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学 位 論 文 題 目　Plastic Deformation to Control Phase Decomposition in Ti-Al Alloy and Development of Hierarchical Nanoporous Structures
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論文内容要約

Chapter 1 Introduction and Background

In past decades, the lamellar Ti-Al alloys have been widely used as high-temperature components due to their high melting point, low density and high specific strengths. The lamellar structure consists of α_2-Ti_3Al lamellae and γ-TiAl lamellae with crystallographic orientation relationship that can be described as: $(0001)\alpha_2$ // $\{111\}\gamma$, $<11\bar{2}0>\alpha_2$ // $<1\bar{1}0>\gamma$, and the lamellar interface is very flat. The lamellar structures are mainly formed by precipitation of γ plates/lamellae from Al-supersaturated α/α_2 matrix during cooling from singe α phase at medium cooling rates or by annealing of Al-supersaturated α_2-Ti_3Al matrix at $\alpha_2+\gamma$ dual phase temperatures. Generally, the precipitation occurs from the heterogeneities in matrix such as dislocations and stacking faults. Thus, the morphologies of lamellar structure should be affected and modified by introducing heterogeneities.

On the other hand, the γ lamellae can be selective dissolved from lamellar Ti-Al alloy by both chemical method and electrochemical method, and periodic nanoarchitectures were produced. The submicron/nano functional periodic structures are very important for many applications. For instance, submicron gratings are widely applied as components for optical devices, and nano-porous/tubular structures are widely utilized for solar energy conversion and capacitance. Thus, novel applications of lamellar Ti-Al alloy such as fabrication of functional nanoarchitectures become possible.

In present study, the macro plastic deformation on Ti-40 at.% Al alloy with the purpose of control and modifying the lamellar structure with subsequent annealing was conducted. On the other hand, the nanoscale plastic deformation behaviors and the control of γ-lamellae precipitation by dislocation bands in Ti-39 at.% Al single crystals were investigated, in order to obtain periodic γ-lamellae for the potential fabrication of submicron grating structures by combination of selective dissolution. Moreover, we tried to fabricate novel hierarchical nano-porous structure with high surface area in lamellar Ti-40 at.% Al alloy by selective dissolution and anodization.

Chapter 2 Refinement of lamellar structure in Ti-40 at.% Al alloy by hot forging

Chapter 2 describes the macro plastic deformation behavior of Ti-40 at.% Al alloy deformed in single α phase. The hot deformation behavior and refinement of grains of Ti-40 at.% Al alloy in single α phase region was investigated by hot compression test, and the temperatures for hot compression were 1423 K, 1473 K and 1523 K, respectively. The strain rates were from 0.001 s^{-1} to 1 s^{-1} with strain from 10 % to 70 % reduction in initial height of samples. On the other hand, the effect of dislocation density on the precipitation of γ-lamellae in the subsequent annealing process was also examined.

The results indicated that the α/α_2 grains of Ti-40 at.% Al alloys were significantly refined by hot forging at single α phase temperatures (1423 K, 1473 K and 1523 K) with high strain rates such as 1 s^{-1} rather than lower strain rates. Moreover, the α/α_2 grains were further refined and homogenized by increasing strain. For instance, the α/α_2 grains were refined from 660 μm (ingot) to 3.5 μm in diameter by hot forging at 1473 K with 1 s^{-1} for 70 % reduction in initial height of samples. Secondly, the lamellar spacing was refined by refinement and introduction of dislocations in the Al-supersaturated α_2 grains, due to the increasement of potential nucleation sites. For instance, the lamellar spacing of lamellae formed in the 70 % forged sample (fine grain sizes with high dislocation density) after annealing at 1073 K for 10 ks is 25 nm, which is finer than the lamellae formed in 50 % forged sample (coarse grain sizes with low dislocation density) with lamellar spacing of 45 nm. Lastly, no significant grain growth was observed during annealing at 1073 K for 2 ks and 10 ks, the α_2-Ti_3Al grains are relatively stable at this temperature. On the other hand, γ-grains were formed along colony boundaries. Moreover, the volumetric fraction of γ-grains increases with the refinement of initial α_2-Ti_3Al grains.

Chapter 3 Nanoplastic deformation in Al-supersaturated α_2-Ti_3Al single crystals

Chapter 3 describes the nanoplastic deformation behaviors of Ti-39 at.% Al single crystals. The effects of nanoscale plastic deformation including nanoimprinting, nanoindentation and nanogrooving on the formation of periodic dislocation bands in single crystals were investigated, with a focus on the formation of periodic parallel basal dislocations. The results indicated that slip traces of both basal and prism slips were produced on the nano-indented crystal's surface, while only basal slip traces were formed on the nano-imprinted and nano-grooved crystals' surfaces.

A dislocation band as shown in Fig. 1 was produced beneath the nanogrooved trench, and the dislocation band consists of basal dislocations with relatively high density and non-basal dislocation tangles with exceedingly high density. However, low-density basal and non-basal dislocations were produced beneath the nanoimprinted indentations, and the plastic zones formed were relatively narrow. Moreover, non-basal slip traces or dislocations were connected to the basal slip traces and dislocations. The reasons for these formations were examined based on the motion of dislocations affected by antiphase domain boundaries as well as the cross-slip of prism dislocations onto the (0001) basal planes. According to the dislocation band characteristics, nanogrooving is the most appropriate among the three processes to produce periodic basal dislocation bands with tunable intervals.

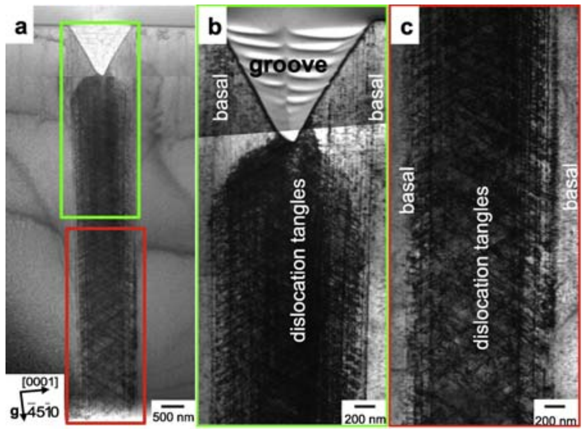

Fig. 1. (a–c) TEM images of cross-sectional area below groove. (b, c) Magnified images of the areas indicated by rectangles in (a). **B** // [40$\bar{4}$1], **g** = $\bar{4}5\bar{1}0$.

Chapter 4 Control of γ lamellae precipitation in Ti-39 at.% Al single crystals

Chapter 4 describes the control of γ lamellae precipitation in Ti-39 at.% Al single crystals by dislocation bands introduced by nanogrooving process (NGP) with subsequent ageing. In NGP, grooves were formed along the trace of (0001) basal plane on the surfaces of single crystal of α_2- phase supersaturated with Al-atoms by nano-scale plastic deformation using diamond knives with the edge angle of 60°. The widths of grooves ranged from 180 nm to 1860 nm for the load per knife-edge length in the range from 0.3 N/mm to 8.3 N/mm. Beneath the grooves, dislocation bands consisting of both basal dislocations and non-basal dislocations were formed. After aging at 1073 K for 1×10^4 s, pairs of γ lamellae were found to form only beneath the grooves to depths greater than 30 μm, meaning that the location of γ lamellae could be controlled by NGP. Increasing the aging temperature to 1173 K provided even greater control, with arrays of γ lamella bundles exhibiting a periodicity identical to that of the nanogrooves, and even near the surface no γ lamellae were formed in un-deformed regions. Fig. 2 shows the microstructure beneath an array of 10 grooves fabricated by combination of NGP and ageing, the γ lamellae formed only beneath grooves and no γ lamellae was present in the non-deformed region. It is clear that precipitation was successfully controlled. No concentration gradient was found within individual γ lamellae, which had a near-equilibrium Al concentration; thinner γ lamellae tended to have a slightly lower Al concentration. These results indicate that the precipitation of γ lamellae can be effectively controlled by introducing periodic dislocation bands using NGP, which opens new avenue for the manufacturing of near- or sub-wavelength grating structures with ultra-high aspect ratios through the selective dissolution of these γ lamellae.

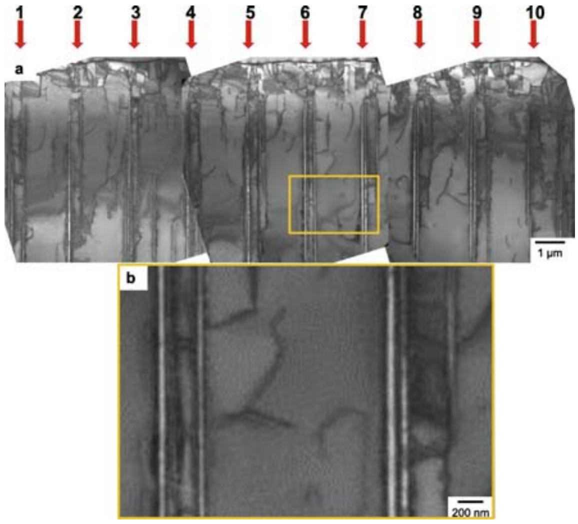

Fig. 2. (a, b) Bright field TEM images of cross-sectional area of the groove formed by loading 5 N after annealing at 1173 K for 1×10^4 s. (b) Magnified images of the areas indicated by rectangles in (a).

Chapter 5 Fabrication of hierarchical nano lamellar porous structures

Chapter 5 describes the fabrication of high aspect-ratio sub-micron lamellar porous/gratings by electrochemical selective dissolution of γ lamellae from lamellar Ti-40 at.% Al alloy in 0.5 M NaCl aqueous solution. We also investigated the effect of hot forging on the modification of lamellar characteristics, which indirectly affect the selective dissolution behaviors and the morphologies of lamellar porous/grating structures. In hot forging, the α/α_2 grains were significant refined and homogenized from diameter of 460 μm to 35 μm at 1473 K with a true strain of 0.7 and strain rate of 1 s^{-1}. In electrochemical etching, the γ lamellae and γ grains were dissolved as Ti^{4+} and Al^{3+}, and layers of reaction products were formed covering the surfaces of samples. After removing the layers, various high-aspect ratio lamellar porous structures were observed. For instance, relatively homogeneous gratings consisting of α_2-lamellae and crevasses with average lamellae thickness of 451 nm and crevasses thickness of 526 nm were produced. On the other hand, the morphologies were affected by the hot forging prior to the ageing.

Moreover, a novel hierarchical nano-porous structure with laminated and tubular pores was fabricated by two step method in which selective dissolution of lamellar Ti-40 at.% Al alloy followed by anodization. In the first step, grating structure consisting of α_2-Ti_3Al lamellae and crevasses was produced by

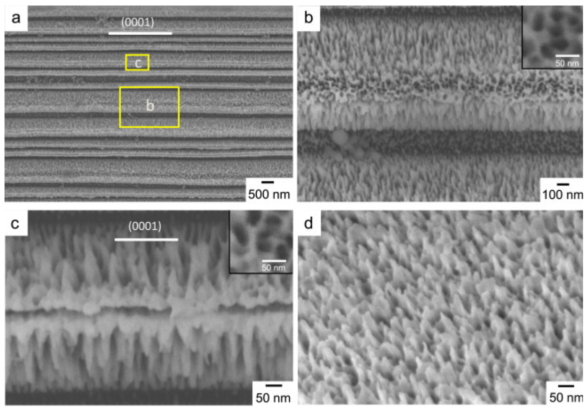

Fig. 3. SEM images of nano-lamellar/nano-tubular hierarchical porous structure produced by anodization of gratings in 1M $(NH_4)_2SO_4$ containing 0.5 wt.% NH4F at 40V for 300s. (b) and (c) maginified SEM images of areas b and c in Fig. 3a, respectively. (d) aerial view of porous structure. The inset figures in (b) and (c) are highly magnified images of top-view of pores.

selective dissolution of γ lamellae from the lamellar alloy. The spacing of gratings was controlled close to visible light wavelength. In the second step, the gratings were anodized and hierarchical porous structure consisting of nanolaminated crevasse and nanopores was formed. The XPS result indicates that the porous structure consists of oxide and hydroxide containing Ti and Al with a molar proportion of 1.5 : 1. Fig. 3 shows the novel nano architectures. The self-organized pores were homogeneous with a diameter of approximately 20 nm, and the depth of pores is 100~200 nm. The dimensions gratings and of pores can tuned with the combination of alloy composition and conditions of heat treatment, selective dissolution and anodization.

Chapter 6 Conclusions

Chapter 6 describes the summary and conclusions of this study. The macro scale plastic deformation behaviors of Ti-40 at.% Al alloy were investigated, and both the lamellar colonies and lamellar spacing were refined by plastic deformation with subsequent ageing. The nanoscale plastic deformation behaviors of single α_2-Ti_3Al phase and the precious control of individual γ-lamellae precipitation from supersaturated α_2-Ti_3Al matrix were investigated for the first time. We succeeded introducing tunable periodic dislocation bands by nanogrooving process. Moreover, the precipitation of γ-lamellae from supersaturated α_2-Ti_3Al matrix was controlled successfully by such dislocation bands combined with appropriate ageing. On the other hand, we fabricated a novel hierarchical nanolamellar porous/tubular structures in lamellar Ti-Al alloy. Several applications are possible for this structure, and a new field relating to the novel applications of Ti-Al alloys is opened.