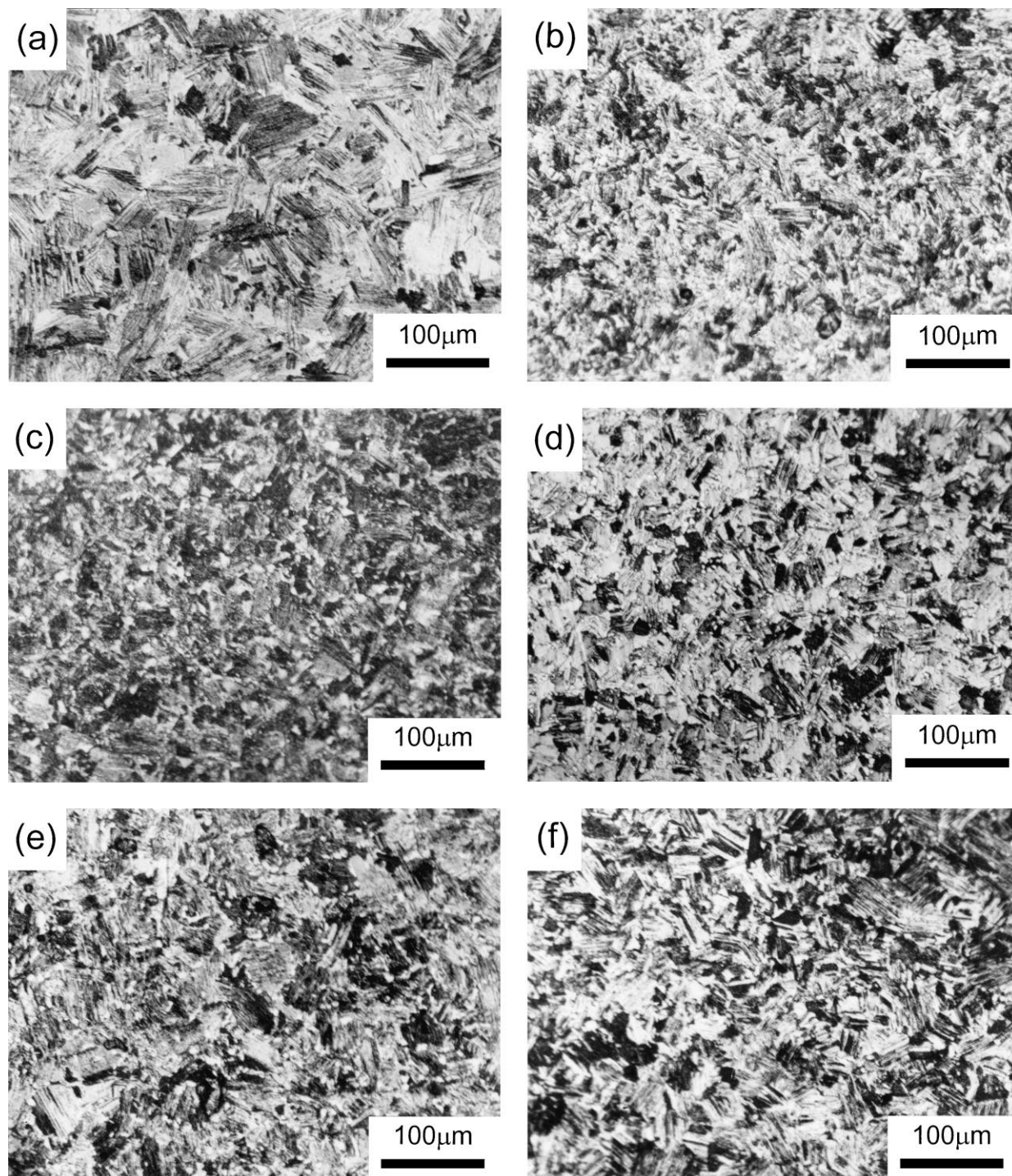


Figure 4 Optical micrographs of Ti-48.5Al-1.5Mo-1.0N alloy after the various heat treatments: (a) 2 hours, (b) 12 hours, (c) 24 hours and (d) 48 hours at 1300°C and (e) 24 hours and (f) 48 hours at 1250°C, respectively.

alloys as a function of nitrogen addition. In the case of fully lamellar alloys, room temperature elongation of the aging-treated alloys after microstructure control is much better than that of only microstructure controlled alloys in all alloy compositions. Moreover, as can be seen in the figure, room temperature elongation decreased markedly in the 0.3N alloys, but recovered to the level of the mother alloy (the 1.5Mo alloy) in the 1.0N and saturated in the 2.0N. As far as yield stress is concerned, the more nitrogen is added, the higher the yield stresses that are obtained.

It seems that precipitation-hardening and grain refinement are two conflicting effects that contribute to

room temperature elongation. When only the effect of grain refinement on room-temperature tensile elongation is considered, the 1.0N alloy with the fine fully lamellar grains obtain higher room temperature tensile elongation than the 1.5Mo alloy and the 0.3N alloy. The finer the grain size is, the higher the room temperature elongation obtained. However, the alloys containing more nitrogen grow harder due to a precipitation-hardening mechanism. Therefore, the 0.3N alloys show poor tensile elongation due to their relatively coarse grains, which compared to enough precipitation hardening effects. In contrast, in those alloys with more than 1.0 at.% N added, tensile elongation recovered to

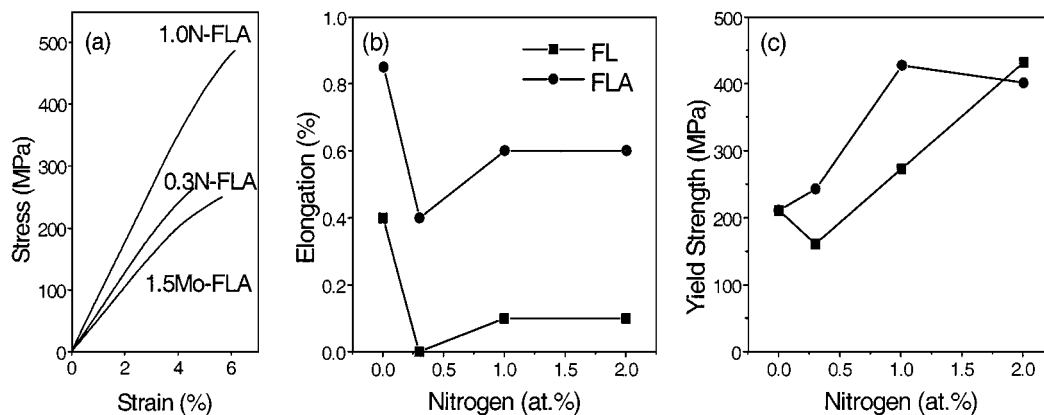


Figure 5 (a) Stress-strain curves and (b) elongation and (c) yield strength of room-temperature tensile tests of the fully lamellar TiAl alloys as a function of nitrogen additions.

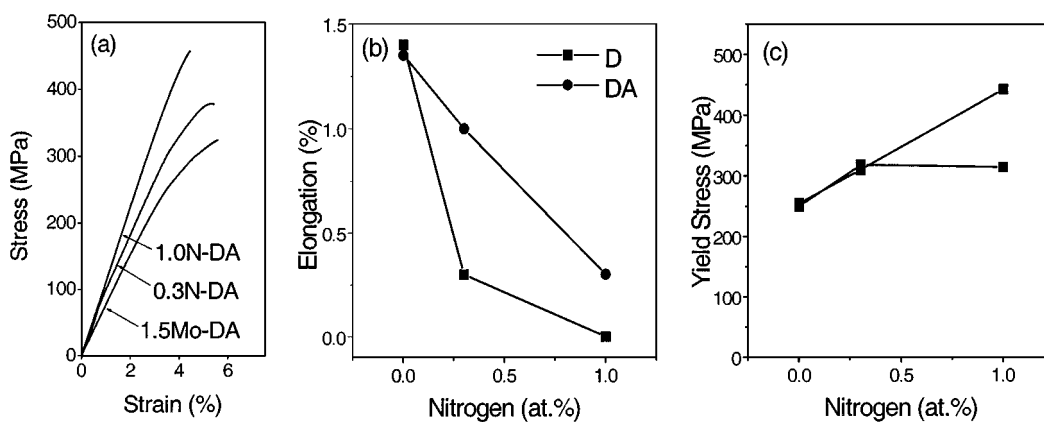


Figure 6 (a) Stress-strain curves and (b) elongation and (c) yield strength of room-temperature tensile tests of the duplex TiAl alloys as a function of nitrogen additions.

the level of the mother alloy because the grain refinement effect was more prominent than the precipitation-hardening effect.

Fig. 6 shows the stress-strain curves and the room temperature tensile properties of duplex TiAl alloys as a function of nitrogen addition. In the case of duplex alloy, the elongation decreased, and the yield strength increased with adding nitrogen. This fact means that grain refinement by nitrogen is ineffective to increase room temperature ductility. Though 1.0 at.% N addition decreased the size of the gamma phase and lamellar grain from $50 \mu\text{m}$ to $30 \mu\text{m}$, such a slight difference had no effect on room temperature ductility in the range of grain size below $100 \mu\text{m}$ [1].

4. Conclusions

In this study, the effects of nitrogen additions on the microstructure and room temperature tensile properties of the TiAl + Mo alloy with the fully lamellar and the duplex microstructure were investigated. Results are summarized as follows.

(1) 1.0 at.% nitrogen addition leads to remarkable grain refinement in the fully lamellar microstructure but had little effect on the duplex microstructure.

(2) Since the formation of the gamma phase is retarded by nitrogen addition, long-term heat treatment

is needed for the duplex microstructure in the 1.0N alloy.

(3) 1.0 at.% nitrogen addition increased the room temperature yield strength by two times without serious reduction of room temperature elongation in the fully lamellar microstructure. It seems that recovery of the room temperature elongation is due to remarkable lamellar grain refinement.

(4) In the duplex microstructure, the room temperature elongation decreased and the room temperature yield strength with nitrogen addition increasing.

Acknowledgements

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