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Doctor Thesis

Mechanical Properties of Microstructure Constituents and  
Microstructure Design in TiAl Base Alloys:  
Role of  $\beta$ -Ti Phase and Effect of Oxygen

TiAl 基合金における組織構成要素の機械的特性と組織設計  
— $\beta$ -Ti 相の役割と酸素の影響—

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# Chapter 1

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## General Introduction

## 1.1 Societal background

In order to stop or slow down global warming, more than 120 countries and regions, including Japan, have declared “carbon neutrality by 2050” [1,2]. Carbon neutrality means achieving a balance between the emission of carbon and the absorption of carbon from the atmosphere in carbon sinks. It is necessary to make efforts to reduce carbon emissions in every field.

The demand of aircrafts has been increasing year after year. **Figure 1-1** shows the projected evolution of the number of passenger aircraft in 2042, as estimated by Airbus [3]. The demand is expected to increase by a factor of two within the next 20 years. Accordingly, it is expected that CO<sub>2</sub> emissions from aircraft will increase, assuming no technological development. The International Civil Aviation Organization (ICAO) has presented three integrated scenarios for future CO<sub>2</sub> emissions from aircraft in the long term global aspirational goal (LTAG) report, as shown in **Fig. 1-2** [4]. Under Scenario 1 (high readiness/attainability and low aspiration), CO<sub>2</sub> emissions in 2050 could reach 160% of the 2019 level, whereas in Scenario 3 (low readiness/attainability and high aspiration), it could reach 33% of the 2019 CO<sub>2</sub> emission level. In order to achieve the outcomes of Scenario 3, a significant advancement in aircraft technology, operation, and fuel is essential. Furthermore, the cost of the advanced fuel for the carbon neutrality, namely sustainable aviation fuel (SAF), is more than twice that of conventional jet fuel [5]. Therefore, from the perspective of both carbon neutrality and cost reduction, it is clearly crucial to enhance the fuel efficiency of aircraft. In order to improve the fuel efficiency of aircraft, a number of approaches are being pursued, including the electrification and hybridization of engines, the development of hydrogen-fueled engines, and the reduction of aircraft weight.

## 1.2 Application of $\gamma$ -TiAl base alloys for aircraft engines

$\gamma$ -TiAl base alloys are a promising material for high-temperature parts of the aircraft engines up to about 1073 K to achieve the weight reduction. **Table 1-1** summarizes various properties of TiAl alloys together with other heat resistant alloys [6]. TiAl alloys have well-balanced properties, and the density of this alloys is approximately half that of Ni base superalloys, which are widely used for high-temperature parts of the engines. The specific strength of TiAl alloys is superior to other alloys as shown in **Fig. 1-3** [7]. Because of the excellent properties of this material, a TiAl alloy was used as low-pressure turbine (LPT) blades for a GENx turbofan jet engine in 2011 for the first in the world by GE Aerospace [8,9]. **Figure 1-4** shows a schematic illustration of GENx-1B engine and turbine blades of the TiAl alloy. The TiAl alloy is applied in the last two of seven stages of the LPT in this engine. The replacement of the conventional Ni base superalloy with the TiAl alloy results in a weight reduction of 180 lb ( $\approx$  80 kg), and the total airframe weight reduction exceeds 400 lb ( $\approx$  180 kg) when engine mounts and other components

are included [8,9]. However, TiAl alloys contain several disadvantages, including limited room-temperature ductility and relatively low toughness. Consequently, there is a need to enhance the properties of these alloys in order to facilitate their further application.

The TiAl LPT blades for GENx have been produced via investment casting [10]. The casting of TiAl alloys presents certain difficulties or problems, despite the process being relatively cost-effective. These include: (1) the production of defect-free components is challenging due to the low fluidity of the alloys, (2) extensive machining is necessary due to the high reactivity of the alloys with crucibles, and (3) the resulting microstructure is inhomogeneous and coarse [10]. The centrifugal casting process was applied to the LPT blades of the LEAP engine, developed by CFM International, a joint company between GE Aerospace and Safran Aircraft Engines, with the objective of eliminating cast-induced defects in an effective manner [10]. In addition to the casting process, wrought process and powder metallurgical process, such as metal injection molding (MIM) and additive manufacturing (AM) methods, have been developed. These processes offer more uniform and refined microstructure than casting, and the powder metallurgical process can produce components with a near net shape with less required machining. The wrought blades were employed in PW1100G engines and the additively manufactured blades are used for GE9X engines.

### 1.3 Phase equilibria and phase transformation in TiAl alloys

It is very important to understand the phase equilibria and phase transformation in TiAl alloys, since the mechanical properties of this material are highly dependent on the microstructure. **Figure 1-5** shows the Ti-Al binary phase diagram reported by Schuster and Palm in 2006 [11]. This phase diagram is based on a re-evaluation of all the literature available at that time and is probably the most reliable one at present, although there is controversy regarding the phase equilibria among the  $\beta$ ,  $\alpha$  and  $\alpha_2$  phases [12]. The crystallographic data and schematics of crystal structure of four phases of  $\beta$ -Ti ( $A2 = \text{bcc}$ ),  $\alpha$ -Ti ( $A3 = \text{hcp}$ ),  $\alpha_2$ -Ti<sub>3</sub>Al ( $D0_{19} = \text{ordered hcp}$ ) and  $\gamma$ -TiAl ( $L1_0 = \text{ordered fct}$ ) existing in Ti-rich side, which are important phases for TiAl alloys, are shown in **Table 1-2** and **Fig. 1-6**, respectively [11]. The  $\gamma$  phase, the most predominant phase in TiAl alloys, is a B2-type intermetallic compound existing at an Al content of between about 47 and 64 at.%. This phase equilibrates with the  $\alpha$  or  $\alpha_2$  phase on the Ti-rich side in the binary system. The  $\alpha_2$  phase is a Kurnakov-type compound existing at an Al content of between about 20 and 38 at.% and a temperature of 1473 K, and it transforms to disordered  $\alpha$  phase at higher temperature. The microstructure of TiAl alloys is controlled variously using a transformation pathway of  $\alpha \rightarrow \alpha + \gamma \rightarrow \alpha_2 + \gamma$ . The  $\gamma$  phase precipitates in a plate-like morphology along the (0001) plane of the  $\alpha$  phase, forming the  $\alpha/\gamma$  lamellar microstructure, and subsequently the  $\alpha$  phase orders into the  $\alpha_2$  phase. There exists the Blackburn orientation

relationship between the  $\alpha$  ( $\alpha_2$ ) and  $\gamma$  phases, as follows [13]:

$$(0001)_\alpha \parallel \{111\}_\gamma, \langle 11\bar{2}0 \rangle_\alpha \parallel \langle \bar{1}10 \rangle_\gamma$$

It should be noted that the  $\gamma$  phase does not equilibrate with  $\beta$  phase at any temperature in the binary system.

In contrast, Takeyama and his co-workers have systematically investigated the phase equilibria of Ti-Al-M (M:  $\beta$  stabilizing elements, V, Nb, Cr, Mo) ternary system [14,15]. **Figure 1-7** shows the isothermal sections of Ti-Al-M ternary phase diagram at 1573 and 1473 K [14]. The addition of the M element results in the  $\beta$  phase becoming in equilibrium with the  $\gamma$  as well as the  $\alpha$  phase, creating a  $\beta + \alpha + \gamma$  three-phase coexisting region. As the temperature decreases, this three-phase region shifts towards the low-Al and low-M concentration side. Consequently, a unique transformation of  $\beta + \alpha \rightarrow \alpha \rightarrow \alpha + \gamma \rightarrow \beta + \alpha + \gamma$  appears in a certain composition range in the M-doped multinary system, as shown in the vertical section of the Ti-Al-Nb ternary system in **Fig. 1-8** [16]. Takeyama et al. first proposed a design principle for wrought TiAl alloys based on this transformation pathway [17–20]. The alloys proposed by Takeyama et al. can be readily forged in the  $\beta + \alpha$  two-phase region at around 1573 K with regular hot forging equipment because of the high deformability of the  $\beta$  phase at elevated temperatures (**Fig. 1-8 (b)**), whereas the conventional alloys, without doping an adequate amount of M element, exhibit poor hot workability and require isothermal working at a relatively low strain rate. The microstructure can be controlled into  $\alpha_2/\gamma$  fully or nearly lamellar microstructure by subsequent heat treatment, and the  $\beta$  phase can be utilized not only for processing but also for in-service purposes (**Fig. 1-8 (d)**). The TiAl alloy applied to PW1100G engines, TNM alloy with a nominal composition of Ti-43.5Al-4Nb-1Mo-0.1B (at.%), is also developed based on this design principle [7]. **Figure 1-9** shows the hot-forged pancakes of the conventional and M-doped developed alloys [19]. There are many cracks observed in the forged pancake of the conventional alloy (**Fig. 1-9 (a)**), whereas no obvious crack is observed in the M-doped alloy (**Fig. 1-9 (b)**). It is clear that the hot workability of the alloy improves with the addition of M element.

#### 1.4 Effect of microstructure on mechanical properties of TiAl alloys

As aforementioned in section 1.3, the mechanical properties of TiAl alloys strongly depend on the microstructure. For  $\alpha_2 + \gamma$  two-phase microstructure, the microstructure typically consists of  $\alpha_2/\gamma$  lamellar grains, resulting from the transformation pathway of  $\alpha \rightarrow \alpha + \gamma \rightarrow \alpha_2 + \gamma$ , and equiaxed  $\gamma$  grains, resulting from heat treatment in  $\alpha + \gamma$  two-phase or  $\gamma$  single phase region. **Figure 1-10** shows typical four microstructures of  $\alpha_2 + \gamma$  two-phase TiAl alloys [21]. These four microstructures are referred to as (a) Near-Gamma (NG), (b) Duplex (DP), (c) Nearly Lamellar (NL) and (d) Fully Lamellar (FL) in increasing order of lamellar volume fraction, and

they exhibit different mechanical properties as shown in **Fig. 1-11** [21]. The NG, DP and NL show relatively high strength and ductility (elongation), whereas FL shows higher fracture toughness, impact resistance and creep resistance.

By introducing the  $\beta$  phase based on the phase diagram study, the range of microstructure design is significantly expanded. Takeyama's research group has demonstrated that the introduction of the  $\beta$  phase to TiAl alloys can improve various mechanical properties by appropriate microstructure design [22,23], whereas there are also some reports on the negative effect of the  $\beta$  phase [24–27]. **Figure 1-12** shows three representative examples of the microstructures of  $\beta$ -containing TiAl alloy with a composition of Ti-43Al-4Nb-5V [22]. These are referred to as (a, d) Nearly Lamellar (NL), (b, e) Lamellar Triplex (LTL) and (c, f) Nearly Globular  $\beta/\gamma$  Duplex (NGDP) microstructures. Even for the same alloy, the microstructure can be controlled in a wide range by heat treatments. The NL microstructure is obtained by the heat treatment in the  $\alpha$  single phase or  $\beta + \alpha$  two-phase region followed by short time aging in  $\beta + \gamma$  two-phase region. The  $\alpha_2/\gamma$  lamellar grains form from the high-temperature  $\alpha$  phase, and their grain boundaries are covered by a small amount of  $\beta$  phase, which exists at higher temperature. The LTL microstructure is obtained by longer time aging in  $\beta + \gamma$  two-phase region. The  $\beta/\gamma$  cellular or lamellar microstructure forms by the discontinuous transformation of  $\alpha_2 + \gamma \rightarrow \beta + \gamma$  from lamellar grain boundaries. The NGDP microstructure is obtained by the long-time heat treatment in  $\beta + \alpha_2 + \gamma$  three-phase region.

Signori et al. have investigated the fatigue crack growth (FCG) properties of the alloys with these three microstructures [22]. **Figure 1-13** shows the FCG curves of the alloys with NL, LTL and NGDP microstructure together with the FL without  $\beta$  phase in comparison. It was found that the introduction of  $\beta$  phase on the lamellar grain boundaries improves the fatigue crack growth resistance by impeding the crack propagation along the lamellar interfaces.

Wakabayashi has investigated the effect of grain boundary  $\beta/\gamma$  duplex on the creep resistance [28]. It was found that the lamellar  $\beta/\gamma$  microstructure on the  $\alpha_2/\gamma$  lamellar grain boundaries is effective for the creep resistance, whereas the globular  $\beta/\gamma$  microstructure deteriorates the creep resistance.

### 1.5 Effect of oxygen on phase equilibria, microstructure and properties of TiAl alloys

It is inevitable that oxygen is introduced into TiAl alloys during the manufacture process, especially in the case of powder metallurgy, due to the high chemical affinity of oxygen for titanium. The amount of oxygen is generally less than 700 wt. ppm for conventional ingot metallurgy using high-purity raw metal [29–31], while it is 700–1000 wt. ppm for electron beam powder bed fusion [32,33] and 1100–2400 wt. ppm for MIM [34–36]. It has been reported that the oxygen in TiAl alloys significantly affects phase equilibria [37–39], microstructures [40–43]

and properties [40–42,44]. Menand et al. have analyzed the oxygen concentration in  $\alpha_2 + \gamma$  two-phase and  $\gamma$  single phase alloys by atom-probe tomography and reported that the oxygen is preferentially partitioned into the  $\alpha_2$  phase [37,38]. In addition, Nakashima et al. recently have investigated the phase equilibria in Ti-Al-O ternary system using soft X-ray emission spectroscopy (SXES) [39]. They also reported that most of the oxygen is dissolved in the  $\alpha_2$  phase, and the  $\alpha + \gamma$  two-phase region expands toward both of the Ti-rich and Al-rich side, as shown in **Fig. 1-14**. Kinetically, the oxygen in TiAl alloys suppresses the formation of the  $\gamma$  grains and favors the  $\alpha_2/\gamma$  lamellar microstructure, as shown in **Fig. 1-15** [41]. In the  $\beta$ -containing alloys, the volume fraction of the  $\beta$  phase decreases with the oxygen addition [40]. Concerning the mechanical properties, it was reported that the alloy becomes harder and less ductile with the oxygen addition, as shown in **Fig. 1-16** [41]. However, in most of the previous research, the microstructure also changes with the oxygen, so that it is necessary to identify whether the change in mechanical properties is caused by the change in nature of the constituent phases due to the solute oxygen itself or by the microstructural changes associated with the change in phase equilibria among the phases concerned.

## 1.6 Significance and objective of this research

The microstructures of TiAl alloys are often complex, where they consist of two or more phases and the morphology of the phases varies. In order to understand the effect and role of each microstructure constituent and design advanced microstructures, it is necessary to investigate the mechanical behavior of the constituents as well as that of whole bulk alloys. The simplest way to evaluate the properties of each microstructure constituent is to prepare alloys with single constituent. However, it is time consuming and sometimes impossible depending on phase equilibria. Recent progress in materials characterization techniques allow to investigate the local mechanical behavior in micro or sub-micro scale in multi-constituent alloys. In this thesis, two techniques of digital image correlation (DIC) and nano-indentation are used to characterize the mechanical behavior of the microstructure constituents of TiAl alloys. The DIC technique allows us to calculate the local strain by comparing images of a material before and after deformation. We can design microstructures with high ductility, which is one of the disadvantages of TiAl alloys, by investigating the deformation behavior of each constituent, or we can estimate the onset of the fracture by investigating the accumulated local strain. The nano-indentation technique allows us to measure the mechanical properties, such as elastic modulus and hardness, of constituent phases in alloys with multiple-phase microstructure. The Young's modulus is known to be correlated with creep resistance and fatigue crack growth resistance [45], and the hardness is qualitatively correlated with the strength. The knowledge of the properties of the constituent phases obtained by nano-indentation can be useful to understand the mechanical behavior of bulk

alloys and design a microstructure with required properties.

As aforementioned in section 1.5, the effect of oxygen on the microstructure and the properties is important, especially in case of MIM process. The knowledge of the microstructure formation in the alloys containing  $\beta$  phase is lacking, despite of the importance of the  $\beta$  phase. Concerning the mechanical properties, it can be possible to understand how the ductility of TiAl alloys decreases with the oxygen addition by evaluating the effect of solute oxygen on the mechanical properties of each phase with nano-indentation.

In this thesis, the deformation behavior of the microstructure constituents during tensile loading and the mechanical properties of the constituent phases in TiAl alloys are investigated using DIC and nano-indentation technique, respectively. Moreover, the effect of oxygen on the microstructure formation and the mechanical properties are evaluated. Based on the findings, the microstructure design principle is proposed.

## 1.7 Outline of this thesis

The flowchart of this thesis is shown in **Fig. 1-17**.

In Chapter 1, “General Introduction”, the current situation of TiAl alloys as aircraft engine parts, the microstructure-property relationship in TiAl alloys and the effect of oxygen on the properties in TiAl alloys are described. The importance of the evaluation of mechanical properties of microstructure constituents in advanced alloy and microstructure design is emphasized. Then, the objective and the outline of this research are explained.

In Chapter 2, “Local Deformation Analysis Using DIC Technique under *In-situ* Tensile Test”, the deformation behavior of  $\alpha_2/\gamma$  lamellar microstructure,  $\beta$  grains and  $\gamma$  grains during tensile loading are investigated using DIC technique.

In Chapter 3, “Formation and Characterization of  $\beta$ -Ti Phase in TiAl Alloys without and with Oxygen”, the microstructure change during aging in a TiAl alloy with oxygen addition is investigated and the obtained microstructure is observed in three dimensions, focusing on  $\beta$  phase along  $\alpha_2/\gamma$  lamellar microstructure. The effect of oxygen on the microstructure formation in TiAl alloy is discussed, and the three-dimensional characteristics of the  $\beta$  phase along  $\alpha_2/\gamma$  lamellae are presented.

In Chapter 4, “Cr Effect on Young’s Modulus and Hardness of the  $\beta$ ,  $\alpha_2$  and  $\gamma$  Phases Evaluated by Nano-indentation”, the Young’s modulus and the hardness of the  $\beta$ ,  $\alpha_2$  and  $\gamma$  phases in Ti-Al-Cr ternary alloys are measured, and the effect of chromium content on the properties is evaluated.

In Chapter 5, “Oxygen Effect on Young’s Modulus and Hardness of the Constituent Phases Evaluated by Nano-indentation”, the oxygen concentration and the mechanical properties of the  $\beta$ ,  $\alpha_2$  and  $\gamma$  phases in a Ti-Al-Cr-O quaternary alloy are investigated, and the effect of the solute



oxygen on the Young's modulus and the hardness of the phases is evaluated.

In Chapter 6, "Temperature Effect on Young's Modulus and Hardness of the Constituent Phases Evaluated by Nano-indentation", the Young's modulus and the hardness of the  $\beta$  and  $\gamma$  phases are measured at elevated temperatures, and the effect of temperature on the properties of the phases is presented.

In Chapter 7, "Utilization of Mechanical Properties of the Constituent Phases for Alloy Design", from the obtained findings in this research, the alloy and microstructure design to satisfy required properties is proposed, and the achievement of advanced alloy development is presented.

In Chapter 8, "Conclusions", the obtained findings in this thesis are summarized.

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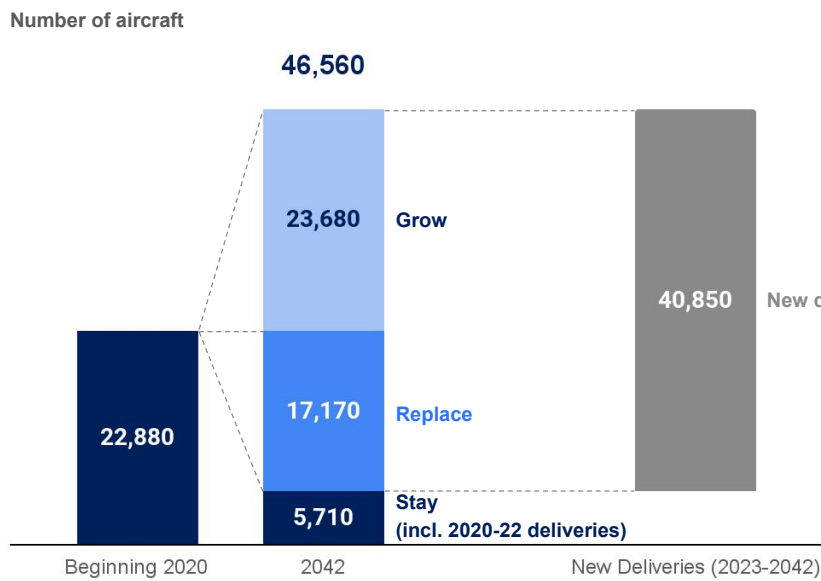
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**Table 1-1** Physical, mechanical and environmental properties of TiAl alloys together with titanium alloys and superalloys [6].

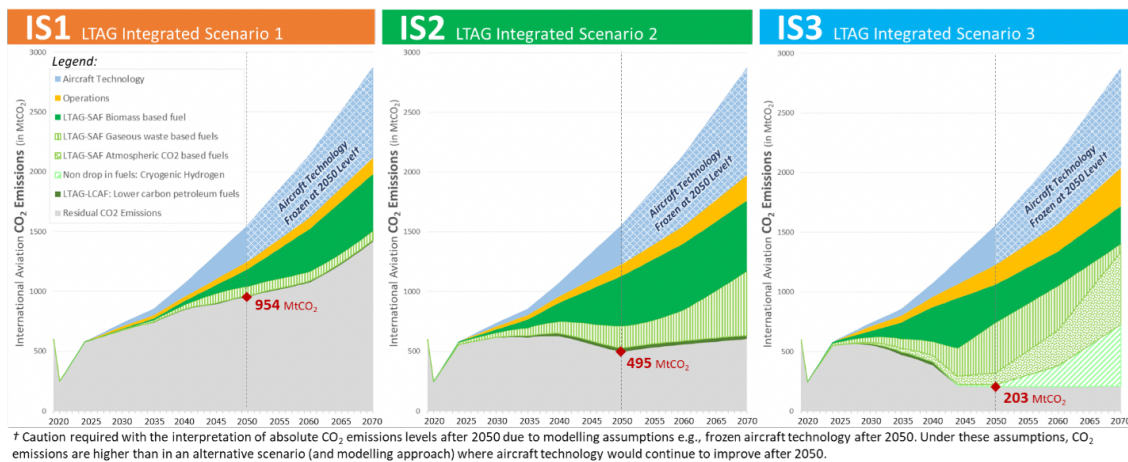
| Property                                            | Ti-Base   | Ti <sub>3</sub> Al-Base | TiAl-Base       | Superalloy          |
|-----------------------------------------------------|-----------|-------------------------|-----------------|---------------------|
| Structure                                           | hcp/bcc   | D0 <sub>19</sub>        | L1 <sub>0</sub> | fcc/L1 <sub>2</sub> |
| Density (g/cm <sup>3</sup> )                        | 4.5       | 4.1-4.7                 | 3.7-3.9         | 7.9-8.5             |
| Modulus (GPa)                                       | 95-115    | 110-145                 | 160-180         | 206                 |
| Yield Strength (MPa)                                | 380-1,150 | 700-990                 | 350-600         | 800-1,200           |
| Tensile Strength (MPa)                              | 480-1,200 | 800-1,140               | 440-700         | 1,250-1,450         |
| Room-Temp.Ductility (%)                             | 10-25     | 2-10                    | 1-4             | 3-25                |
| High-Temp.Ductility (%/°C)                          | 12-50     | 10-20/660               | 10-600/870      | 20-80/870           |
| Room-temp.Fracture Toughness (MPam <sup>1/2</sup> ) | 12-50     | 13-30                   | 12-35           | 30-100              |
| Creep Limit (°C)                                    | 600       | 750                     | 750-950         | 800-1,090           |
| Oxidation (°C)                                      | 600       | 650                     | 800-950         | 870-1,090           |

**Table 1-2** Crystallographic data of important phases for TiAl alloys [11].

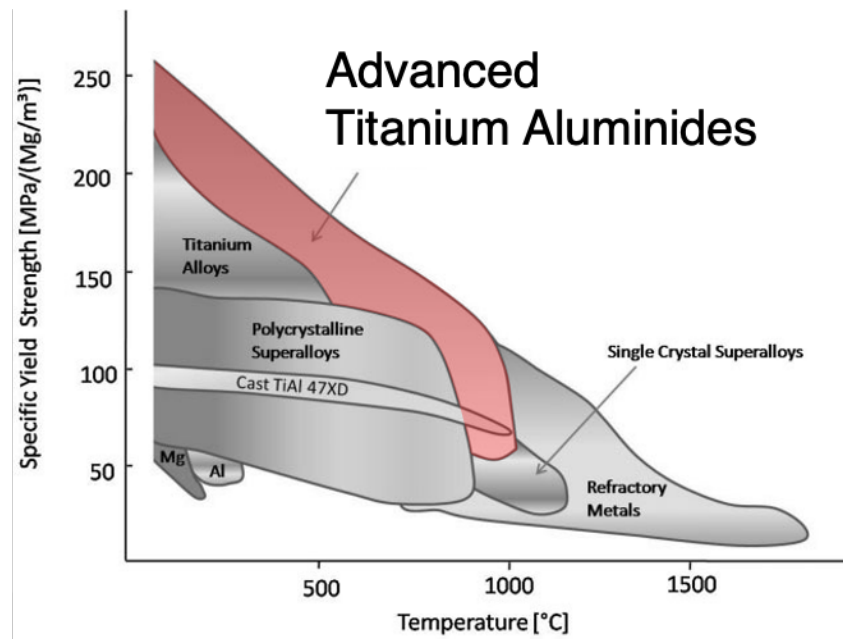
| Phase                              | Pearson symbol | Space Group          | Strukturbericht designation | Prototype          | Lattice parameters / nm    | Remarks       |
|------------------------------------|----------------|----------------------|-----------------------------|--------------------|----------------------------|---------------|
| β-Ti                               | cI2            | Im $\bar{3}$ m       | A2                          | W                  | a = 0.33065                | at 1173 K     |
| α-Ti                               | hP2            | P6 <sub>3</sub> /mmc | A3                          | Mg                 | a = 0.29504<br>c = 0.46833 |               |
| α <sub>2</sub> -Ti <sub>3</sub> Al | hP8            | P6 <sub>3</sub> /mmc | D0 <sub>19</sub>            | Ni <sub>3</sub> Sn | a = 0.5765<br>c = 0.4625   | at 25 at.% Al |
| γ-TiAl                             | tP4            | P4/mmm               | L1 <sub>0</sub>             | AuCu               | a = 0.3997<br>c = 0.4062   | at 50 at.% Al |



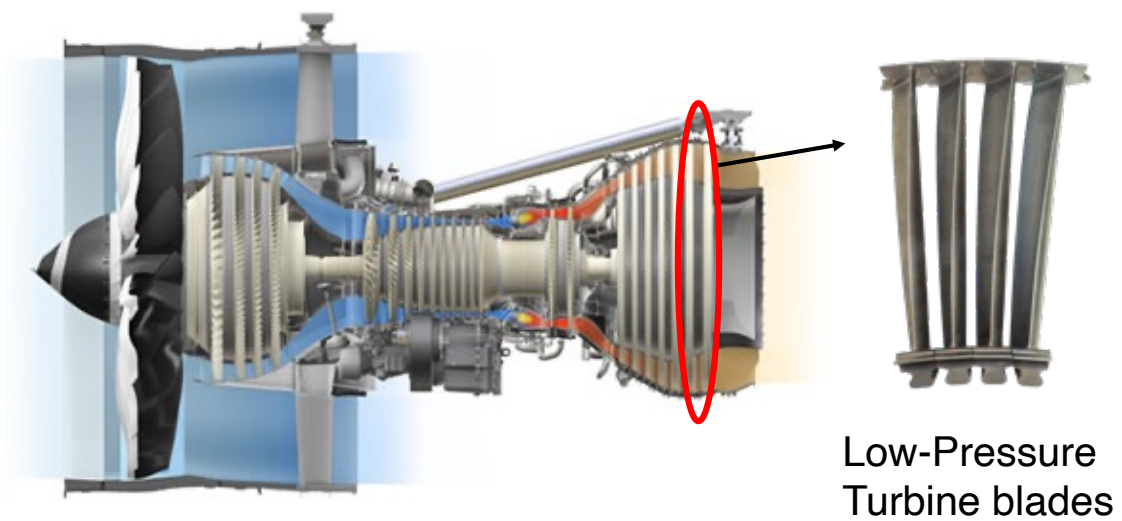
**Fig. 1-1** Evolution of the number of passenger aircraft in 2042 [3].



**Fig. 1-2** Three integrated scenarios for future CO<sub>2</sub> emissions from aircraft in the long term global aspirational goal (LTAG) report [4]. Scenario 1: high readiness/attainability and low aspiration, Scenario 2: middle readiness/attainability and middle aspiration, Scenario 3: low readiness/attainability and high aspiration.

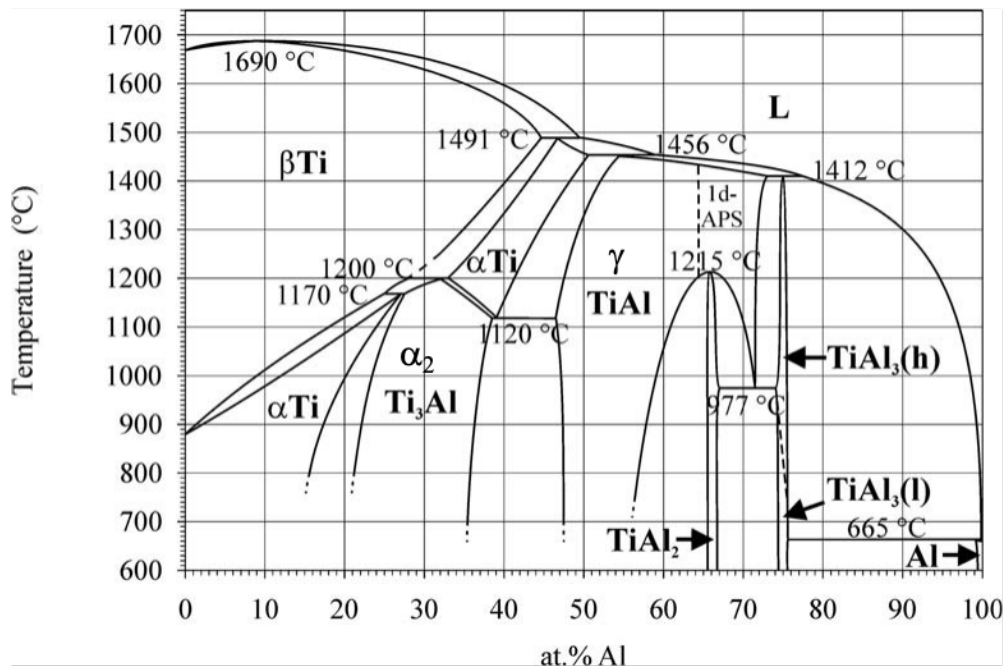


**Fig. 1-3** Change in specific yield strength of various structural alloys with temperature [7].

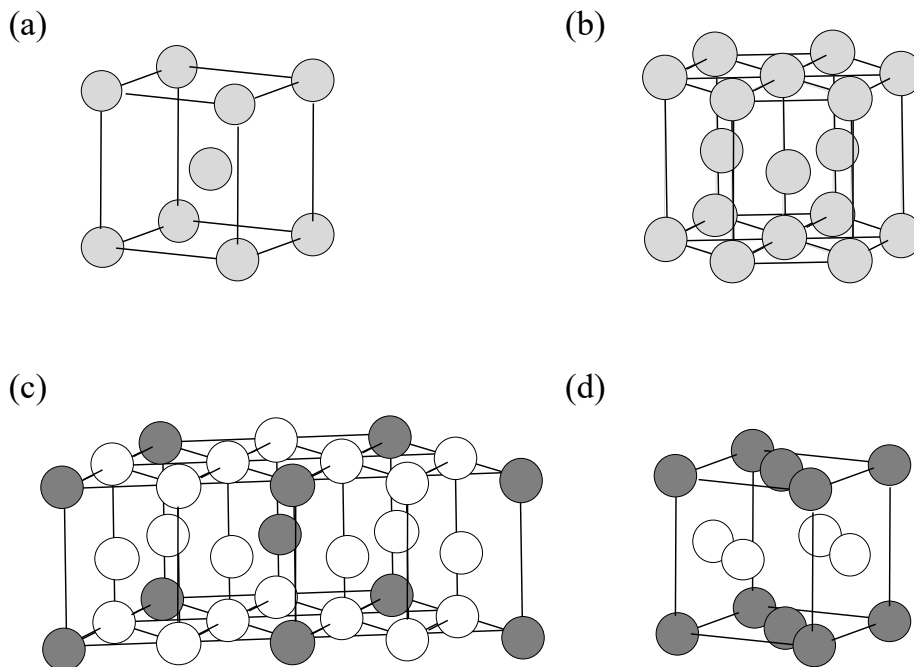


**Fig. 1-4** Schematic illustration of the commercial turbofan engine, GEnx-1B, and low-pressure turbine (LPT) blades of TiAl alloys used in the last two stages of LPT.

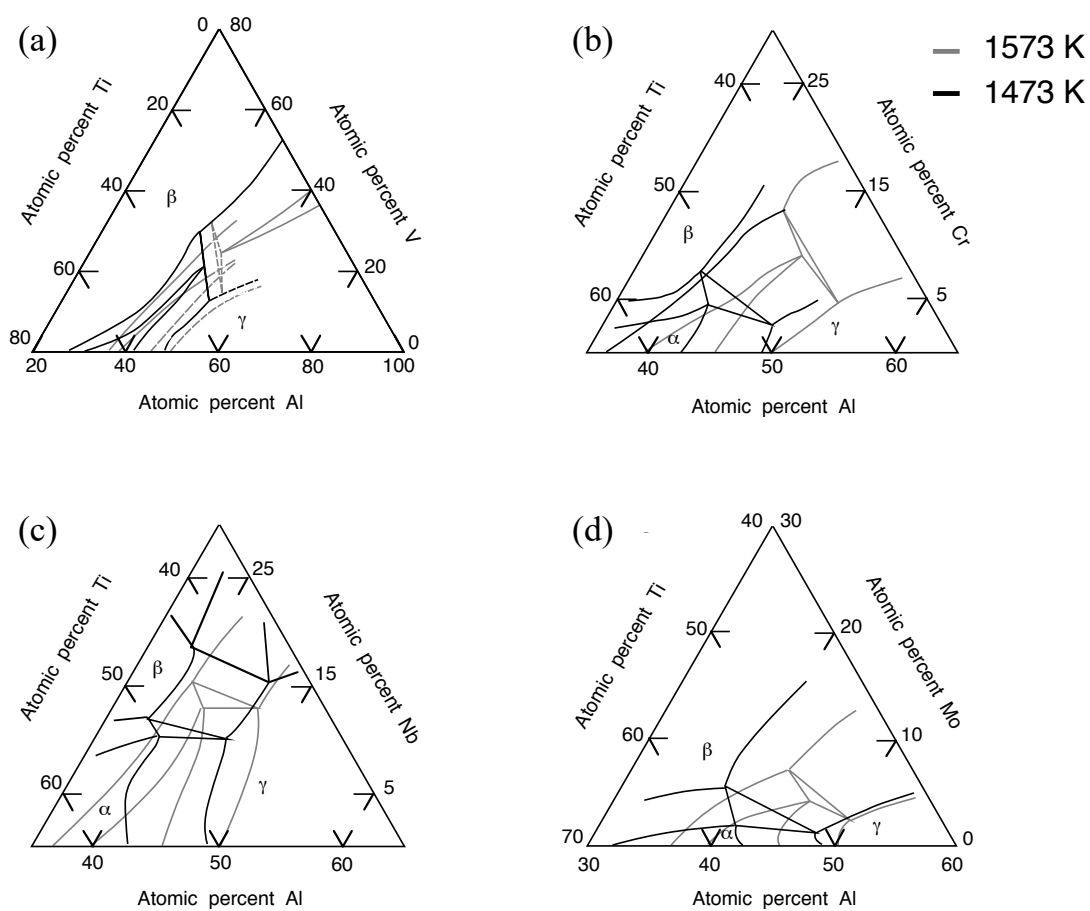




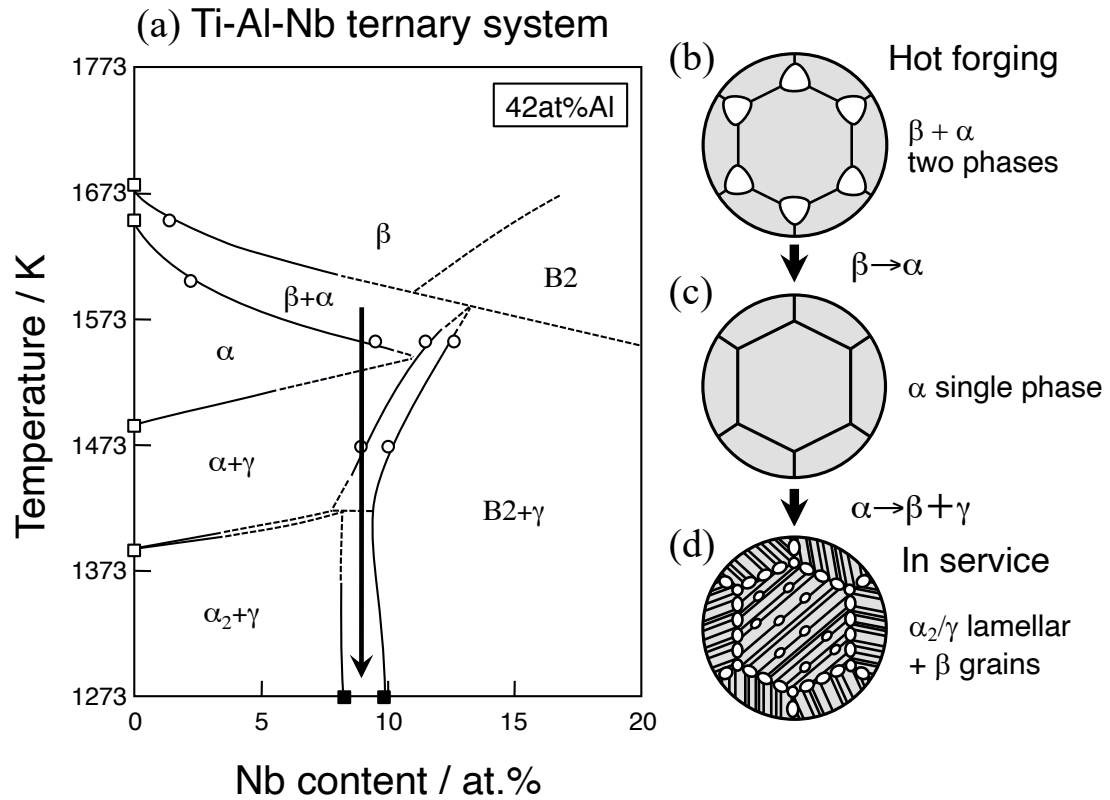
**Fig. 1-5** Ti-Al binary phase diagram reported by Schuster and Palm in 2006 [11].



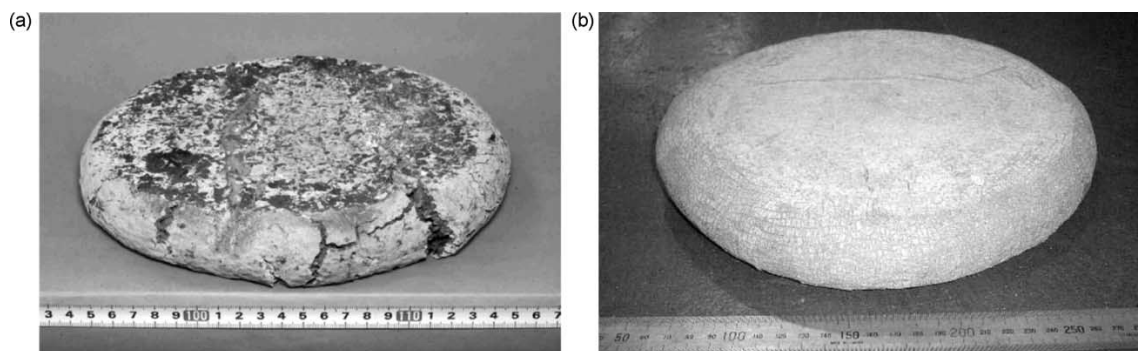
**Fig. 1-6** Crystal structure of (a)  $\beta$ -Ti ( $\text{A}_2 = \text{bcc}$ ), (b)  $\alpha$ -Ti ( $\text{A}_3 = \text{hcp}$ ), (c)  $\alpha_2$ - $\text{Ti}_3\text{Al}$  ( $\text{D}_{019}$  = ordered hcp) and (d)  $\gamma$ -TiAl ( $\text{L}_{10}$  = ordered fct) phases.



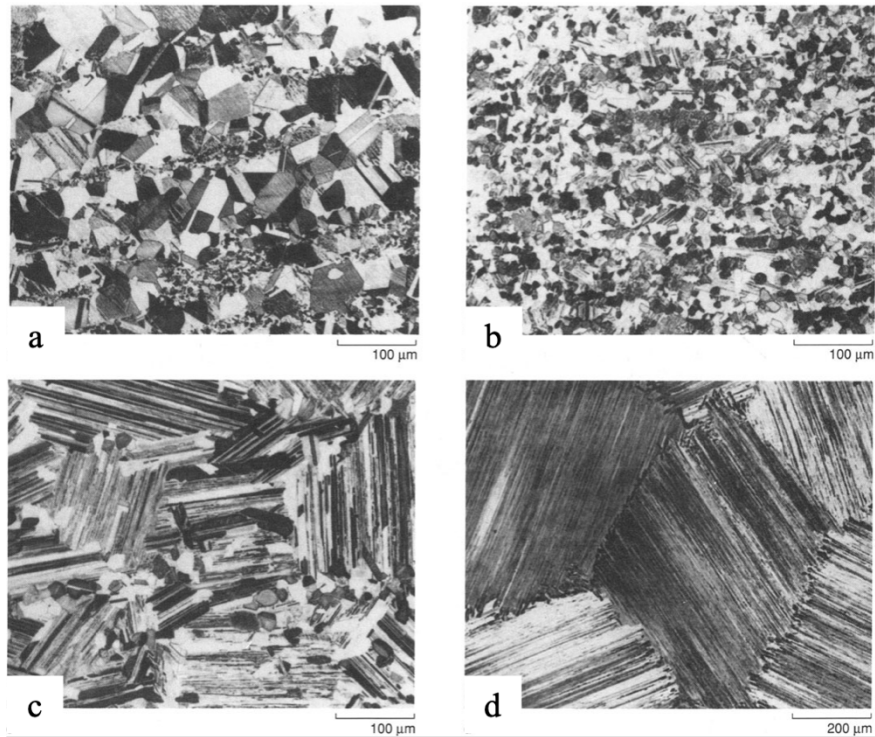
**Fig. 1-7** Isothermal sections of Ti-Al-M (M = (a) V, (b), Cr, (c) Nb, (d) Mo) ternary phase diagram at 1573 and 1473 K reported by Nakamura et al. [14].



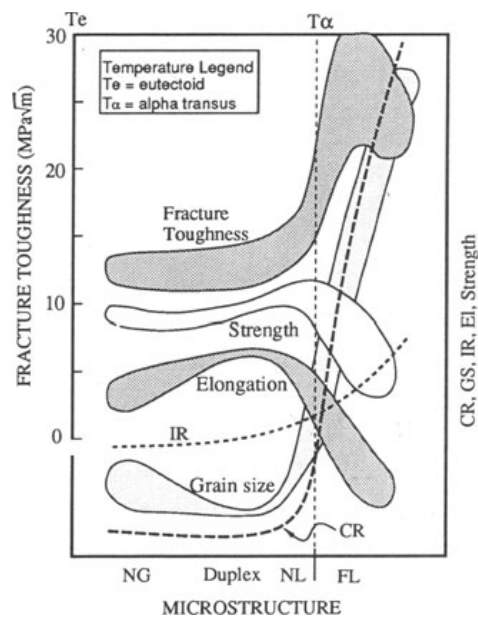
**Fig. 1-8** (a) Vertical section of Ti-Al-Nb ternary system at 42 at.% Al and (b–d) schematic illustrations of the microstructure control process based on the design principle proposed by Takeyama et al. [16].



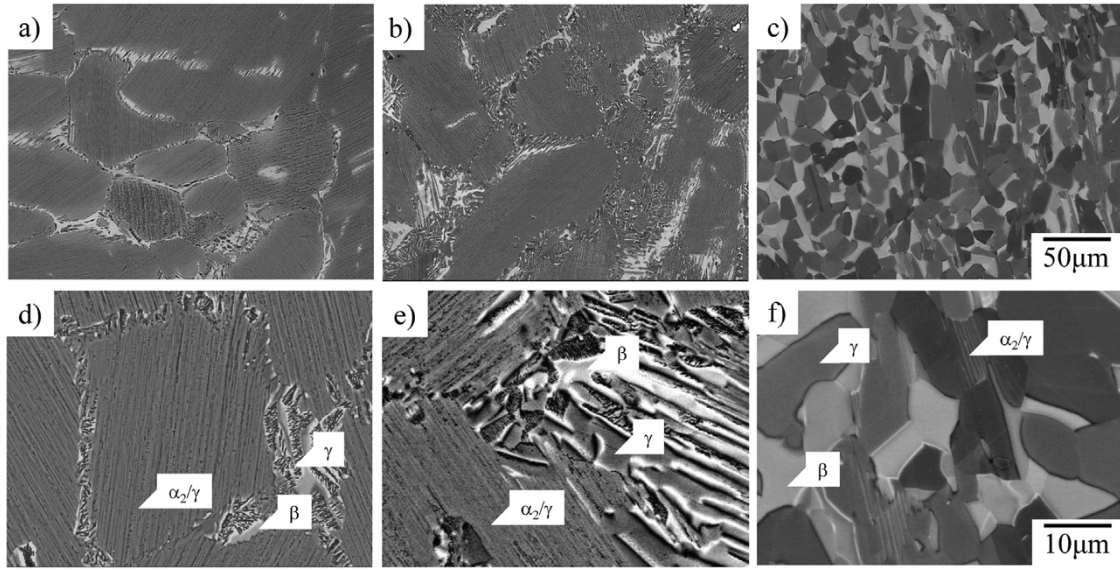
**Fig. 1-9** Hot-forged pancakes of (a) conventional and (b)  $\beta$ -stabilizing element doped alloy [19].



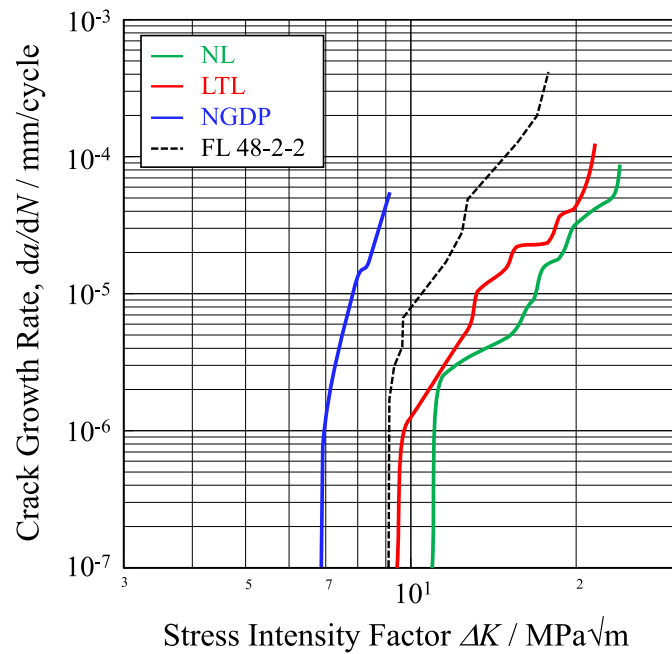
**Fig. 1-10** Four typical microstructures of TiAl alloys obtained by heat treatments: (a) Near-Gamma (NG), (b) Duplex (DP), (c) Nearly Lamellar (NL) and (d) Fully Lamellar (FL) [21].



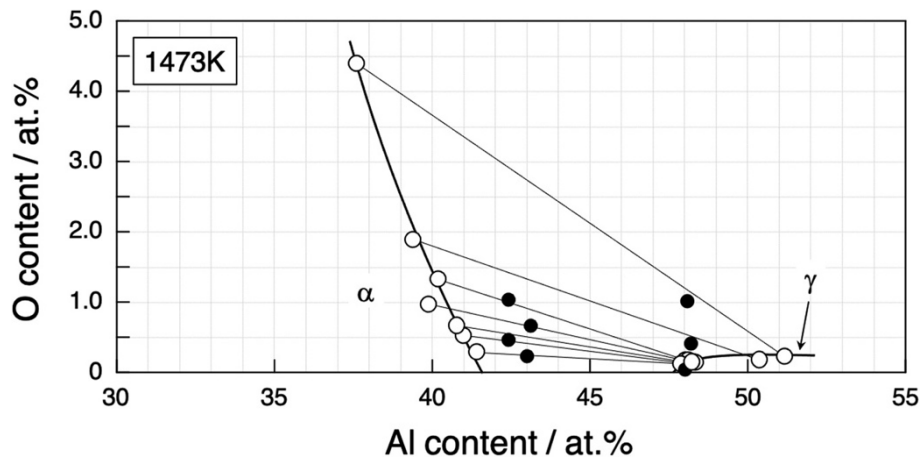
**Fig. 1-11** Schematic relationships between microstructure and grain size (GS) and mechanical properties including fracture toughness, tensile strength, elongation (El), impact resistance (IR) and creep resistance (CR) [21].



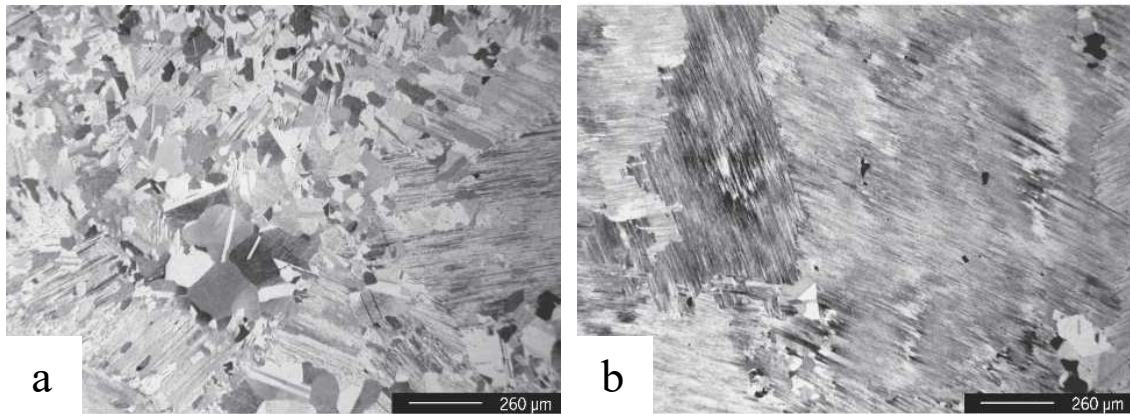
**Fig. 1-12** Three representative microstructures of  $\beta$ -containing TiAl alloy with a composition of Ti-43Al-4Nb-5V [22]: (a, d) Nearly Lamellar (NL), (b, e) Lamellar Triplex (LTL) and (c, f) Nearly Globular  $\beta/\gamma$  Duplex (NGDP).



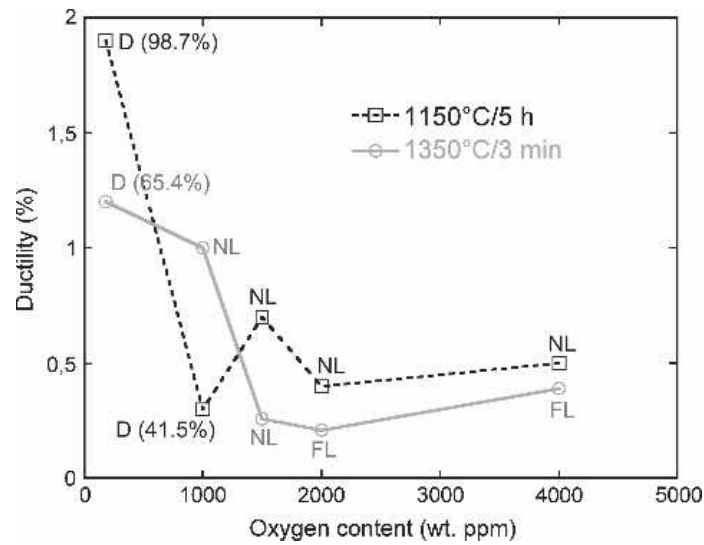
**Fig. 1-13** Fatigue crack growth curves of Ti-43Al-4Nb-5V alloy with microstructures of NL, LTL and NGDP shown in Fig. 1-12 reported by Signori et al. [22], together with GE 48-2-2 alloy with FL microstructure.



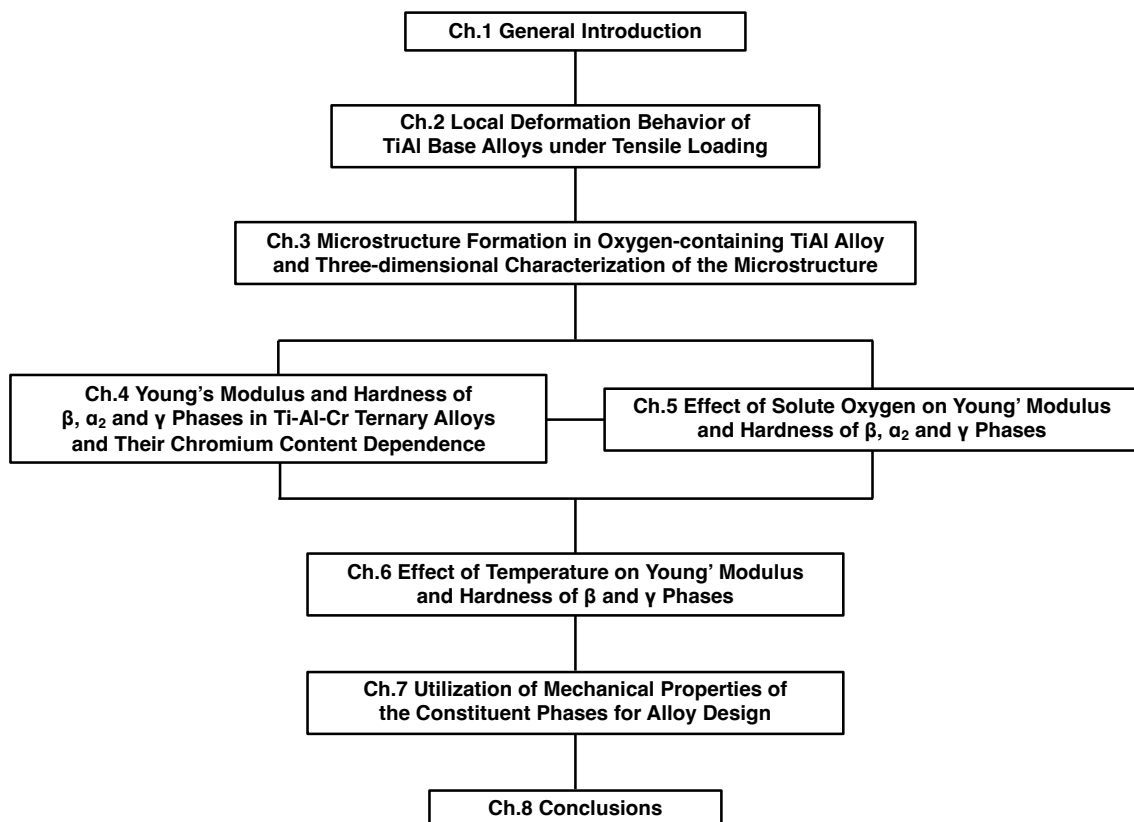
**Fig. 1-14** Partial isothermal section of Ti-Al-O ternary system at 1473 K reported by Nakashima et al. [39].



**Fig. 1-15** Optical micrographs of the Ti-48Al-2Cr-2Nb alloys, cooled and annealed at 1423 K for 5 h and then cooled at 35 K/min, containing (a) 185 and (b) 1500 wt. ppm oxygen, reported by Lamirand et al. [41].



**Fig. 1-16** Change in fracture strain with oxygen content in TiAl alloys. The value in parentheses corresponds to the percentage volume fraction of equiaxed  $\gamma$  grains [41].



**Fig. 1-17** Flowchart of this thesis.

# Chapter 2

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Local Deformation Analysis Using DIC  
Technique under *In-situ* Tensile Test



## 2.1 Introduction

In chapter 1, it was described that the mechanical properties of TiAl alloys strongly depend on the microstructure. It is important to know the local deformation behavior in order to understand the effect of each microstructure constituent in complex microstructures of TiAl alloys. Understanding of the deformation behavior of microstructure constituents leads to an insight into various mechanical behaviors, such as predicting the onset of fracture, as well as microstructural design to improve ductility. In this chapter, the local deformation behavior of  $\alpha_2/\gamma$  lamellar microstructure,  $\beta$  grains and  $\gamma$  grains during tensile loading are investigated using digital image correlation (DIC) technique, and how the deformation takes place in each microstructure is discussed.

## 2.2 Experimental procedure

### 2.2.1 Alloy preparation

One binary alloy of Ti-48Al (at.%) and two quaternary alloys of Ti-43Al-4Nb-5V and Ti-44Al- $xM_1$ - $yM_2$  ( $M_1$ ,  $M_2$ :  $\beta$  stabilizing V or VI group element) were investigated in this chapter. The binary alloy was prepared by centrifugal casting, and the quaternary alloys were prepared by cold crucible induction melting and gravity casting, followed by forging by one stroke at 1573 K. The binary Ti-48Al alloy was first maintained at 1693 K of  $\alpha$  single phase region for 24 h, and then cooled to 1393 K at a rate of 10 K/min followed by air cooling, as schematically shown in **Fig. 2-1**. Two types of heat treatments were conducted to the Ti-43Al-4Nb-5V alloy based on the phase diagram study in Takeyama's research group (**Fig. 2-2**) [1]. For type A, the alloy was first maintained at 1573 K of  $\beta + \alpha$  two-phase region for 1 h followed by air cooling, and then aged at 1173 K for 1h. For type B, the alloy was held at 1373 K of  $\beta$  (B2) +  $\alpha_2 + \gamma$  three-phase region for 42 h. For the Ti-44Al- $xM_1$ - $yM_2$  alloy, two steps of heat treatments were conducted to control the microstructure into  $\beta + \gamma$  two phases based on the phase diagram study (**Fig. 2-3**).

### 2.2.2 Tensile testing

The heat-treated alloys were cut into flat dog-bone shaped specimens shown in **Fig. 2-4**, where the gage length, gage width and thickness are 14, 3 and about 1 mm, respectively, by electrical discharge machine. Then the specimens were mechanically polished with SiC paper and diamond paste, and they were electrically polished using a solution of 90 vol.% ethanol containing 6 vol.% perchloric acid to remove surface damage. Subsequently, speckle patterns were introduced on the polished surface to analyze local strain by DIC. The tensile tests were performed using an *in-situ* type machine in an FE-SEM chamber as shown in **Fig. 2-5**. The macroscopic strain of the specimen was measured from the displacement of cross head of the tensile machine and the distance of markers introduced with a Vickers hardness tester. Due to the compliance of

the tensile machine, the displacement is larger than the actual specimen elongation as described later.

### 2.2.3 Local strain analysis by digital image correlation technique

In-plane strain fields at microstructural scale were obtained by DIC technique. A commercial software, VIC-2D 6, was used, and correlation was done based on zero-normalized squared differences criterion. Secondary electron (SE) images with a resolution of 4096×4096 pixels were taken with FE-SEM for DIC analyses. **Figure 2-6** shows typical SE images and subsets used for DIC analyses. The speckle pattern was introduced by either chemical etching with 0.75 vol.% HF-1.75 vol.% HCL solution (**Figs. 2-6 (a–c)**) or Pt deposition using focused ion beam (**Figs. 2-6 (d–f)**). The subset size, which corresponds to the spatial resolution of strain analysis, is smaller than 2  $\mu\text{m}$ .

## 2.3 Results and discussion

### 2.3.1 Microstructures

**Figure 2-7** shows an optical micrograph and a backscattered electron (BSE) image of Ti-48Al alloy after the heat treatment. This alloy shows  $\alpha_2/\gamma$  fully lamellar microstructure, and the lamellar grain size is larger than 5  $\mu\text{m}$  (**Fig. 2-7 (a)**). The volume fraction of  $\alpha_2$  phase is approximately 10%, and the  $\alpha_2$  lamellar spacing is approximately 1  $\mu\text{m}$  (**Fig. 2-7 (b)**). This microstructure is hereafter referred to as FL (fully lamellar). **Figure 2-8** shows BSE images of Ti-43Al-4Nb-5V alloy after the heat treatments. This alloy after type A heat treatment shows  $\alpha_2/\gamma$  lamellar microstructure with  $\beta/\gamma$  duplex (DP) microstructure on grain boundaries (**Fig. 2-8 (a)**). In contrast, the alloy after type B heat treatment shows globular  $\beta$  and  $\gamma$  phases with small fraction of  $\alpha_2/\gamma$  lamellar grains (**Fig. 2-8 (b)**). These microstructures are hereafter referred to as NL (nearly  $\alpha_2/\gamma$  lamellar) and NGDP (nearly globular  $\beta/\gamma$  duplex), respectively. The microstructural features of NL and NGDP are summarized in **Table 2-1**.

### 2.3.2 Tensile properties

**Figure 2-9** shows an engineering stress-strain curve of FL sample. The slope of the elastic regime is way too low than the actual Young's modulus value of the material since the stiffness of the *in situ* type tensile machine used in this study is small. The tensile strength and elongation are 147 MPa and 0.6%, respectively. The tensile curve of engineering stress versus total strain (elastic + plastic) and plastic strain of the Ti-43Al-4Nb-5V alloys with NL and NGDP microstructures are given in **Fig. 2-10**. The result obtained from a cylindrical specimen with Instron type machine is also shown as a reference [2]. In the stress versus total strain curve (**Fig. 2-10 (a)**), the slope in elastic regime in the NL sample is 16.9 GPa in this study and 137 GPa with

Instron type machine. Again, this difference is caused by the compliance of the tensile machine. The fracture stress and elongation are 761 MPa and 0.14% from *in-situ* type machine and 893 MPa and 0.10% from Instron type machine, and these values are almost identical as shown in the stress versus plastic strain curve (**Fig. 2-10 (b)**). Therefore, the mechanism of deformation and fracture should be the same in the two tests. The NGDP sample shows a larger fracture stress of 871 MPa and elongation of 0.49% than those of the NL sample.

### 2.3.3 Local deformation behavior

#### (a) $\alpha_2/\gamma$ lamellar microstructure

**Figure 2-11** shows a BSE image of FL sample before the tensile test and a corresponding strain map after the tensile fracture. The loading axis is horizontal. The strain map shows levels of the normal strain component along the loading axis ( $\epsilon_{xx}$ ) by color. The deformation takes place along the lamellar orientation in an inhomogeneous manner. Some regions show no strain (purple color), whereas other regions locally show strain higher than 10% (red color) even though the macroscopic strain is only 0.5%. **Figure 2-12** shows a strain profile along the white arrow shown in **Fig. 2-11**. The black broken lines represent the  $\gamma/\gamma$  lamellar interfaces, and the red bands represent the  $\alpha_2$  lamellae. Note that these lamellar interfaces are identified from the BSE image which is manually superimposed on the strain map. The localized strain tends to occur on the vicinities of the  $\alpha_2/\gamma$  and  $\gamma/\gamma$  lamellar interfaces.

**Figure 2-13** shows a BSE image of NL sample and a corresponding strain map. The deformation is localized along the lamellae in this sample as well. The deformation behavior of lamellar microstructure in this sample seems to be the same as the binary FL sample.

The deformation in the  $\alpha_2/\gamma$  lamellar microstructure probably occurs by the dislocation motion in longitudinal direction since the strain is localized along the lamellar interfaces (**Fig. 2-11**). Besides, the dislocation motion would be enhanced by the existence of lamellar interfaces (**Fig. 2-12**). Umeda et al. has reported that the finer lamellar structure leads to larger tensile elongation [3]. This enlargement of elongation could be caused by the deformation enhancement by lamellar interfaces observed in the present study. Several reasons, such as misfit strain along interfaces and elastic modulus difference between adjacent lamellae, can be cited for this phenomenon, but the precise mechanism is still unclear. However, the author suggests this deformation enhancement by lamellar interfaces can be utilized for improvement of mechanical properties.

#### (b) $\beta/\gamma$ duplex microstructure

**Figure 2-14** shows a BSE image of NGDP sample before the tensile test and a corresponding strain map after the tensile fracture. In this microstructure, localized deformation

occurs in  $\gamma$  grains and in  $\beta$  phase regions near  $\beta/\gamma$  phase boundaries although the grain interior of  $\beta$  phase shows no obvious strain. The magnitude of strain in  $\beta$  and  $\gamma$  is approximately 7% at maximum. Average strain of each phase in the area shown in **Fig. 2-14** was calculated from DIC result in conjunction with EBSD analysis and is shown in **Fig. 2-15**.  $\gamma$  phase shows higher strain than the other phases of  $\beta$  and  $\alpha_2$  by a factor of 2.5–3.

A high magnification SE image and the corresponding strain map of the  $\gamma$  grain region indicated in **Fig. 2-14** are shown in **Fig. 2-16**. Four  $\{111\}$  plane traces and the maximum Schmid factors for  $\{111\} \langle 1\bar{1}0 \rangle$  slip system for each plane are shown in **Fig. 2-16 (a)**. Note that the  $\langle 1\bar{1}0 \rangle$  and  $\langle 10\bar{1} \rangle$  directions are not distinguished because the  $\gamma$  phase was characterized as fcc structure in EBSD analysis. In the  $\gamma$  grains, slip lines or micro twins are observed along the  $\{111\}$  plane traces with high Schmid factor, and high strain localized regions also lie along these plane traces.

**Figure 2-17** shows a high magnification backscattered electron image and the corresponding strain map near the  $\beta/\gamma$  phase boundary region indicated in **Fig. 2-14**. Slip lines or micro twins, and high strain regions along them are observed in the  $\gamma$  grain as described earlier. On the other hand, the  $\beta$  phase region near the  $\beta/\gamma$  phase boundary shows high strain localization whereas the grain interior of the  $\beta$  phase shows no obvious deformation feature.

The yield strength of the  $\beta$  phase is generally much higher than the  $\gamma$  phase at room temperature because  $\beta$  is ordered into the B2 structure. Thus, the strain in  $\beta$  phase regions near phase boundaries shown in **Fig. 2-17** is suggested to be caused by the stress concentration at the phase boundaries which comes from plastic strain in  $\gamma$  grains.

#### 2.3.4 Enhancement of ductility by $\beta$ phase

The  $\gamma$  phase is the most deformable phase in the NGDP sample as described in section 2.3.3. Thus, it is suggested that the  $\gamma$  single phase alloys show high ductility. However, it was demonstrated that an equiaxed  $\gamma$  single phase alloy shows only 0.06% elongation and the strength of this alloy is also much lower than the  $\beta$  containing alloys [4]. The fracture surface of the  $\gamma$  single phase alloy partly shows grain boundary fracture. This indicates that the  $\gamma/\gamma$  grain boundaries are weaker than the  $\beta/\gamma$  phase boundaries and the  $\gamma$  single phase alloys break from grain boundaries before deforming.

The  $\beta$  phase deforms only near the phase boundaries in  $\beta/\gamma$  two phase regions. This suggests that high stress concentration was produced at phase boundaries because of the dislocation pile-ups resulted from the deformation in the  $\gamma$  phase. This stress concentration would induce activation of multiple deformation systems of the  $\gamma$  phase as well as deformation of  $\beta$  phase. This means  $\beta/\gamma$  phase boundaries enhances the room temperature ductility of TiAl alloys although  $\beta$  phase itself is less deformable than  $\gamma$ . Therefore, the high volume fraction of  $\gamma$  grain

and introduction of the  $\beta$  phase in platelet morphology should be effective for enhancement of room temperature ductility in  $\beta$  containing TiAl alloys. Based on this idea, a different microstructure was designed using Ti-44Al- $x$ M<sub>1</sub>- $y$ M<sub>2</sub> as shown in **Fig. 2-18**. This microstructure shows a high volume fraction of  $\gamma$  phase (79%) and mostly platelet  $\beta$  phase. The fracture stress and elongation of this sample are 701 MPa and 0.76%, respectively, with *in-situ* type tensile machine and 812 MPa and 1.4%, respectively, with Instron type tensile machine, as shown in **Fig. 2-19**. Thus, the alloy with this microstructure shows higher ductility than the NL and NGDP sample.

## 2.4 Summary

The local deformation behavior of  $\alpha_2/\gamma$  lamellar microstructure,  $\beta$  grains and  $\gamma$  grains during tensile loading were investigated using digital image correlation (DIC) technique, and a design concept of high ductility TiAl alloy was introduced. The following conclusions were obtained in this chapter:

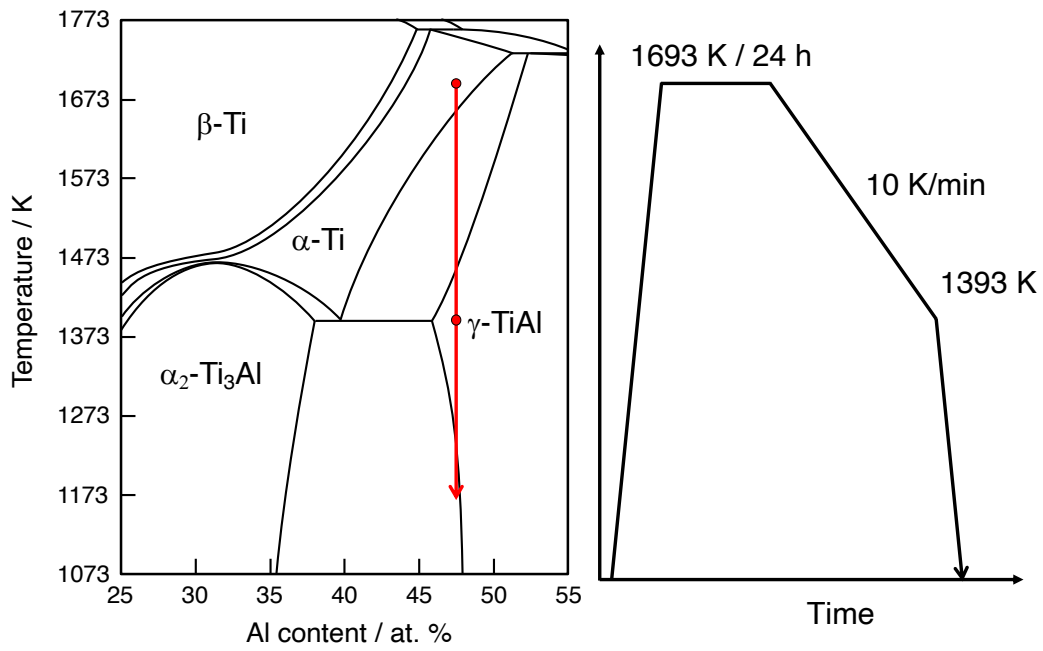
1. In the  $\alpha_2/\gamma$  lamellar microstructure, the deformation occurs inhomogeneously in the  $\gamma$  plates along the longitudinal direction, and the localized deformation tends to lie on the vicinities of the  $\alpha_2/\gamma$  and  $\gamma/\gamma$  lamellar interfaces.
2. In the  $\beta/\gamma$  duplex microstructure, the deformation occurs mainly along  $\{111\}$  planes with high Schmid factor of the  $\gamma$  grains. The  $\beta$  phase regions near  $\beta/\gamma$  phase boundaries also show high strain localization, and this is caused by stress concentration at phase boundaries from plastic deformation in  $\gamma$  grains.
3. High volume fraction of  $\gamma$  phase and high density of  $\beta/\gamma$  phase boundaries are effective for enhancement of room temperature ductility in TiAl based alloys.

## References

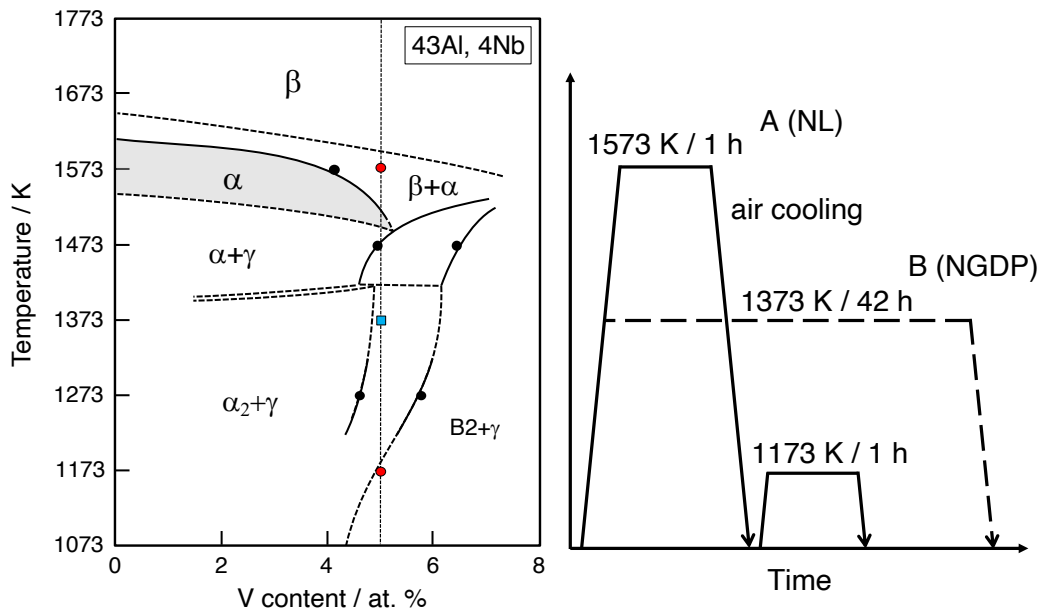
- [1] H. Nakashima, Phase Equilibria in the Quaternary TiAl Alloys with the Combined Addition of Substitutional Elements — Phase Stability of High and Low-temperature  $\beta$ -Ti Phase — , Doctoral Thesis, Tokyo Institute of Technology, 2015. [http://t2r2.star.titech.ac.jp/cgi-bin/publicationinfo.cgi?lv=en&q\\_publication\\_content\\_number=CTT100682866](http://t2r2.star.titech.ac.jp/cgi-bin/publicationinfo.cgi?lv=en&q_publication_content_number=CTT100682866) (accessed December 17, 2024).
- [2] S. Usui, H. Nakashima, S. Kobayashi, M. Takeyama, In-situ Observation of Deformation and Cracking Behavior in TiAl alloy with Lamellar Microstructure Decorated by  $\beta/\gamma$  Dual Phase, Report of the 123rd Committee on Heat-Resisting Materials and Alloys 56 (2015) 87–97.
- [3] H. Umeda, K. Kishida, H. Inui, M. Yamaguchi, Effects of Al-concentration and lamellar spacing on the room-temperature strength and ductility of PST crystals of TiAl, Materials Science and Engineering: A 239–240 (1997) 336–343. [https://doi.org/10.1016/S0921-5093\(97\)00601-1](https://doi.org/10.1016/S0921-5093(97)00601-1).
- [4] R. Yamagata, Y. Okada, H. Wakabayashi, H. Nakashima, M. Takeyama, Microstructure Design for Enhancement of Room-temperature Ductility in Multi-component TiAl Alloys, MRS Adv 4 (2019) 1523–1529. <https://doi.org/10.1557/adv.2019.230>.

**Table 2-1** Microstructural features of Ti-43Al-4Nb-5V alloy with NL and NGDP microstructures.

| Microstructure | $\alpha_2/\gamma$ lamellar colonies |                      | $\beta/\gamma$ Duplex |                      |                | $\beta/\gamma$ ratio |
|----------------|-------------------------------------|----------------------|-----------------------|----------------------|----------------|----------------------|
|                |                                     |                      | $\gamma$ grains       |                      | $\beta$ grains |                      |
|                | Fraction / %                        | Size / $\mu\text{m}$ | Fraction / %          | Size / $\mu\text{m}$ | Fraction / %   |                      |
| NL             | $89.6 \pm 0.4$                      | $101.8 \pm 34.9$     | $6.4 \pm 0.4$         | $4.8 \pm 1.4$        | $4.0 \pm 0.4$  | 0.63                 |
| NGDP           | $5.8 \pm 1.2$                       | $13.9 \pm 2.6$       | $73.7 \pm 2.4$        | $16.4 \pm 5.1$       | $20.5 \pm 3.5$ | 0.28                 |

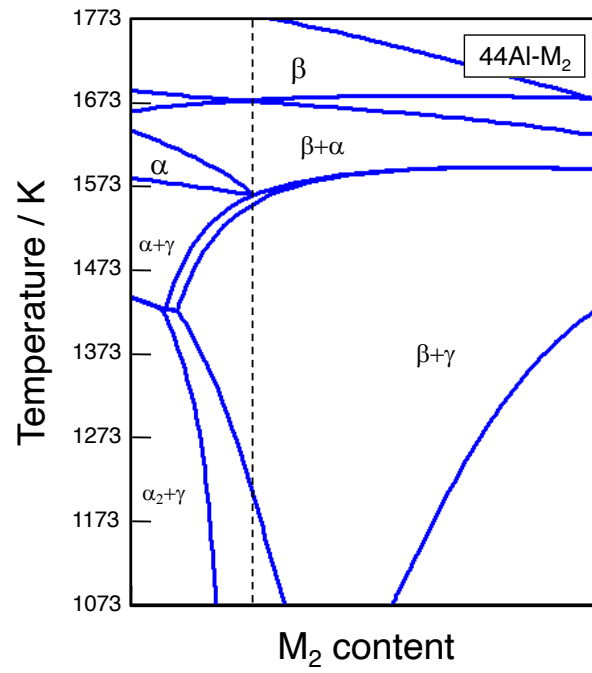


**Fig. 2-1** Ti-Al binary phase diagram and schematic diagram of heat treatment on Ti-48Al alloy.

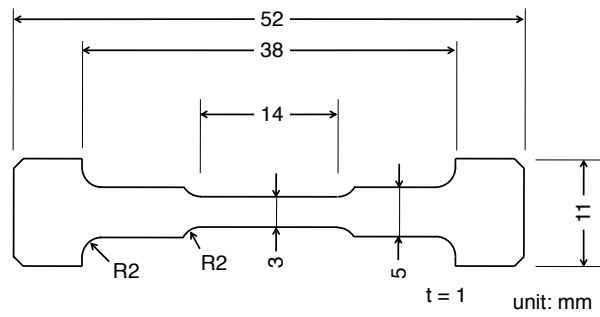


**Fig. 2-2** Vertical section of Ti-Al-Nb-V quaternary phase diagram at 43 at.% Al-4 at.% Nb [1] and schematic diagram of heat treatments on Ti-43Al-4Nb-5V alloy.

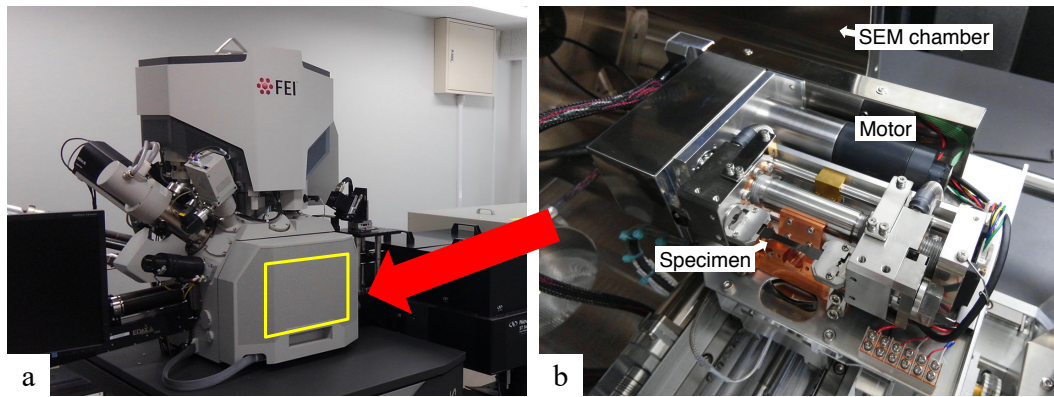




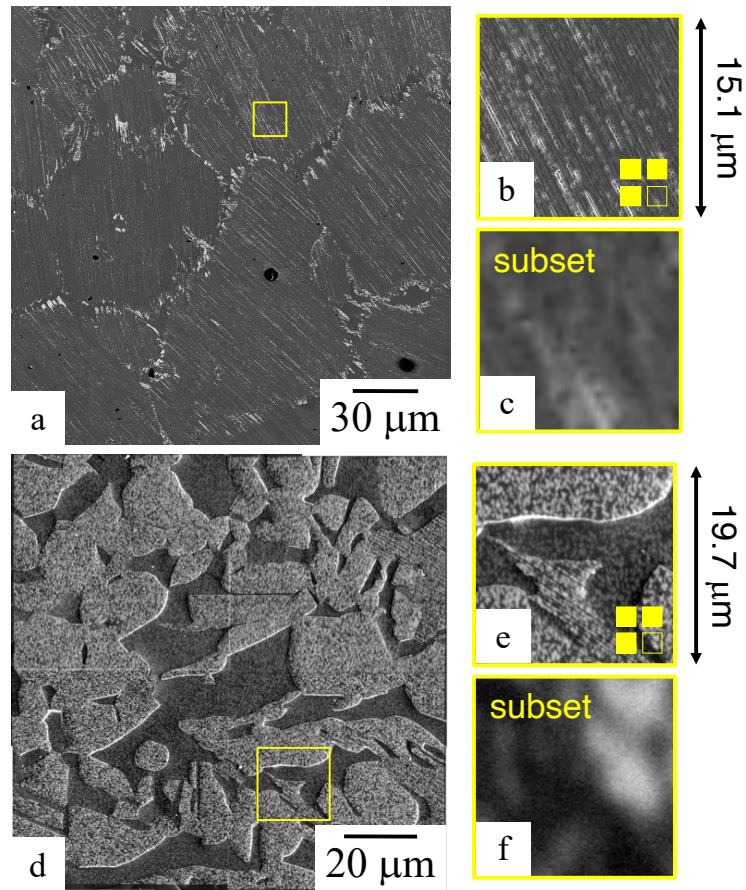
**Fig. 2-3** Vertical section of Ti-Al- $M_1$ - $M_2$  quaternary phase diagram at 44 at.% Al-x at.%  $M_1$ .



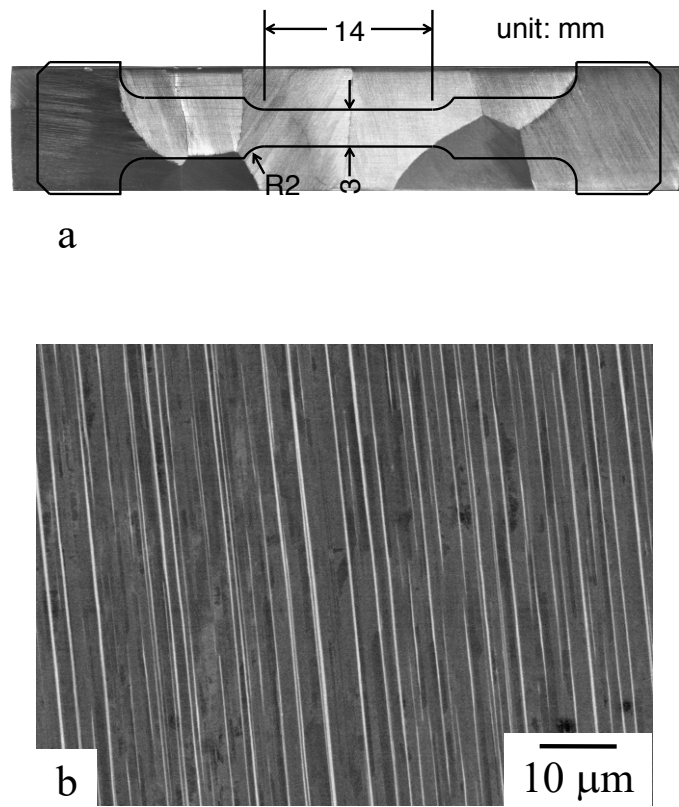
**Fig. 2-4** Dimension of the flat dog-bone shaped tensile specimen used in this study.



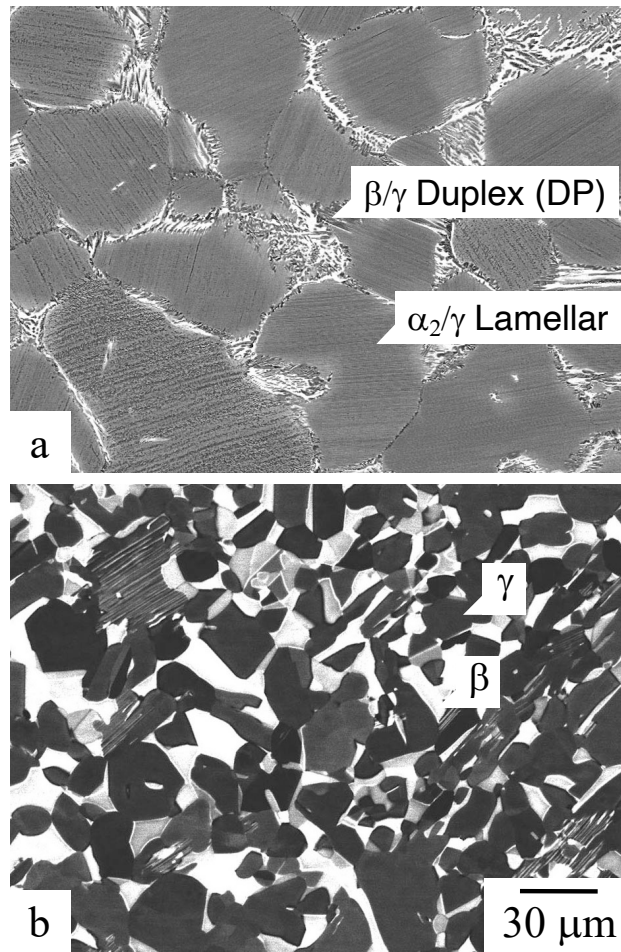
**Fig. 2-5** Appearance of (a) FE-SEM and (b) *in-situ* type tensile machine used in this study.



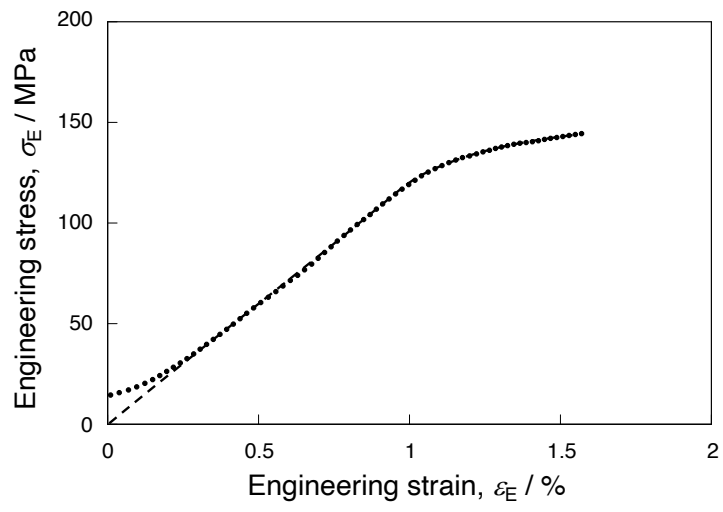
**Fig. 2-6** Reference images for DIC analysis and subset for each image: (a–c) NL and (d–f) NGDP.



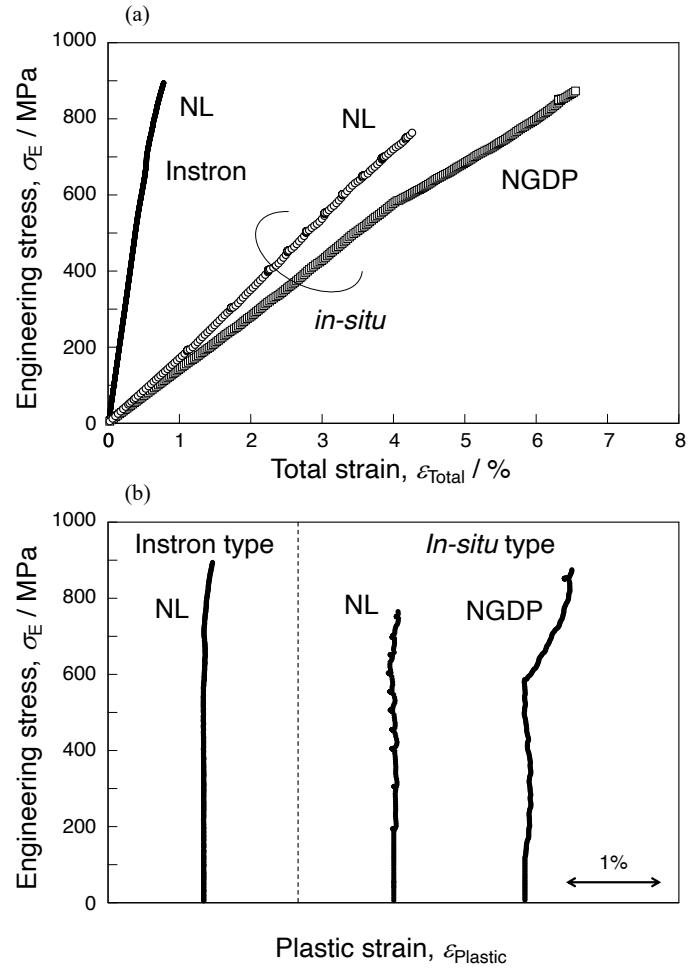
**Fig. 2-7** (a) Optical and (b) backscattered electron (BSE) micrographs of Ti-48Al alloy after the heat treatment, exhibiting a fully lamellar microstructure.



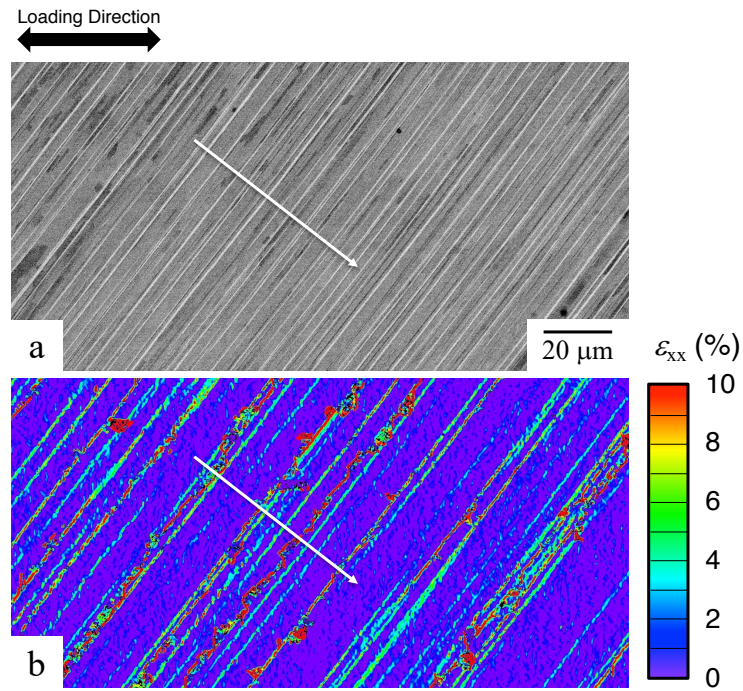
**Fig. 2-8** BSE micrographs of Ti-43Al-4Nb-5V alloys after (a) type A heat treatment, showing NL microstructure and (b) type B heat treatment, showing NGDP microstructure.



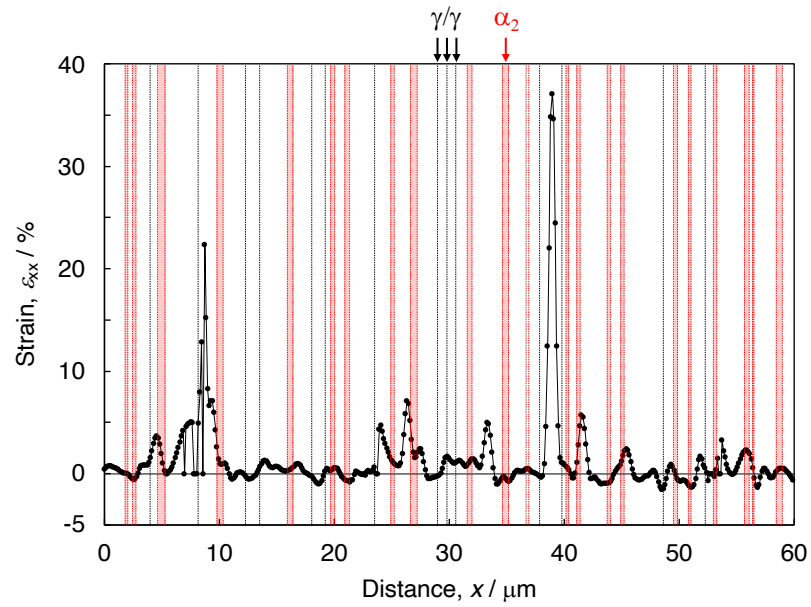
**Fig. 2-9** Stress-strain curve of the FL sample.



**Fig. 2-10** Stress-strain curves of NL and NGDP sample together with the result of NL sample obtained with Instron type machine [2]: (a) Engineering stress versus total strain, and (b) engineering stress versus plastic strain.

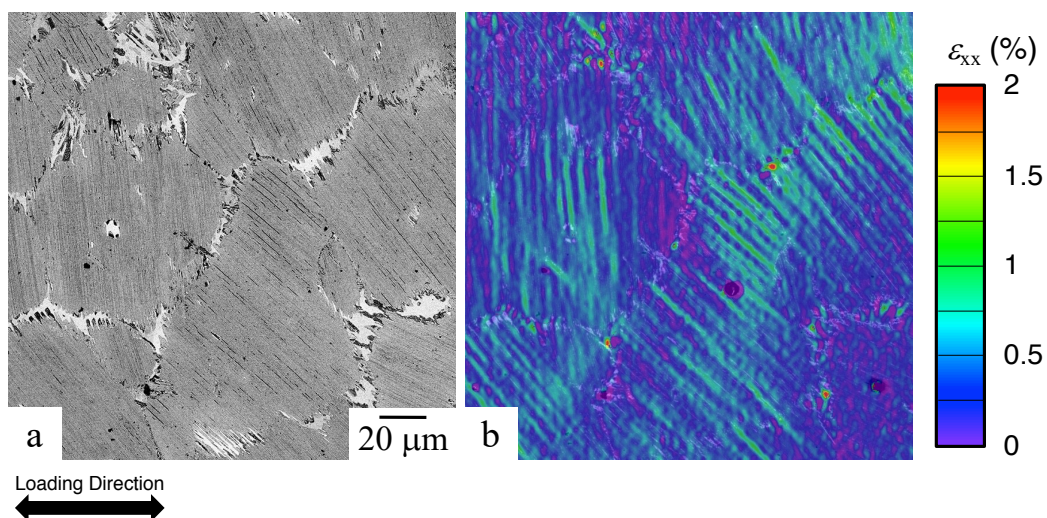


**Fig. 2-11** (a) BSE micrograph of FL sample before tensile loading and (b) strain map for corresponding region after fracture calculated by DIC.

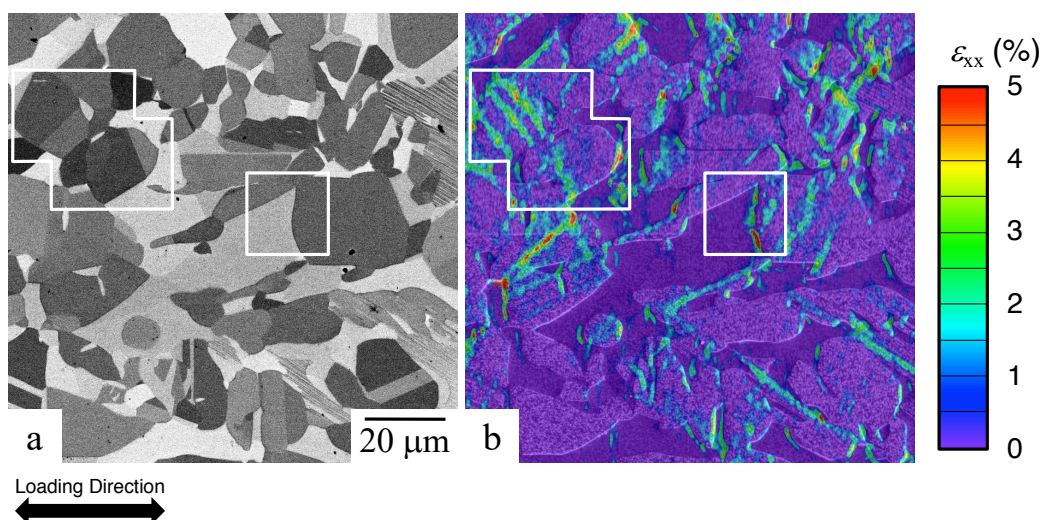


**Fig. 2-12** Strain along the white arrow shown in Fig. 2-11.



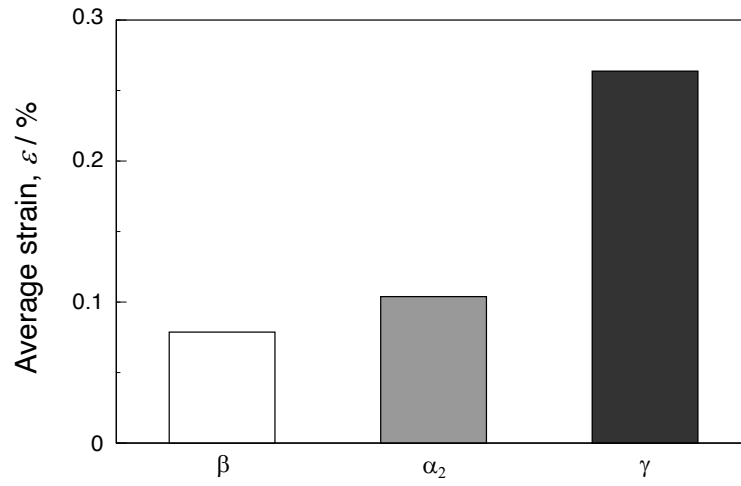


**Fig. 2-13** (a) BSE micrograph of NL sample before tensile loading and (b) strain map for corresponding region after fracture calculated by DIC.

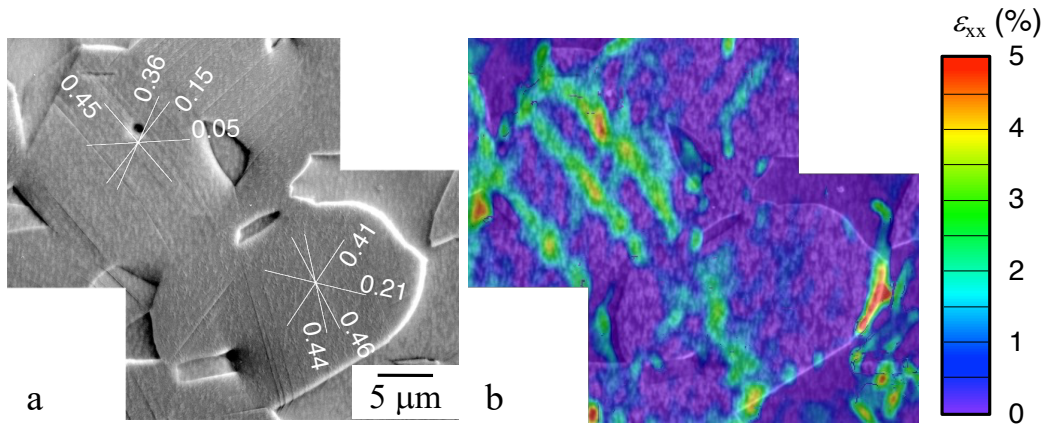


**Fig. 2-14** (a) BSE micrograph of NGDP sample before tensile loading and (b) strain map for corresponding region after fracture calculated by DIC.

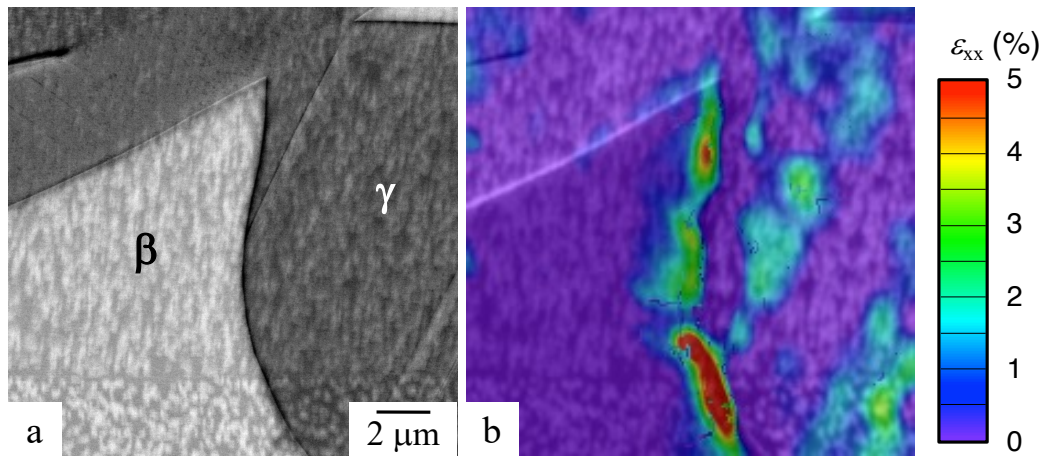




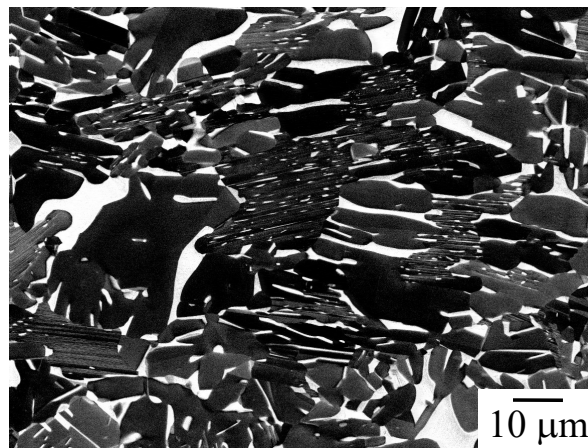
**Fig. 2-15** Average strain of each phase calculated in the area of Fig. 2-14 by DIC.



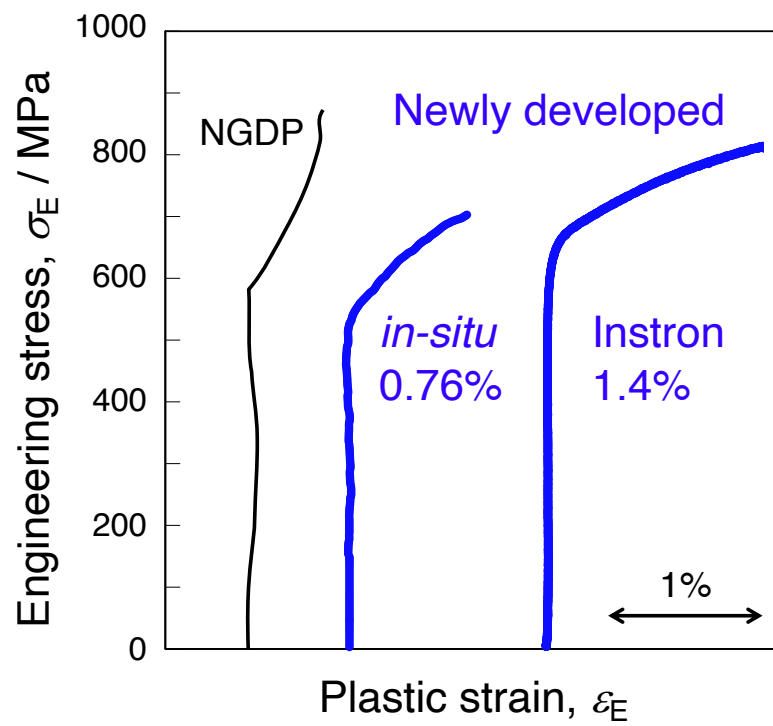
**Fig. 2-16** High magnification of (a) secondary electron image and (b) strain map after fracture in  $\gamma$  grain region shown in Fig. 2-14.  $\{111\}$  plane traces and the maximum Schmid factor for each  $\{111\}$  plane are shown in (a).



**Fig. 2-17** High magnification of (a) BSE image and (b) strain map after fracture near  $\beta/\gamma$  phase boundary region shown in Fig. 2-14.



**Fig. 2-18** BSE micrograph of Ti-44Al-xM<sub>1</sub>-yM alloy after heat treatment.



**Fig. 2-19** Stress-plastic strain curves of Ti-44Al-xM<sub>1</sub>-yM alloy with newly designed microstructure, together with NGDP sample.

# Chapter 3

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Formation and Characterization of  $\beta$ -Ti Phase  
in TiAl Alloys without and with Oxygen

### 3.1 Introduction

In chapter 2, the  $\beta$  phase or the  $\beta/\gamma$  cellular microstructure was found to be effective for enhancement in mechanical properties. However, it has been reported that the oxygen in TiAl alloys suppresses the formation of  $\beta$  phase and stabilizes the  $\alpha_2/\gamma$  lamellar microstructure [1]. We need to investigate the effect of oxygen on the  $\beta$  phase formation.

Kobayashi et al. has reported following two types of formation mode of the  $\beta$  phase from the  $\alpha$  phase, depending on the alloy composition: (1) a pearlitic mode where both  $\beta$  and  $\gamma$  phases simultaneously precipitate ( $\alpha \rightarrow \beta + \gamma$ ) and (2) a sequential mode where  $\gamma$  plates precipitate first followed by the  $\beta$  phase formation ( $\alpha \rightarrow \alpha + \gamma \rightarrow \beta + \gamma$ ) [2]. The  $\beta/\gamma$  cellular microstructure shown in chapter 2 was formed through the type 1 mode. In contrast, in the type 2 mode, the  $\beta$  phase forms along the lamellar microstructure. It has been demonstrated that both types of  $\beta$  phase formation are effective for the mechanical properties.

In this chapter, the microstructure formation in an oxygen-containing TiAl alloy was investigated, especially focusing on the  $\beta$  phase, and the obtained microstructure was characterized by three-dimensional observation.

### 3.2 Experimental procedure

#### 3.2.1 Alloy preparation

An alloy with a nominal composition of Ti-45Al-6Cr-0.75O (at.%) was investigated in this chapter. This alloy was prepared by cold crucible induction melting and gravity casting, followed by forging by one stroke at 1573 K. The oxygen was intentionally added by using  $\text{TiO}_2$  to control its concentration to a level of that in the MIM-processed alloys. Two steps of heat treatments were employed to the forged alloy based on the experimental phase diagram in Takeyama's group, as shown in **Figs. 3-1 and 3-2**. For the first step, the alloy was maintained at 1573 K for 24 h and cooled to 1523 K slowly at a rate of 0.5 K/min, followed by air cooling. In this step, the  $\beta + \alpha$  two-phase microstructure forms at high temperature and the  $\alpha$  phase grows during controlled cooling. Secondly, the alloy was aged at 1273 K for 3 to 100 h to precipitate the  $\beta$  phase.

#### 3.2.2 Microstructure observation

The as-forged microstructure and heat-treated microstructures were observed with a field emission scanning electron microscope (FE-SEM). The volume fraction of the  $\beta/\gamma$  cellular microstructure was measured by drawing grid lines on the image and counting the number of intersections on the microstructure.

#### 3.2.3 Three-dimensional observation

The microstructure of the sample aged for 3 h was also observed in three dimensions (3D). The sample preparation and observation procedure are described in this subsection.

The heat-treated alloy was cut into a cylindrical shape with a diameter of 3 mm by electrical discharge machine (EDM) and sliced into a 200  $\mu\text{m}$ -thick disc by fine cutter. Subsequently, the disc was mechanically polished with a SiC paper followed by electro-polishing in a solution of 10 vol.% perchloric acid-ethanol using a twin jet polisher to make a thin film with a hole of about 250  $\mu\text{m}$ . The electro-polishing was conducted under conditions of 248 K for temperature, 22 V for voltage and 10 mA for electric current. The film was cut into two pieces as shown in **Fig. 3-3**. One of the cut pieces was attached on a pre-tilted holder with silver paste, and the holder was set in an SEM chamber equipped with a focused ion beam (FIB), as schematically shown in **Fig. 3-4**. By emitting  $\text{Ga}^+$  ion beam perpendicularly, the film was milled, and a pillar of  $20 \times 20 \times 20 \mu\text{m}$  in size was prepared for 3D observation, as shown in **Fig. 3-5**. The area of interest was protected with platinum deposition prior to the ion milling in order to prevent from damage by FIB.

The cross section microstructure of the pillar was analyzed with electron backscatter diffraction (EBSD) technique prior to the 3D observation. After that, a serial sectioning method using FIB and FE-SEM was applied to the pillar. By repeating the milling by FIB and imaging by FE-SEM, the microstructure was observed in three dimensions. The milling thickness was set to 20 nm per slice, and 568 slices were observed in total. The acceleration voltage and the probe current are 30 kV and 0.5 nA, respectively, for FIB milling and 5 kV and 3.2 nA, respectively, for SEM imaging. The obtained 568 images were reconstructed into a three-dimensional image. After the serial sectioning observation, the pillar was milled with weaker beam conditions of 5 kV for the acceleration voltage and 0.77 nA for the probe current. Then, the EBSD orientation analysis was conducted on the cross section. The reason for weak beam milling is described in section 3.3.2.

### 3.3 Results and discussion

#### 3.3.1 Microstructure change during heat treatments

**Figure 3-6** shows backscattered electron (BSE) micrographs of the as-forged sample of Ti-45Al-6Cr-0.75O. The microstructure consists of  $\alpha_2/\gamma$  lamellar grains with granular  $\beta$  and  $\gamma$  phases surrounding the lamellar grains. The lamellar grains exhibit a flattened shape perpendicular to the forging direction, and the length of major and minor axes is approximately 30 and 10  $\mu\text{m}$ .

**Figure 3-7** shows BSE images of the sample after the first-step heat treatment (1573 K for 24 h and controlled cooling to 1523 K, followed by air cooling). The microstructure consists of  $\alpha_2/\gamma$  lamellar grains with  $\beta + \gamma$  two-phase microstructure on the grain boundaries. The lamellar

grains exhibit a nearly circular (or spherical) shape, and the grain size is approximately 50  $\mu\text{m}$ . The  $\beta + \gamma$  two-phase microstructure can be divided into two types of  $\beta$ -dominant and  $\gamma$ -dominant microstructures. It can be deduced that the  $\beta$ -dominant microstructure was the  $\beta$  phase at high temperatures of 1573–1523 K, and the  $\gamma$  phase was precipitated during the air cooling, according to the phase diagram (**Fig. 3-1**). This region is hereafter referred to as prior  $\beta$ . The  $\gamma$ -dominant microstructure is called  $\beta/\gamma$  cell, and this microstructure was formed during cooling. The area fraction of the prior  $\beta$  phase region and the  $\beta/\gamma$  cell region is 11.4 and 4.4%.

**Figure 3-8** shows BSE micrographs of the sample aged at 1273 K. Compared to the first-step heat-treated sample, the  $\beta/\gamma$  cell region expands with aging time, and the fine  $\beta$  particles precipitates along the lamellae in the  $\alpha_2/\gamma$  lamellar grains at all the aging time of 3, 10 and 100 h. By 3 h of aging at 1273 K, the area fraction of the  $\beta/\gamma$  cell region increases from 4.4 to 24.1%, and at the aging time of 100 h, it reaches 79.2%. Also, the spacing between  $\beta$  and  $\gamma$  phases in the cell gets wider with aging time. **Figure 3-9** shows the change in volume fraction of the  $\beta/\gamma$  cell in prior  $\alpha$  grains with aging at 1273 K in Ti-45Al-6Cr-0.75O alloy, together with that in Ti-44Al-4Cr and Ti-45Al-6Cr alloys with no intentional oxygen addition reported by Wakabayashi [3]. As of the first-step heat treatment (aging time = 0 h), the volume fraction of the cell in Ti-45Al-6Cr-0.75O alloy is significantly lower than that in no oxygen alloys. This means that the formation of the  $\beta/\gamma$  cell during the air cooling of first-step heat treatment is suppressed by the oxygen addition. This would be due to the reduction of supersaturation by the phase equilibrium change and the suppression of Cr atoms diffusion by the interstitial oxygen atoms. After the first-step heat treatment, the cell volume can be controlled to a preferred value by aging to satisfy the required mechanical properties. Therefore, the microstructure control range is expanded by the addition of oxygen.

### 3.3.2 Three-dimensional characterization of $\alpha_2/\gamma$ lamellar microstructure with $\beta$ precipitates

In this section, the results of the 3D observation of the sample aged for 3 h is presented focusing on the  $\beta$  precipitates on the lamellar interfaces, and the characteristic is discussed.

**Figure 3-10** shows BSE images before and after the serial sectioning and corresponding phase and inverse pole figure (IPF) maps obtained from EBSD analysis. In the EBSD analysis before the serial sectioning, almost whole surface was indexed as  $\alpha_2$  phase ( $\text{D0}_{19}$ , ordered hcp) (**Figs. 3-10 (b) and (c)**). This should be due to the transformation induced by FIB damage. After the serial sectioning, therefore, the pillar was milled with smaller acceleration voltage of 5 kV prior to EBSD analysis. Consequently, the result that seems correct was obtained (**Figs. 3-10 (e) and (f)**).

**Figure 3-11** shows a high magnification BSE micrograph of the  $\alpha_2/\gamma$  lamellar microstructure with  $\beta$  precipitates. Most of the  $\beta$  phase are in contact with an  $\alpha_2$  lamella, and they

grow toward the adjacent  $\gamma$  lamella, whereas it looks like some of the  $\beta$  phase are not on  $\alpha_2$  lamellae, as indicated with white arrows in **Fig. 3-11**.

**Figure 3-12** shows the reconstructed 3D BSE image and several selected images of lamellar interfaces in the reconstructed image, and **Fig. 3-13** shows  $\beta$  precipitates extracted from one lamellar interface corresponding to **Fig. 3-12 (f)**. The  $\beta$  precipitates exhibit an elongated plate-like shape, and they show Widmanstätten pattern. The size is approximately 1  $\mu\text{m}$  in width, 10  $\mu\text{m}$  in length and 100 nm in thickness. The precipitation density is different for each lamellar interface.

**Figure 3-14** shows one lamellar interface corresponding to **Fig. 3-12 (f)**, observed from the plane normal, and the corresponding stereographic projection of the  $\gamma$  phase obtained from the EBSD analysis. In this lamellar interface, six variants of the  $\beta$  phase exist, and the longitudinal directions of the precipitates are offset by approximately  $\pm 12.5^\circ$  from the  $\langle 110 \rangle$  directions of the  $\gamma$  phase. It has been reported that there is Kurdjumov-Sachs (K-S) orientation relationship, where close-packed planes and directions of two phases are parallel, between the  $\gamma$  lamella and the continuous precipitated  $\beta$  phase along the lamellar interface, as schematically shown in **Fig. 3-15** [4]. The three  $\langle 110 \rangle$  directions of a (111) plane in the  $\gamma$  phase are parallel to the two  $\langle 111 \rangle$  directions of a (110) plane in the  $\beta$  phase, and consequently, the six variant were produced.

### 3.4 Summary

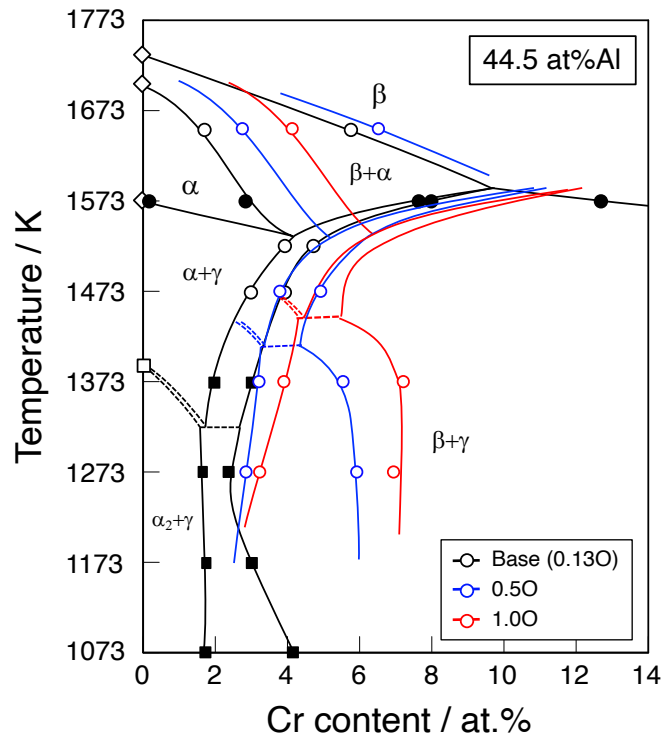
The microstructure formation in an oxygen-containing TiAl alloy was investigated, especially focusing on the  $\beta$  phase on lamellar grain boundaries and along lamellar interfaces. Also, the  $\alpha_2/\gamma$  lamellar microstructure with the  $\beta$  precipitates on lamellar interfaces was observed using a serial sectioning technique in 3D, and the characteristic of the precipitated  $\beta$  phase was investigated. The following conclusions were obtained in this chapter:

1. The microstructure control using the  $\beta/\gamma$  cellular precipitation and the  $\beta$  phase precipitation along lamellar interfaces is possible even in the TiAl alloys containing certain amount of oxygen.
2. The cellular precipitation reaction during cooling from high temperature  $\beta + \alpha$  region is suppressed by the addition of oxygen. As a consequence of the suppression of cellular reaction, the control range of volume fraction of the cellular microstructure is expanded.
3. The  $\beta$  phase precipitates along the lamellar interfaces exhibit an elongated plate-like shape, and they have six orientation variants, showing Widmanstätten pattern.

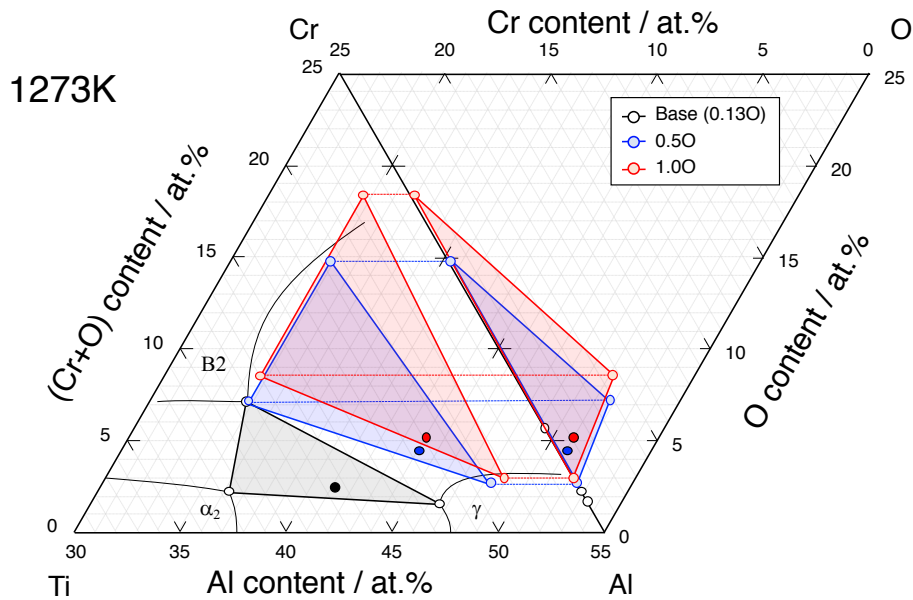


## References

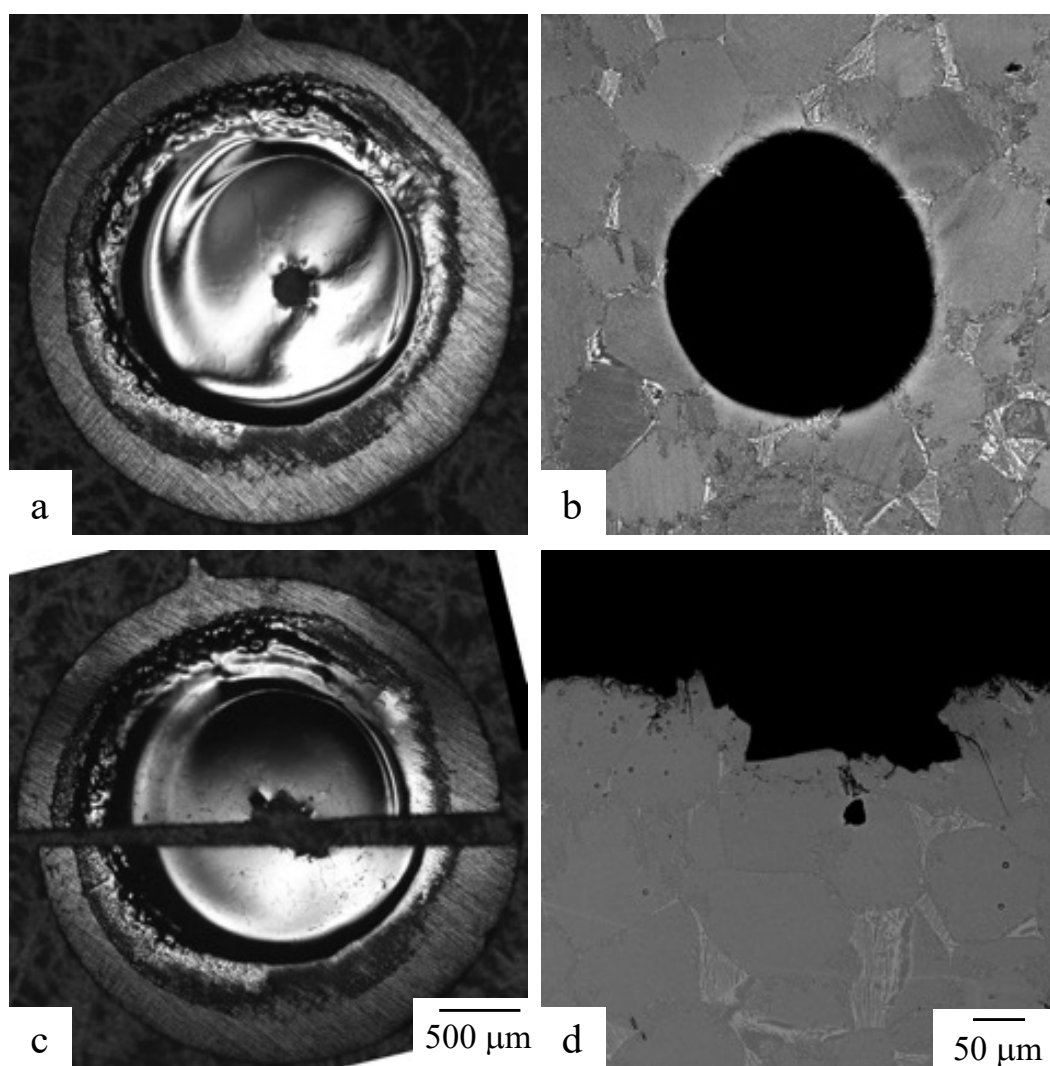
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- [4] H. Fukushima, S. Kobayashi, T. Matsuo, M. Takeyama, Transmission Electron Microscopy and Formation Mechanism of  $\beta$ -Ti Phase Precipitated within Lamellae in Ti-47Al-2.5Mo, Report on the 123rd Committee on Heat-Resisting Materials and Alloys, Japan Society for Promotion of Science Vol. 45 (2004) 327–335.



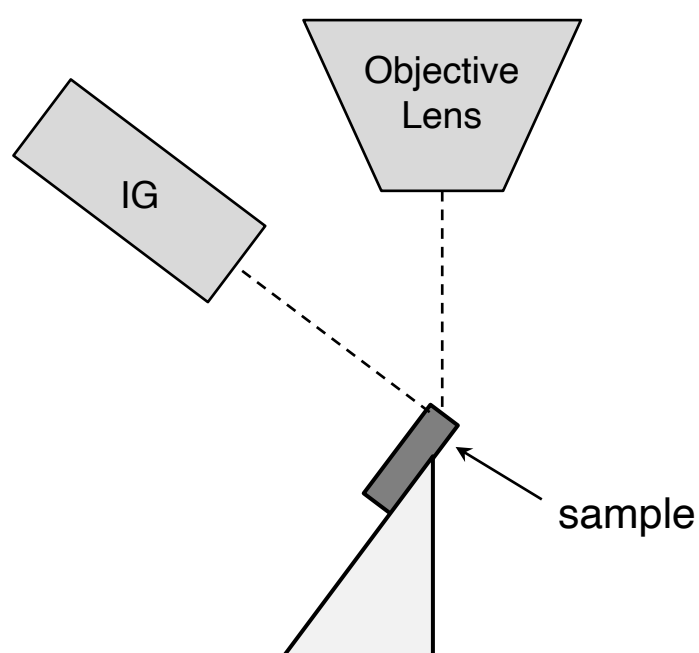
**Fig. 3-1** Vertical section of Ti-Al-Cr ternary system at 44.5 at.% Al without oxygen and with 0.5 and 1.0 at.% oxygen.



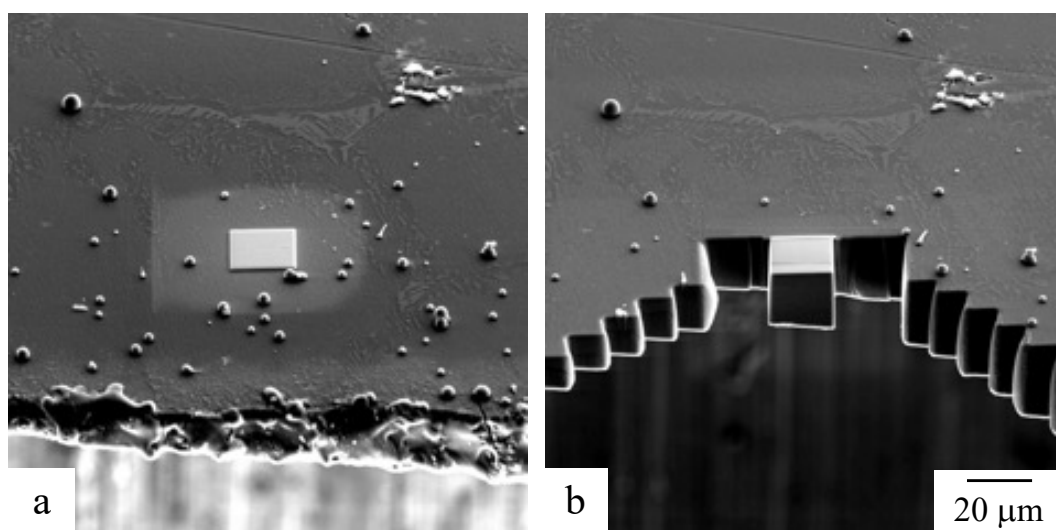
**Fig. 3-2** Parallel projection of  $\beta + \alpha_2 + \gamma$  three-phase tie triangles in Ti-Al-Cr-O quaternary system at 1273 K.



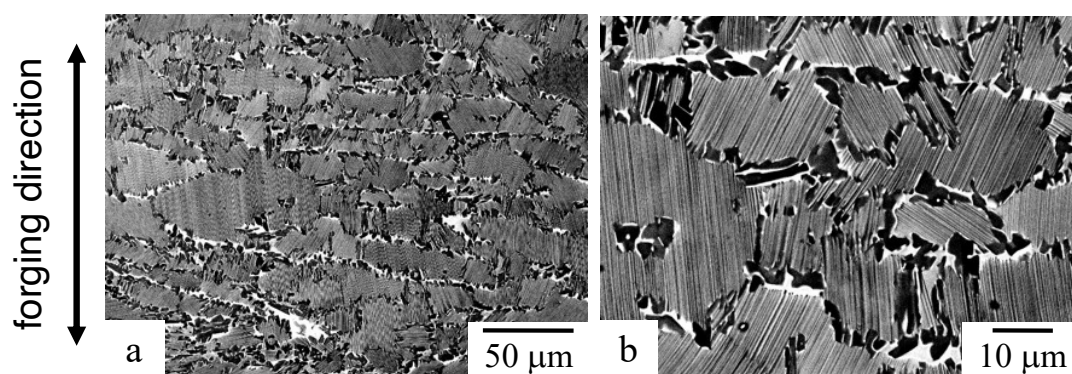
**Fig. 3-3** (a, c) Optical micrographs and (b, d) backscattered electron (BSE) micrographs of the thin film used for three-dimensional observation (a, b) before and (c, d) after cutting.



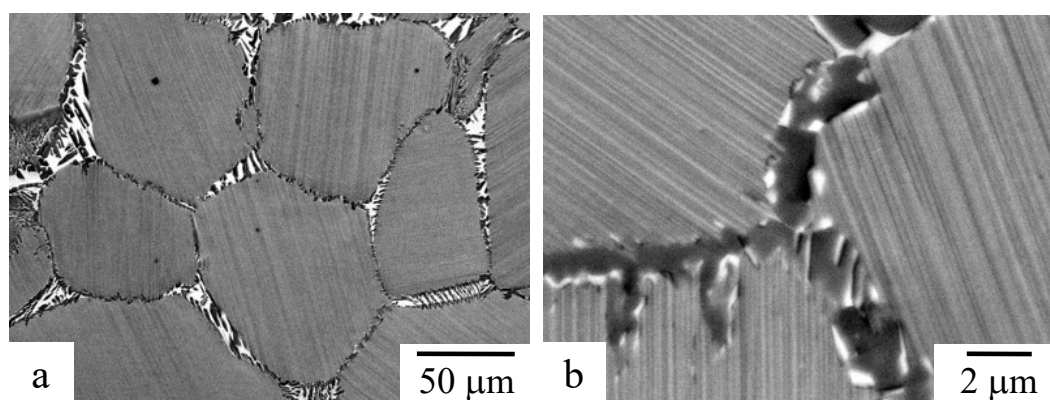
**Fig. 3-4** Schematic illustration showing the arrangement of the sample, objective lens of SEM and Ga<sup>+</sup> ion gun (IG).



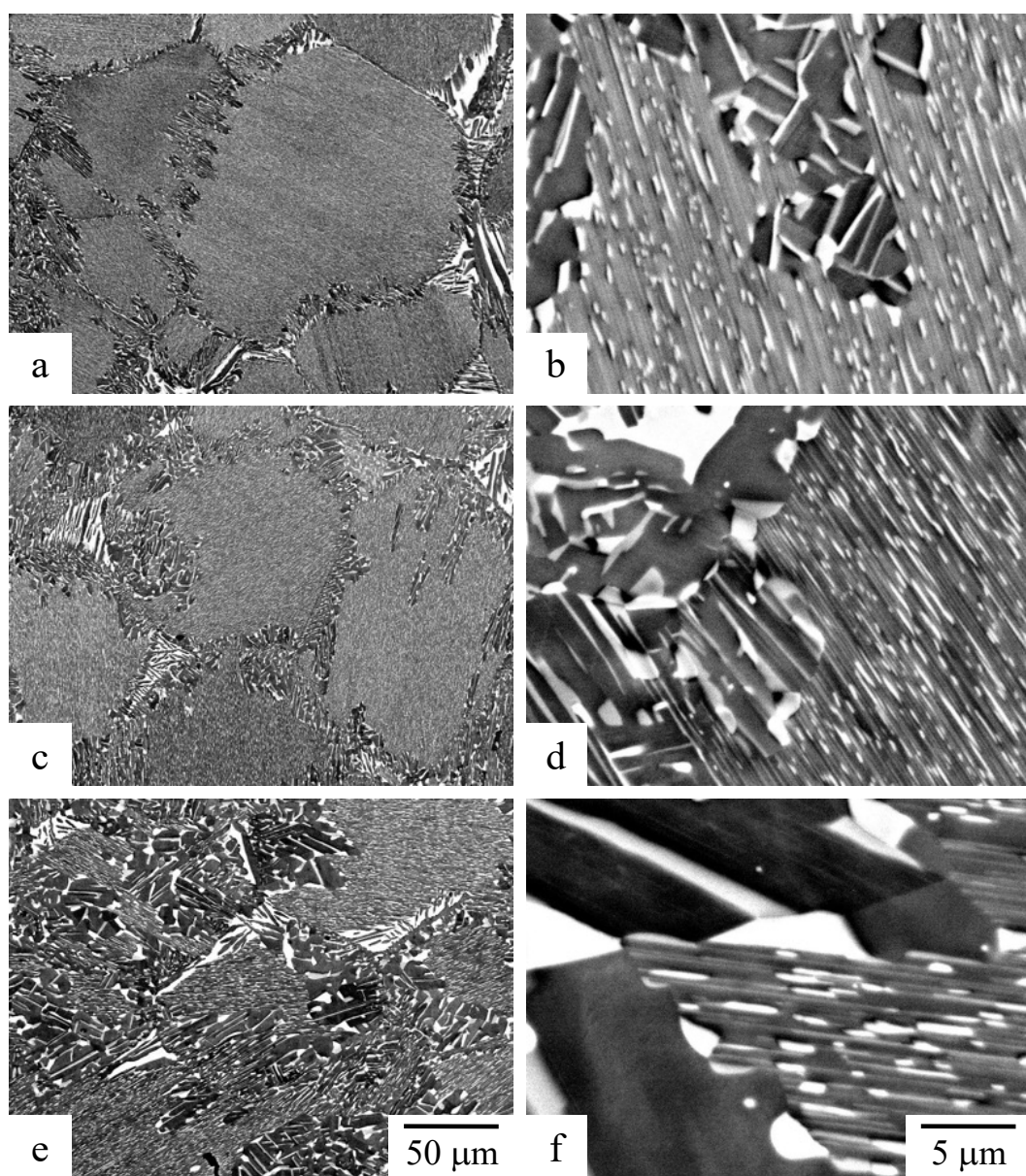
**Fig. 3-5** BSE micrographs of the thin film (a) before and (b) after the FIB milling.



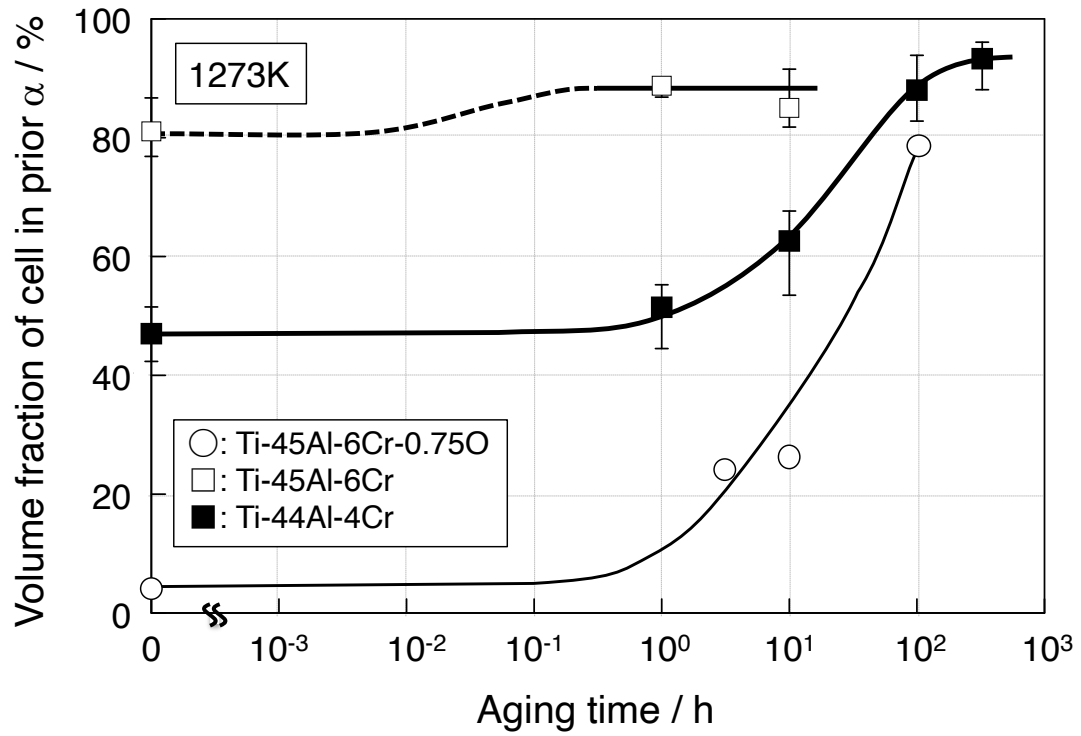
**Fig. 3-6** BSE micrographs of the as-forged sample of Ti-45Al-6Cr-0.75 alloy in (a) low and (b) high magnification.



**Fig. 3-7** BSE micrographs of the sample after the first-step heat treatment (1573 K for 24 h and controlled cooling to 1523 K, followed by air cooling) in (a) low and (b) high magnification.

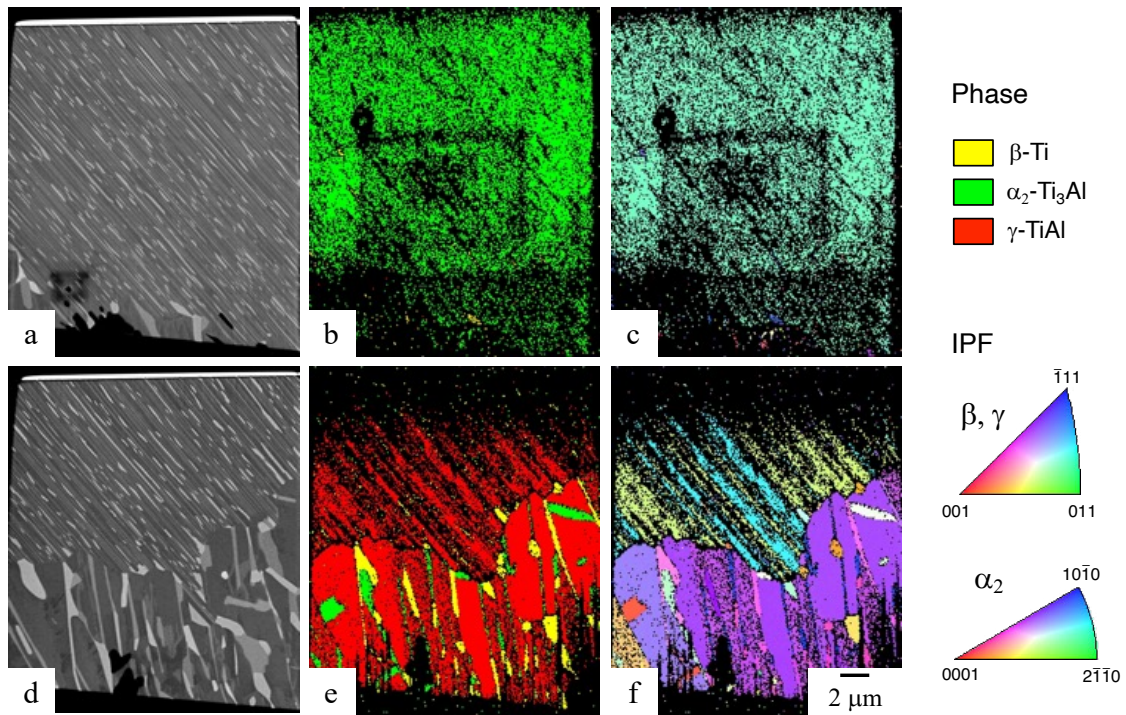


**Fig. 3-7** BSE micrographs of the sample aged at 1273 K for (a, b) 3 h, (c, d) 10 h and (e, f) 100 h followed by air cooling in (a, c, e) low and (b, d, f) high magnification.

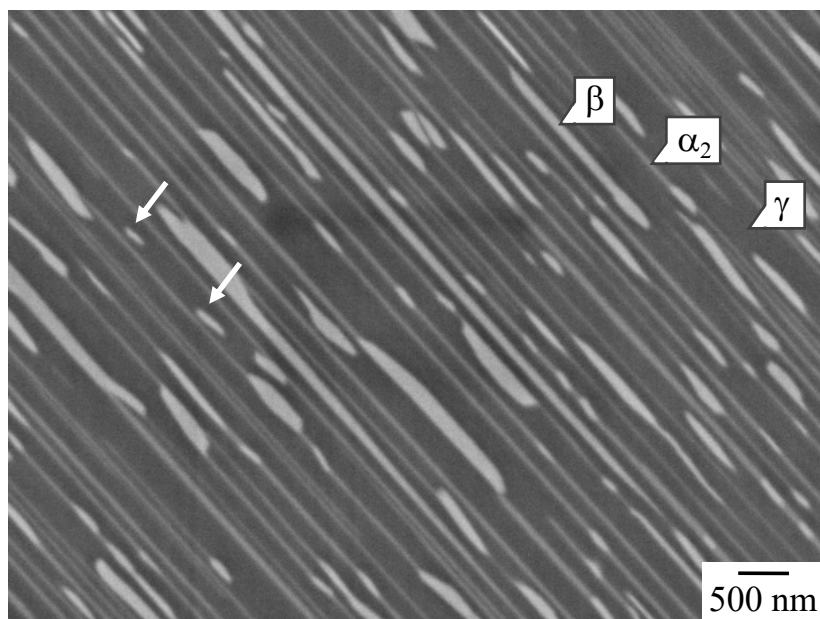


**Fig. 3-9** Change in volume fraction of the  $\beta/\gamma$  cell in prior  $\alpha$  grains with aging at 1273 K in Ti-45Al-6Cr-0.75O alloy, together with that in Ti-44Al-4Cr and Ti-45Al-6Cr alloys with no intentional oxygen addition reported by Wakabayashi [3].



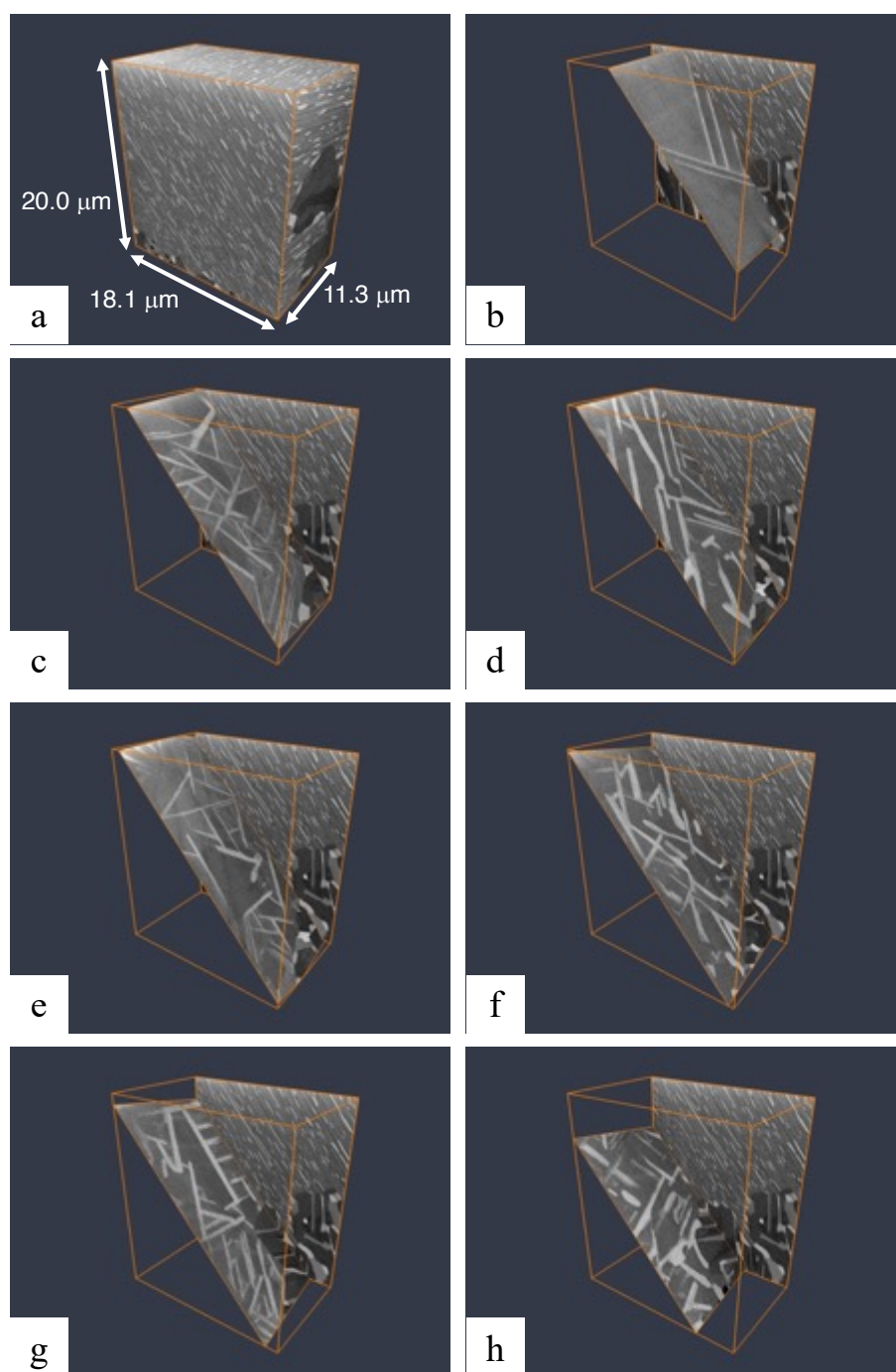


**Fig. 3-10** (a, d) BSE micrographs of the pillar of the 3 h aged sample for 3D observation and corresponding (b, e) phase and (c, f) IPF maps obtained from EBSD analysis (a–c) before and (d–f) after the serial sectioning.

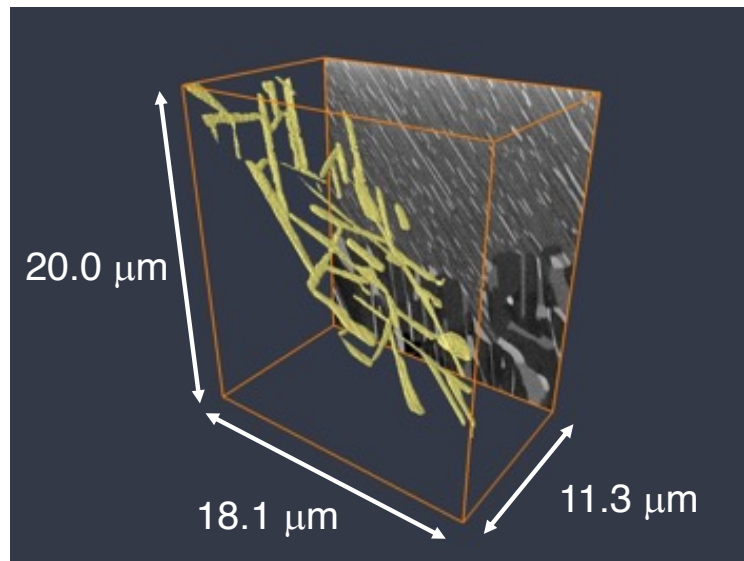


**Fig. 3-11** High magnification BSE micrograph of the  $\alpha_2/\gamma$  lamellar microstructure with  $\beta$  precipitates.

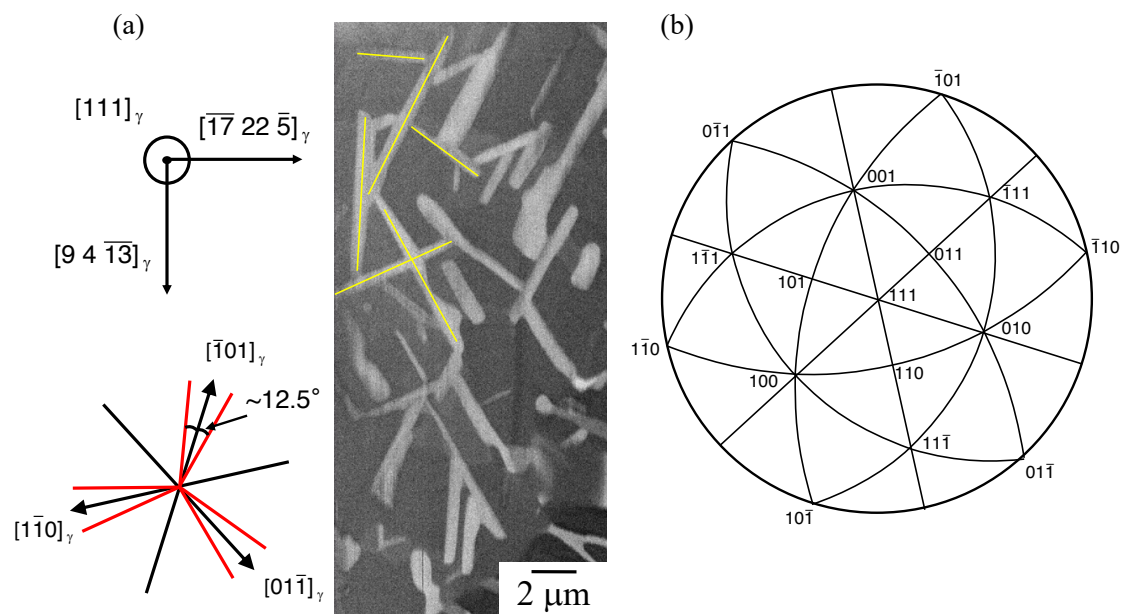




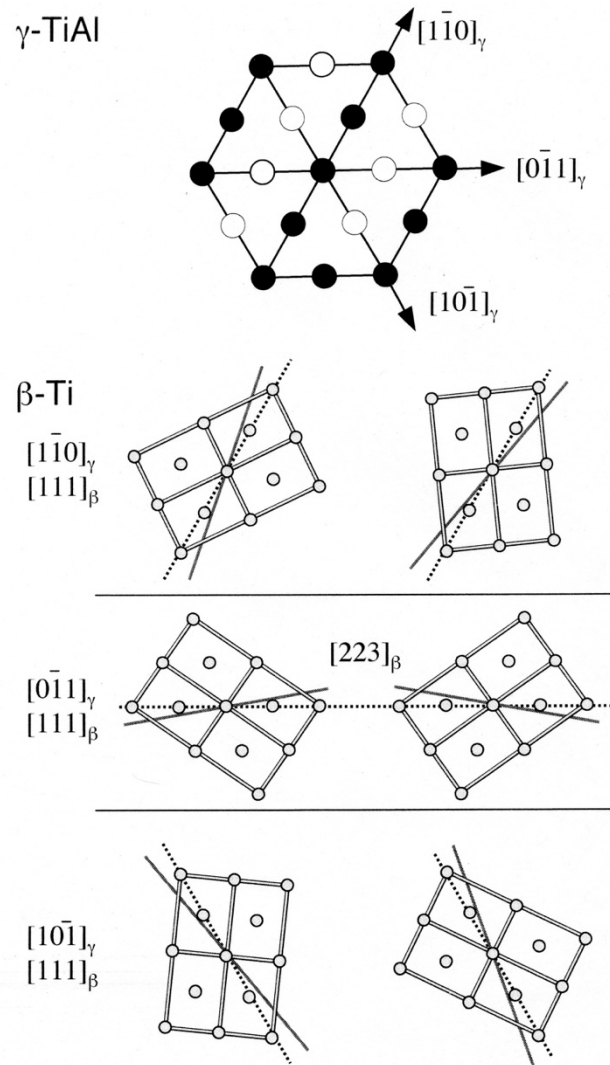
**Fig. 3-12** (a) Reconstructed 3D BSE image and (b–h) selected images of lamellar interfaces in the reconstructed image.



**Fig. 3-13** 3D image of the  $\beta$  phase precipitates extracted from one lamellar interface corresponding to Fig. 3-12 (f).



**Fig. 3-14** (a) One lamellar interface observed from the plane normal and (b) the corresponding stereographic projection of the  $\gamma$  phase obtained from the EBSD analysis.



**Fig. 3-15** Schematic illustration of atom arrangement of close-packed planes of  $\beta$  and  $\gamma$  phase with K-S orientation relationship, showing six variants. In the  $\beta$  phase, dotted line and solid line represent  $\langle 111 \rangle$  direction and the preferred growth orientation, respectively [4].

# Chapter 4

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Cr Effect on Young's Modulus and Hardness of the  
 $\beta$ ,  $\alpha_2$  and  $\gamma$  Phases Evaluated by Nano-indentation

## 4.1 Introduction

As mentioned in chapter 1 and demonstrated in chapter 2, the introduction of the  $\beta$  phase in TiAl alloys is effective for the mechanical properties. In order to make the role of  $\beta$  phase clear, it is important to identify the mechanical properties of the  $\beta$  phase itself in equilibrium with the other phases. One of the effective ways to evaluate the properties of the constituent phases is nano-indentation method [1,2], which allows you to have Young's modulus and hardness although orientation effect is somehow considered in the evaluation.

The composition dependence on the mechanical properties of each phase must also be taken into account in the evaluation. According to our phase diagram study on Ti-Al-M system, the composition of  $\beta$  phase in equilibrium with  $\alpha$  ( $\alpha_2$ ) and  $\gamma$  phases, especially in case of Cr, varies widely, depending on heat treatment temperatures [3,4]. There is some literature reported on the hardness of phases in TiAl alloys [5–7]. However, in most cases, only the alloy compositions, not the phase compositions, were considered.

The database on the relationship between the chemical composition and mechanical properties of the constituent phases would be useful to design the microstructure to meet the required properties for the components from a viewpoint of materials integration based on the computational materials engineering. In this chapter, therefore, the author intentionally selected several Ti-Al-Cr alloys having the  $\beta$  phase in equilibrium with  $\alpha_2$  and  $\gamma$  phases, and analyzed the chemical composition of each phase first. Then, the Young's modulus and hardness of the phases were measured in terms of nano-indentation method, and the effect of Cr on these properties of the  $\beta$  phase was quantitatively evaluated, in conjunction with the  $\alpha_2$  and  $\gamma$  phases.

## 4.2 Experimental procedure

### 4.2.1 Sample preparation

Three ternary alloys with nominal compositions of Ti-43Al-3Cr, Ti-44Al-4Cr and Ti-45Al-6Cr, together with two binary alloys of Ti-40Al and Ti-48Al, were used in this chapter. These alloys are hereafter referred to as 43-3, 44-4, 45-6, 40 and 48. The preparation methods of these alloys and the heat treatment conditions are summarized in **Table 4-1**. The oxygen content of these alloys was identified to be a level of 450 to 500 wt. ppm by wet chemical analysis. Note that the difference in alloy preparation method of these alloys (**Table 4-1**) comes from different purposes such as the studies on the phase equilibria and creep behavior, and all these alloys were homogenized prior to the equilibrium heat treatment, so that the nano-indentation method to examine the mechanical properties of the constituent phases is independent of the alloy preparations. In the heat treatments, the samples with a size of approximately  $6 \times 6 \times 10 \text{ mm}^3$  were wrapped with Ta foil and encapsulated in quartz tube evacuated and backfilled with Ar gas to minimize oxidation. The ternary alloy samples were first homogenized in the  $\beta$  single phase

region to eliminate composition fluctuation, followed by water quenching, and then equilibrated at 1373 K for 672 h (**Table 4-1**). The binary alloys 40 and 48 were also homogenized in the  $\alpha$  and  $\gamma$  single phase region, respectively, followed by rapid quenching. The heat-treated samples were mechanically polished with SiC paper and diamond paste, and they were electrically polished using a solution of 90 vol.% ethanol containing 6 vol.% perchloric acid to remove surface damage.

#### 4.2.2 Microstructure characterization and composition analysis

The microstructures of the specimens were observed using a field emission scanning electron microscope (FE-SEM). The crystallographic orientation was examined using electron backscatter diffraction (EBSD) technique. For the EBSD analyses, the  $\beta$ ,  $\alpha_2$  and  $\gamma$  phases were indexed as bcc, ordered  $D0_{19}$  (hcp) and ordered  $L1_0$  (fct) structures, respectively. The chemical composition of the individual phases was determined using a field emission electron probe micro-analyzer, equipped with a wavelength-dispersive X-ray spectrometer under an accelerating voltage of 20 kV and a probe current of 20 nA using pure metals as standards.

#### 4.2.3 Nano-indentation testing

Young's modulus,  $E$ , and hardness,  $H$ , of the  $\beta$ ,  $\alpha_2$  and  $\gamma$  phases were measured by nano-indenter equipped with a continuous stiffness measurement (CSM) device. The CSM method allows to measure the properties as a function of indentation depth continuously by oscillating the tip [1,8,9] as schematically shown in **Fig. 4-1 (a)**, different from the conventional method known as Oliver-Pharr (O-P), where the properties can be measured only at the maximum indentation depth [1,10] (**Fig. 4-1 (b)**). In the CSM method, the contact stiffness, from which the properties of the tested materials can be calculated, can be derived continuously during loading from the load amplitude, displacement amplitude, and phase of the oscillation, whereas in the O-P method, it is obtained from the slope of the unloading curve. The oscillation frequency of 110 Hz and the displacement amplitude of 2 nm were used in the present study. For the calculation of the Young's modulus, Poisson's ratio of the measured material was set to 0.25. The tests were performed using a diamond Berkovich tip with a maximum indentation depth of at least 400 nm, and the obtained properties were averaged over a depth range of 380 to 400 nm as described in the following section 3.2. Prior to the sample measurements, a reference specimen of fused silica was measured with the same condition to determine the load frame stiffness and the area function of the tip [1] for the data reliability. Before the tests, the indentation areas of the samples were predetermined based on the EBSD analyses, and several tests were conducted in each phase with indentation spacing greater than 10 times of the maximum indentation depth to obtain accurate results, as indicated in [11]. After the nano-indentation tests, the indentation impressions were observed by FE-SEM to verify that each test was correctly conducted.

### 4.3 Results

#### 4.3.1 Microstructures and phase analyses

**Figure 4-2** shows backscattered electron images of the three ternary alloys, together with two binary alloys, after the equilibration. The ternary 43-3 shows granular microstructure having an approximately 50  $\mu\text{m}$  in diameter, together with a small amount of lamellar region. The granular phase with the brightest, intermediate and darkest contrast was identified as  $\beta$ ,  $\alpha_2$  and  $\gamma$  phase, respectively, and the lamellar region consists of the  $\alpha_2$  and  $\gamma$  phases, in terms of EBSD together with the composition analyses (**Fig. 4-2 (a)**). In contrast, the other ternary 44-4 and 45-6 consist of two phases of  $\beta$  and  $\gamma$ , having the granular  $\gamma$  phase larger than 50  $\mu\text{m}$  in diameter as a dominant phase (**Figs. 4-2 (b, c)**). Note that the phase with the gray contrast observed in these specimens were identified as either  $\beta$  phase or  $\gamma$  phase, due to the channeling effect. The binary 40 exhibits the  $\alpha_2$  single phase microstructure (**Fig. 4-2 (d)**), and the 48 shows nearly  $\gamma$  single phase microstructure, although a small amount of  $\alpha_2$  particles are sparsely observed (**Fig. 4-2 (e)**).

The analyzed chemical composition of each phase present in the alloys shown in **Fig. 4-2** are summarized in **Table 4-2** and plotted on the isothermal section in **Fig. 4-3**. The binary data are referenced from the literature [12] as well. The terminal compositions of the three-phase coexisting region in the 43-3 are in good agreement with the previous reports [3,4]. The Cr content in the  $\beta$  phase in equilibrium with  $\gamma$  phase increases tremendously from 5.2 to 13.9 at.% with increase in the Cr content of the alloys from 3 to 6 at.%, whereas that of  $\gamma$  phase in equilibrium with  $\beta$  phase increases slightly from 1.4 to 3.1 at.%. Thus, it is obvious that Cr is preferentially partitioned to  $\beta$  phase against  $\gamma$  phase with the partition coefficient of Cr between the  $\beta$  and  $\gamma$  phases,  $k_{\text{Cr}}^{\beta/\gamma}$ , ranging from 3.7 to 4.5, although it is also partitioned to  $\alpha_2$  phase slightly larger than in  $\gamma$  phase with  $k_{\text{Cr}}^{\alpha_2/\gamma}$  of 1.6 (**Table 4-2**), where a partition coefficient was calculated as follows:  $k_{\text{Cr}}^{\text{A/B}} = X_{\text{Cr}}^{\text{A}}/X_{\text{Cr}}^{\text{B}}$  ( $X_{\text{Cr}}^{\text{A}}$  is the Cr concentration in A phase). It should be noted that Al content of the  $\beta$  and  $\gamma$  phases in equilibrium each other remains almost unchanged with deviation less than 1 at.%. Thus, Cr dependence of the mechanical properties can be evaluated from these samples.

As previously reported, lowering the temperature from 1373 to 1073 K changes the Cr content of the  $\beta$  phase in equilibrium with other phases from 5 to 12 at.%, i.e., the mechanical properties of the  $\beta$  phase would change, depending on the heat treatment conditions, because of the composition change. Although the composition change in  $\beta$  phase is controlled by changing the alloy composition at the fixed temperature in this case, the range of composition change shown in **Fig. 4-3** corresponds to that by changing the temperature, as intended.

#### 4.3.2 Young's modulus and hardness of each phase

**Figure 4-4** shows an example of the backscattered electron images of each phase in the

43-3 showing the indentation impressions, together with the phase maps of the corresponding area. The maximum indentation load is 30 mN for the  $\beta$  and  $\gamma$  phases, whereas it is 25 mN for the  $\alpha_2$  phase due to the small area relative to those of the others. The size of impressions in the  $\beta$  phase area (**Figs. 4-4 (a) and (d)**) is smaller than that in the  $\gamma$  phase area (**Figs. 4-4 (c) and (f)**) under the same maximum load, indicating that the  $\beta$  phase is harder than the  $\gamma$  phase. All these impressions, excluding those on or close to the phase boundary, were used for the evaluation of the properties, in order to secure the data reliability. The typical CSM curves of the  $E$  and  $H$  of each phase present in the 43-3 are shown in **Fig. 4-5**, as a function of indentation depth. In the small depth less than 50 nm, both values of each phase are widely scattered. However, as the depth increases the scatter range of these values becomes smaller, and although the  $E$  and  $H$  tend to slightly increase and decrease, respectively (**Figs. 4-5 (a) and (b)**), they become almost constant at the depth of 400 nm. In this study, thus, the values of the properties obtained from each indentation were averaged in the depth range of 380 to 400 nm. In addition, since the region corresponds to a single crystal for this indentation test, the orientation dependence of the properties must be considered. Therefore, the regions having low index orientation parallel to indentation axis are intentionally selected by EBSD prior to the tests.

All the results of nano-indentation tests are summarized in **Table 4-3**. Since the  $E$  and  $H$  of the three phases are somehow dependent on the crystallographic orientation, some of the representative data of each phase are selected and shown in **Fig. 4-6** as a bar graph. In the  $\beta$  phase obtained from the 44-4, the  $E$  varies from 140 to 160 GPa among the three major orientations of [001], [011] and  $\bar{1}\bar{1}1$ . In contrast, the  $H$  is about 6.7 GPa, regardless of the orientation (**Fig. 4-6 (a)**). In the  $\alpha_2$  phase from 43-3, both of the  $E$  and  $H$  vary in a range of 166 to 183 GPa and from 5.7 to 7.2 GPa, respectively, among the three orientations of [0001],  $10\bar{1}0$  and  $2\bar{1}\bar{1}0$  (**Fig. 4-6 (b)**). The  $E$  and  $H$  of the  $\gamma$  phase also vary from 154 to 179 GPa and 3.1 to 4.4 GPa, respectively, among the five orientations of [001], [010], [011],  $\bar{1}10$  and  $\bar{1}\bar{1}1$  (**Fig. 4-6 (c)**). Even by taking into account the orientation effect on the  $E$  and  $H$ , the  $E$  of the  $\beta$  phase basically shows smaller values and less orientation dependent than that of the others, whereas the  $H$  of the  $\beta$  phase is similar to that of the  $\alpha_2$  phase but much larger than the  $\gamma$  phase. The feature among the phases is held regardless of the composition of the phases. Even under the fixed composition, the values of the properties change to some extent depending on the orientation. These data clearly suggested that the results having different Cr composition but the same orientation must be compared, in order to identify the effect of Cr on these properties.

**Figures 4-7 and 4-8** show the  $E$  and  $H$  as a function of Cr content in each phase obtained under the same orientation, respectively. Note that the properties of  $\alpha_2$  and  $\gamma$  phases with no Cr content were obtained from the binary 40 and 48. The  $E$  of the three phases increases with the Cr content in any orientations, except  $\gamma$  phase with [011] orientation. The  $E$  of the  $\beta$  phase with [001]



and [011] orientations increase from about 140 to 160 GPa in a similar manner as Cr content increases from 5 to 14 at.% (**Fig. 4-7 (a)**). The  $E$  of the  $\alpha_2$  phase with [0001] orientation increases from 173 to 183 GPa with increasing Cr content from 0 to 2.2 at.% (**Fig. 4-7 (b)**). In case of the  $\gamma$  phase, the  $E$  basically increases up to 180 GPa with increasing the limited range on Cr content up to 3 at.%, and the rate of increase is different from the orientations tested (**Fig. 4-7 (c)**). On the other hand, the  $H$  of the  $\beta$  phase increases from about 6 to 7 GPa with increasing Cr from 5 to 8 at.%, and it remains unchanged with further Cr content up to 14 at.% (**Fig. 4-8 (a)**). The  $H$  of the  $\alpha_2$  phase increases slightly from 6.8 to 7.2 GPa with the limited increase in Cr content up to 2.2 at.% (**Fig. 4-8 (b)**). Unlike the other phases, the  $H$  of the  $\gamma$  phase is insensitive to Cr content in any orientations, although the values vary in the range of 3 to 4.5 GPa, depending on the orientation (**Fig. 4-8 (c)**).

#### 4.4 Discussion

The present results clearly demonstrated that Young's modulus,  $E$ , and hardness,  $H$ , of the constituent phases of  $\beta$ ,  $\alpha_2$  and  $\gamma$  in equilibrium each other in the alloys studied depend on Cr content as well as loading orientation, and the  $\beta$  phase exhibits the lowest  $E$  whereas it shows relatively high  $H$  value nearly the same as that of  $\alpha_2$  and 1.5 times higher than that of  $\gamma$  phase. As mentioned earlier, the concentration of Cr in the  $\beta$  phase in equilibrium with  $\alpha_2$  and  $\gamma$  phases changes with temperature even in the same alloy [3,4], so that the understanding of the change in the properties with the Cr content and other elements based on the reliable data for each phase, is important for alloy design.

The values of the  $E$  and  $H$  for each phase obtained by the nano-indentation method in this study would be reliable to figure out the features of the effect of Cr content on the properties in each phase. **Table 4-4** summarizes the compositions and properties of the three phases in equilibrium each other in Ti-43Al-3Cr, together with the reported values [6,13–16] in comparison. Note that the values of  $E$  and  $H$  in this table are averaged over all orientations shown in **Table 4-3**, assuming a polycrystal with randomly orientated grains. As far as the literature survey is concerned, there are some published data on the  $E$  and  $H$  of each phase, but most of them are obtained by either calculation [15] or experiments using the specimens with nearly single-phase microstructure of each phase [13,14]. However, like this study, there are no data obtained from the phases in equilibrium each other as the constituent phases of the alloys, except the one reported by Schloffer et al. [6]. The  $E$  and  $H$  of the  $\beta$  phase in this study ( $E = 141$  GPa,  $H = 5.9$  GPa) are lower than those of their values ( $E = 172$  GPa,  $H = 7.2$  GPa). The higher values of the  $\beta$  phase reported by Schloffer et al. is attributed to the enrichment of Nb and Mo in the phase [17,18], since they used a commercial TNM alloy with a nominal composition of Ti-43.5Al-4Nb-1Mo-0.1B (at.%). In contrast, the  $E$  and  $H$  of the  $\gamma$  phase between the two studies become nearly the

same values ( $E = 163\text{--}167$  GPa,  $H = 3.9\text{--}4.2$  GPa), since those elements are not enriched in the  $\gamma$  phase [18], just like the Cr content in the  $\gamma$  phase in this study. In addition, the  $E$  of  $\gamma$  phase obtained in this study is also in good agreement with that of polycrystalline GE alloy with a nominal composition of Ti-48Al-2Cr-2Nb having near- $\gamma$  microstructure [16]. The facts that the properties of  $\gamma$  phase in this study are almost the same as those of the published data indicate clearly that the present values of  $E$  and  $H$  of  $\beta$  and  $\alpha_2$  phases in this study are reliable since they are evaluated under the same conditions in the same specimen.

**Figure 9** shows the change in the measured properties against increment of Cr content in each phase. The curves in this figure are drawn under the averaged values, just like **Table 4-4**. The  $E$  increases with Cr content in all of the three phases, and the increasing rate for the  $\beta$  phase is approximately 2.0 GPa/at.%, the smallest among the three phases of 4.5 GPa/at.% for the  $\alpha_2$  phase and 3.4 GPa/at.% for the  $\gamma$  phases (**Fig. 4-9 (a)**). On the other hand, the increasing rate of  $H$  with Cr content for the  $\beta$  phase becomes 0.4 GPa/at.%, twice as high as that for the  $\alpha_2$  phases (0.2 GPa/at.%). It should be interesting to note that the  $H$  of the  $\gamma$  phase is unaltered regardless of the Cr content (**Fig. 4-9 (b)**). The Cr concentration dependencies of the  $E$  and  $H$  for the three phases are such that the following three distinguished features will be discussed: (1) the dependency of  $E$  for the  $\beta$  phase, (2) the dependency of  $H$  for the  $\beta$  phase, (3) no dependency of  $H$  for the  $\gamma$  phase.

The increase in  $E$  with Cr content in the  $\beta$  phase as well as other phases is related to the strengthening of the chemical bonding in the atmosphere around Cr atoms. Holec et al. recently calculated the phase stabilities of various phases possibly present in  $\gamma$ -TiAl alloys by alloying, in terms of the density functional theory [19], and reported that Cr atoms preferentially occupy Al sublattice sites in B2 ordered phase and strengthen the formation energy. In this study, the  $\beta/\beta+\gamma$  phase boundary is found to locate along the equi-Al concentration line of 37 at.% Al in Ti-Al-Cr ternary system (**Fig. 3**), and the  $\beta$  phase is possibly ordered to B2 phase, according to the studies reported by other researchers [20–22]. In contrast, as far as the  $\gamma$  phase is concerned, Kawabata et al. experimentally revealed the reduction of the unit cell volume of  $\gamma$  phase by Cr addition in  $\gamma$ -TiAl alloys [23,24], and suggested the increase in chemical bonding. In addition, Morinaga et al. also reported the strengthening of atomic bonding in  $\gamma$  phase by Cr addition in  $\gamma$  phase, based on the calculation of DV-X $\alpha$  (discrete variational X $\alpha$ ) cluster method [25], although the contradictory calculated result was reported [19]. The present result of the increase in  $E$  with increasing Cr content strongly supports their calculated prediction, since the magnitude of Young's modulus is highly associated with the formation energy originated from chemical bonding. The fact that the magnitude of the Cr effect on the  $E$  per atomic percent addition is less pronounced in the  $\beta$  phase than that in the other phases (**Fig. 4-9 (a)**) is presumably due to the weaker enhancement of chemical bonding caused by the open crystal structure (bcc) with less

coordination number, in comparison with the  $\alpha_2$  and  $\gamma$  phases where both are basically close-packed structures.

The more pronounced effect of the Cr on the  $H$  in the  $\beta$  phase than the other phases with the increment of Cr content up to 3 at.% (**Figs. 4-8 and 4-9 (b)**) would be associated with the increase in the degree of order in the B2 phase by Cr in solution. As mentioned earlier, the Cr atoms theoretically prefer to occupy the Al sublattice site where the excess Ti atoms occupied as anti-site defects, in order to stabilize the B2 phase [19]. As the Cr content in the  $\beta$  phase in equilibrium with the  $\gamma$  phase increases from 5 at.% to 14 at.% under the equi-Al concentration line of 37 at.% Al (**Fig. 4-3**), the degree of order should increase since the composition of the  $\beta$  phase approaches to the stoichiometric composition of Ti(Al, Cr) with B2 structure. The hardness is related to the plastic deformation involving dislocation motion around the indent, and the ordering to B2 changes the translation vector of  $\langle 111 \rangle$  twice as large as that of the disordered bcc phase, making more difficult to activate the dislocation motion. This is responsible for the increase in the hardness of the  $\beta$  phase with Cr content. Since the ordering to B2 phase is the second order transformation, it is reasonable that the increasing rate of  $H$  levels out as the Cr content in the  $\beta$  phase increases and approaches to the stoichiometric composition of the B2 phase.

The no effect of Cr on the  $H$  in the  $\gamma$  phase suggests an important implication in improving the mechanical properties of the alloys containing the  $\beta$  phase. It is known that the Cr addition to TiAl alloys enhances that room temperature ductility [23,24,26]. The improvement of the ductility has been interpreted from various viewpoints of the bonding energy,  $c/a$  ratio, dislocation motion and so on [23–27]. Among them, the commonly accepted explanation for the Cr effect on ductility enhancement is based on dislocation behavior. According to the report by Woodward and MacLaren [27], the addition of Cr lowers the superlattice intrinsic stacking fault (SISF) and antiphase boundary (APB) energy on the  $\{111\}$  plane of  $\gamma$  phase, so that they attributed the ductility improvement to enhancing the mobility of the super-partials by dissociation of the  $\langle 101 \rangle$  super-dislocations. However, if the Cr dissolved in the  $\gamma$  phase affects the dislocation motion, the  $H$  should decrease with Cr content, unlike the present results. In fact, Kawabata et al. reported that the ductility of  $\gamma$  single phase alloy decreases with increasing Cr content [23,24]. In addition, the present results show no indication of the enhancement of deformation of the  $\gamma$  phase itself by Cr in solution. From these results, it is not easily acceptable that the ductility enhancement is only explained by the dislocation characters, although it is not ruled out. It is rather strongly suggested that the improvement of the mechanical properties of TiAl alloys containing the  $\beta$  stabilizing elements [28] is not just caused by enhancement of the deformability of the  $\gamma$  phase itself but the existence of the  $\beta$  phase inducing the deformation of the  $\gamma$  phase. As shown in **Figs. 4-7–4-9**, the  $E$  and  $H$  of the  $\beta$  phase as well as  $\alpha_2$  phase increases with increasing the Cr content, and their hardness is nearly twice as high as that of the  $\gamma$  phase, so that the  $\gamma$  phase is undoubtedly

responsible for the deformation of the alloys. Therefore, let us consider the plastic deformation in the TiAl alloys with  $\beta$  phase. The  $\gamma$  phase is the softest among the three phases, the dislocations in the  $\gamma$  phase start to move at first, and once they meet the  $\gamma/\beta$  phase boundaries as the deformation proceeds, the stress concentration takes place at there, which could activate the secondary slip in the  $\gamma$  phase since the  $\beta$  phase is much harder than the  $\gamma$  phase. Kawabata et al. reported the improvement of ductility in Ti-rich TiAl alloys by Cr addition [23,24]. In those alloys, the  $\beta$  phase was found to exist, but they did not mention anything on the role of the  $\beta$  phase on the ductility and attributed the improvement to the structure change and dislocation characters of the  $\gamma$  phase. This could mislead the subsequent interpretation of the Cr effect on the ductility, and it is the existence of the  $\beta$  phase that gives rise to the ductility enhancement, as is suggested above. Note that the similar effect could also be expected for the  $\alpha_2$  phase since the phase is also harder, as reported by Takeyama where the introduction of Widmanstätten-like  $\alpha_2$  plates in  $\gamma$  grains improves the room temperature ductility of TiAl alloys [29].

The present study clearly reveals how the introduction of  $\beta$  phase in TiAl alloys is effective in improving the mechanical properties by identifying the mechanical properties of the constituent phases in terms of the nano-indentation method. These databases are useful to design the microstructures to meet the required properties for the TiAl components. The orientation dependence of the properties for each phase may be considered under the nano-indentation method, but it is beyond the scope of this study since all of the TiAl alloys are polycrystalline and the orientation of each grain is uncontrollable. In this study, we focus on Cr as one of the alloying elements, but the same systematic studies on the other alloying elements such as Nb and Mo, are needed. However, it should be noted that the reliable phase diagrams in the systems concerned are also needed for the alloy design and development since the composition of each phase changes by the heat treatment conditions, as mentioned earlier. In addition to the substitutional elements, the database on the phases containing the interstitial elements such as oxygen becomes important in case of fabricating the component by powder processes of additive manufacturing (AM) and metal injection molding (MIM). Such studies including the oxygen as an alloying element are currently in progress.

## 4.5 Summary

In order to identify the effect of Cr on the Young's modulus and hardness of the  $\beta$ -Ti phase, in equilibrium with  $\alpha_2$ -Ti<sub>3</sub>Al and  $\gamma$ -TiAl phases, several Ti-Al-Cr ternary alloys were intentionally prepared based on the phase diagram, and the properties of each phase were measured by nano-indentation method. The following conclusions were obtained in this chapter:

1. The Cr concentration of the  $\beta$  phase in equilibrium with the  $\alpha_2$  and  $\gamma$  phases can widely be changed from 5.2 at.% to 13.9 at.% with nearly the same Al concentration of 37 at.%, whereas that of the  $\gamma$  phase in equilibrium with the  $\beta$  phase is limited in the range of 1.4 at.% to 3.1 at.%.
2. The  $\beta$  phase shows the lowest Young's modulus of 141 GPa among the three phases in equilibrium each other, 173 GPa for the  $\alpha_2$  phase and 167 GPa for the  $\gamma$  phase. The hardness of the  $\beta$  phase is 5.9 GPa, comparable to that of the  $\alpha_2$  phase (6.3 GPa) and much harder than that of the  $\gamma$  phase (3.9 GPa).
3. The increasing rate of the Young's modulus per atomic percent of the Cr addition in the  $\beta$  phase is the smallest (2.0 GPa/at.%) among the three phases, whereas that of the hardness becomes the highest (0.4 GPa/at.%) in a range of 5 to 8 at.% Cr. It was found that the hardness of the  $\gamma$  phase remains unchanged regardless of the Cr content.
4. The present study suggests that the improvement of the mechanical properties by the addition of Cr is caused by the existence of the  $\beta$  phase in the microstructure, rather than the change in the nature of the  $\gamma$  phase itself by Cr in solution.

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**Table 4-1** Nominal compositions, heat treatment conditions, and preparation methods of the alloys studied.

| Mark               | Nominal Composition / at. % |    |      | Heat treatment                       |                         |
|--------------------|-----------------------------|----|------|--------------------------------------|-------------------------|
|                    | Al                          | Cr | Ti   | Homogenization                       | Equilibration           |
| 43-3 <sup>1)</sup> | 43                          | 3  | Bal. | 1673 K for 30 min → W.Q. ( $\beta$ ) | 1373 K for 672 h → W.Q. |
| 44-4 <sup>2)</sup> | 44                          | 4  | Bal. |                                      |                         |
| 45-6 <sup>1)</sup> | 45                          | 6  | Bal. |                                      |                         |
| 40 <sup>2)</sup>   | 40                          | 0  | Bal. | 1473 K for 1 h → A.C. ( $\alpha$ )   | —                       |
| 48 <sup>3)</sup>   | 48                          | 0  | Bal. | 1373 K for 240 h → W.Q. ( $\gamma$ ) | —                       |

1) induction melting followed by hot forging, 2) arc melting, 3) centrifugal casting

W.Q.: Water Quench, A.C.: Air Cool

**Table 4-2** Analyzed compositions of each phase in the alloys studied.

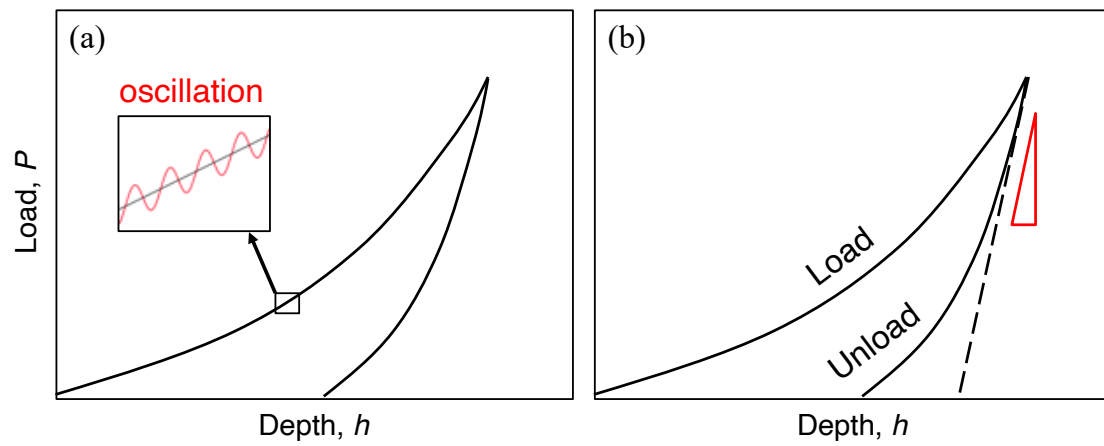
| Alloy | Phase present      | Composition / at. % |      |      | Partition coefficient of Cr |                            | Remarks                                                                    |
|-------|--------------------|---------------------|------|------|-----------------------------|----------------------------|----------------------------------------------------------------------------|
|       |                    | Al                  | Cr   | Ti   | $k_{Cr}^{\beta/\gamma}$     | $k_{Cr}^{\alpha_2/\gamma}$ |                                                                            |
| 43-3  | $\beta$            | 37.2                | 5.2  | Bal. | 3.7                         | 1.6                        | $\beta/\alpha/\gamma$ or $\beta/\alpha_2/\gamma$<br>three phases at 1373 K |
|       | $\alpha_2(\alpha)$ | 38.9                | 2.2  | Bal. |                             |                            |                                                                            |
|       | $\gamma$           | 47.4                | 1.4  | Bal. |                             |                            |                                                                            |
| 44-4  | $\beta$            | 36.5                | 8.5  | Bal. | 4.3                         | —                          |                                                                            |
|       | $\gamma$           | 47.8                | 2.0  | Bal. |                             |                            |                                                                            |
| 45-6  | $\beta$            | 36.3                | 13.9 | Bal. | 4.5                         | —                          |                                                                            |
|       | $\gamma$           | 48.1                | 3.1  | Bal. |                             |                            |                                                                            |
| 40    | $\alpha_2(\alpha)$ | not analyzed        |      |      | —                           | —                          | $\alpha$ single phase at 1473 K                                            |
| 48    | $\gamma$           | not analyzed        |      |      | —                           | —                          | small amount of $\alpha_2$ exist                                           |

**Table 4-3** Nano-indentation test results of the three phases in each alloy.

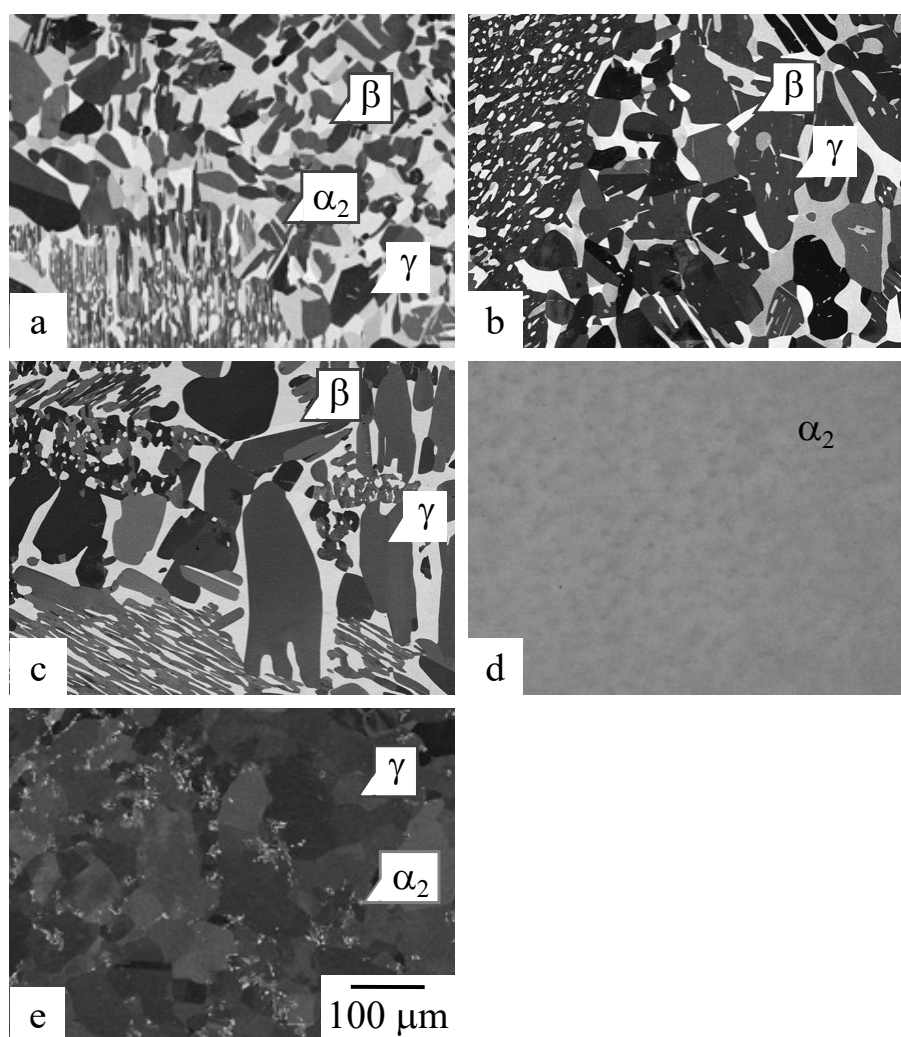
| Alloy | Phase      | Orientation  |               | Number of measurements | Young's modulus / GPa |         |         | Hardness / GPa |         |         |
|-------|------------|--------------|---------------|------------------------|-----------------------|---------|---------|----------------|---------|---------|
|       |            | Measured     | Approximation |                        | Average               | Maximum | Minimum | Average        | Maximum | Minimum |
| 43-3  | $\beta$    | 2 3 22       | 001           | 4                      | 135.3                 | 138.9   | 130.4   | 6.12           | 6.19    | 6.05    |
|       |            | -1 9 10      | 011           | 10                     | 146.5                 | 154.8   | 141.5   | 5.60           | 5.75    | 5.42    |
|       | $\alpha^2$ | 2 0 -2 15    | 0001          | 3                      | 182.8                 | 183.3   | 182.0   | 7.21           | 7.30    | 7.13    |
|       |            | 19 0 -19 6   | 10-10         | 7                      | 171.4                 | 178.7   | 167.9   | 5.94           | 6.12    | 5.84    |
|       |            | 25 -12 -13 6 | 2-1-10        | 9                      | 165.9                 | 170.9   | 163.2   | 5.67           | 5.80    | 5.54    |
|       | $\gamma$   | -1 2 17      | 001           | 3                      | 153.9                 | 154.1   | 150.3   | 3.07           | 3.09    | 3.04    |
|       |            | -1 1 30      | 001           | 3                      | 143.6                 | 143.9   | 143.3   | 3.17           | 3.19    | 3.13    |
|       |            | -3 26 1      | 010           | 3                      | 178.6                 | 182.1   | 174.8   | 4.26           | 4.36    | 4.16    |
|       |            | -3 25 2      | 010           | 4                      | 168.0                 | 171.5   | 164.8   | 4.44           | 4.52    | 4.36    |
|       |            | -1 30 0      | 010           | 7                      | 160.3                 | 165.1   | 154.8   | 4.50           | 4.58    | 4.36    |
|       |            | -1 9 7       | 011           | 4                      | 178.7                 | 182.4   | 174.5   | 4.38           | 4.49    | 4.22    |
|       |            | -9 12 13     | -111          | 13                     | 173.4                 | 179.3   | 164.2   | 3.72           | 3.99    | 3.54    |
| 44-4  | $\beta$    | -1 3 30      | 001           | 10                     | 140.4                 | 147.8   | 137.1   | 6.82           | 7.05    | 6.63    |
|       |            | 0 15 19      | 011           | 10                     | 153.7                 | 155.7   | 152.3   | 6.66           | 6.94    | 6.47    |
|       |            | -13 14 16    | -111          | 8                      | 160.4                 | 164.9   | 157.7   | 6.71           | 6.83    | 6.60    |
|       | $\gamma$   | -1 1 17      | 001           | 11                     | 154.1                 | 160.7   | 149.7   | 3.14           | 3.23    | 3.05    |
|       |            | -2 23 3      | 010           | 7                      | 170.3                 | 172.9   | 168.0   | 4.03           | 4.11    | 3.90    |
|       |            | -1 22 21     | 011           | 6                      | 177.3                 | 180.0   | 174.2   | 4.37           | 4.59    | 4.03    |
|       |            | -14 17 2     | -110          | 5                      | 173.9                 | 176.2   | 172.4   | 3.25           | 3.36    | 3.18    |
|       |            | -8 8 9       | -111          | 21                     | 179.2                 | 185.9   | 174.2   | 3.76           | 4.06    | 3.63    |
| 45-6  | $\beta$    | -1 1 9       | 001           | 5                      | 151.3                 | 152.4   | 150.1   | 6.78           | 6.92    | 6.64    |
|       |            | -1 21 22     | 011           | 6                      | 164.5                 | 167.7   | 162.9   | 6.74           | 6.82    | 6.52    |
|       | $\gamma$   | -1 18 0      | 010           | 9                      | 170.0                 | 172.0   | 167.7   | 4.11           | 4.20    | 4.05    |
| 40    | $\alpha^2$ | 3 -1 -2 24   | 0001          | 16                     | 172.7                 | 178.4   | 168.3   | 6.77           | 6.93    | 6.56    |
| 48    | $\gamma$   | 2 3 22       | 001           | 19                     | 140.7                 | 144.7   | 136.1   | 3.05           | 3.15    | 2.95    |
|       |            | -15 16 15    | -111          | 14                     | 165.7                 | 168.6   | 160.9   | 4.06           | 4.17    | 3.87    |

**Table 4-4** The compositions and properties of the three phases in equilibrium each other in Ti-43Al-3Cr, together with the reported values in comparison [6,13–16].

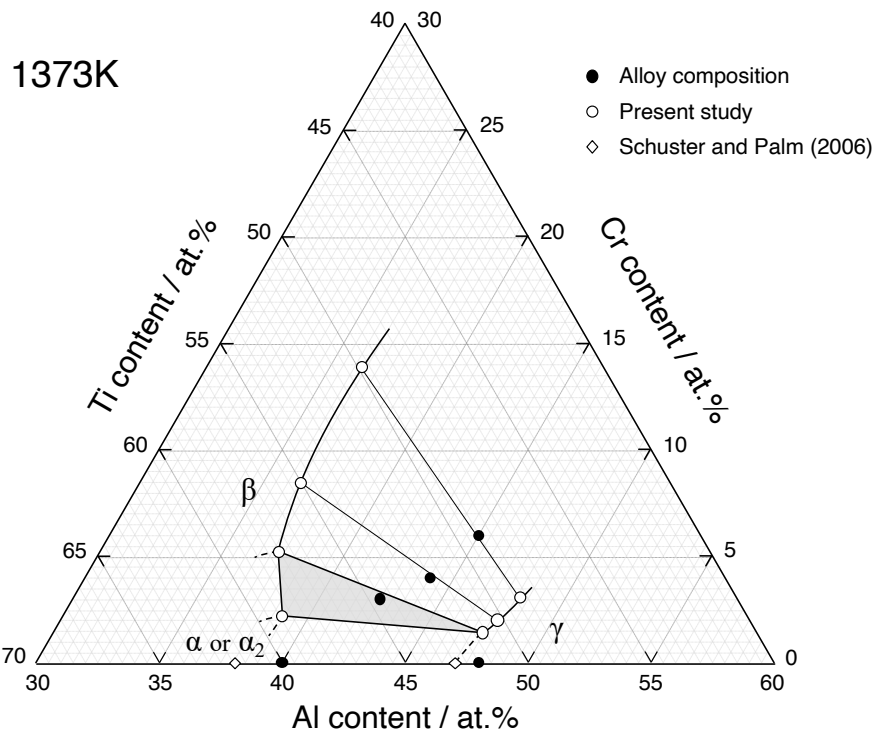
|                   | Phase               | $\beta$         | $\alpha^2$      | $\gamma$        | Remarks                                   |
|-------------------|---------------------|-----------------|-----------------|-----------------|-------------------------------------------|
| Present results   | Composition / at. % | Ti-37.2Al-5.2Cr | Ti-38.9Al-2.2Cr | Ti-47.4Al-1.4Cr | EPMA-WDS                                  |
|                   | $E$ / GPa           | 141             | 173             | 167             | Nano-indentation                          |
|                   | $H$ / GPa           | 5.9             | 6.3             | 3.9             |                                           |
| Literature survey | $E$ / GPa           | —               | 149             | 172             | Resonance method, binary alloys [13,14]   |
|                   |                     | —               | 184             | 146             | First principle calc., binary alloys [15] |
|                   |                     | —               | —               | 165             | Polycrystalline GE alloy [16]             |
|                   |                     | 172             | 149             | 163             | Nano-indentation, TNM alloy [6]           |
|                   | $H$ / GPa           | 7.2             | 5.3             | 4.2             |                                           |



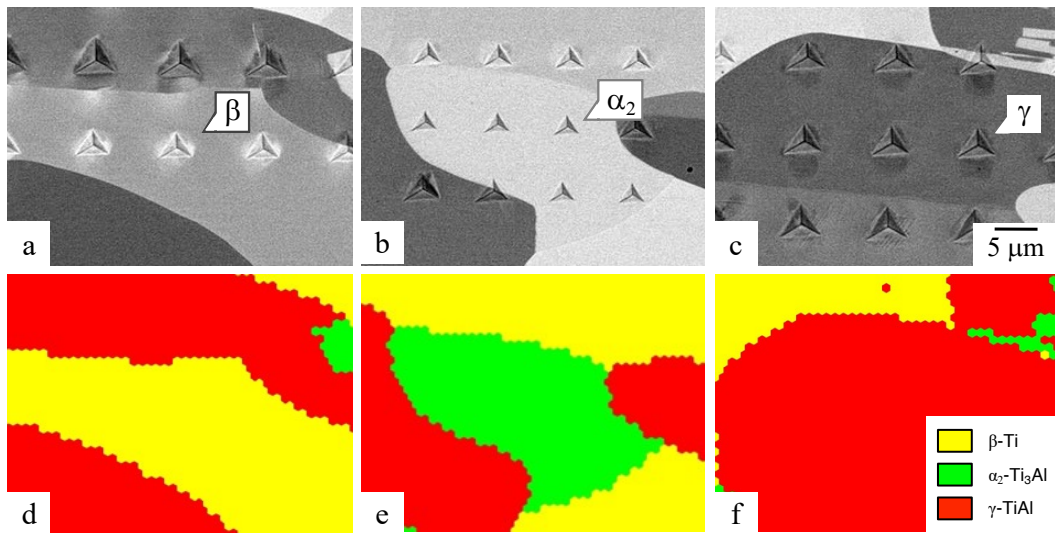
**Fig. 4-1** Schematic illustrations of loading curve of nano-indentation: (a) continuous stiffness measurement (CSM) method, (b) conventional Oliver-Pharr (O-P) method.



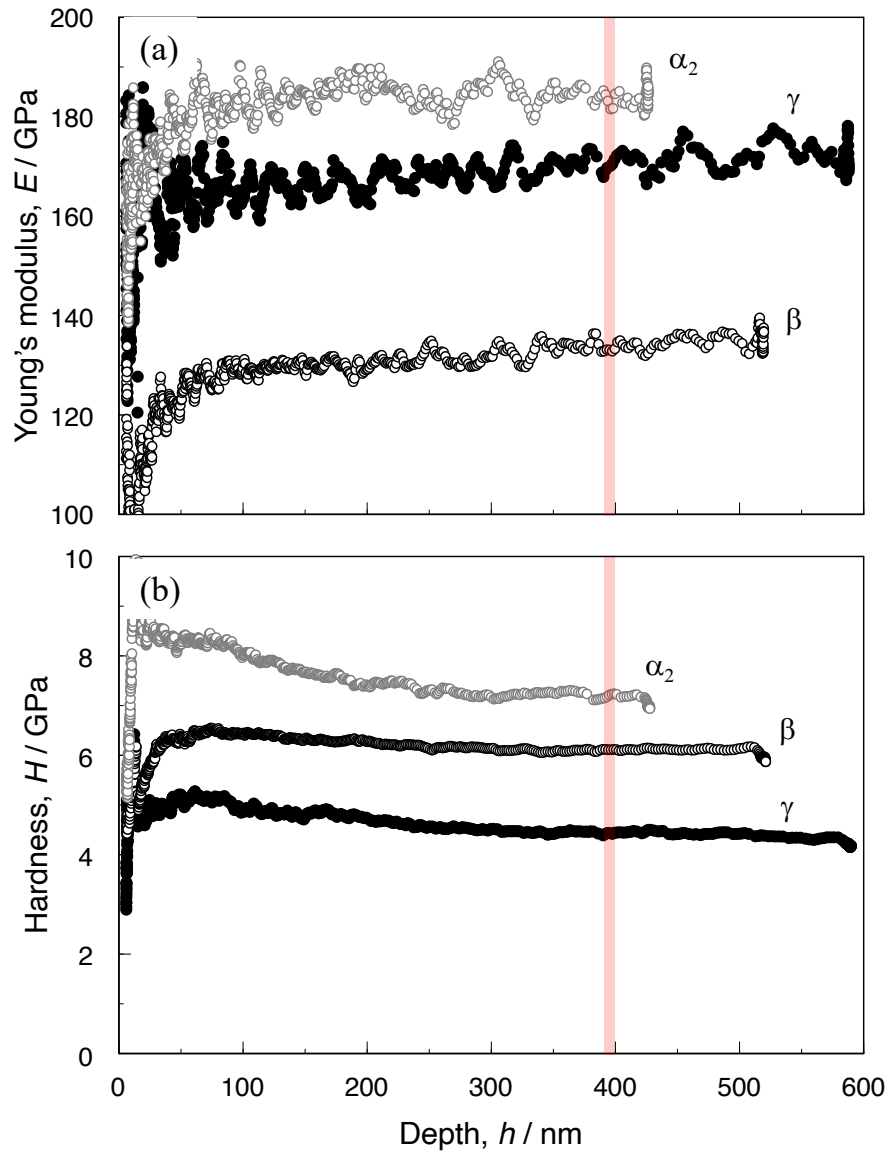
**Fig. 4-2** Backscattered electron images of (a) 43-3, (b) 44-4, (c) 45-6, (d) 40, and (e) 48 after the heat treatments.



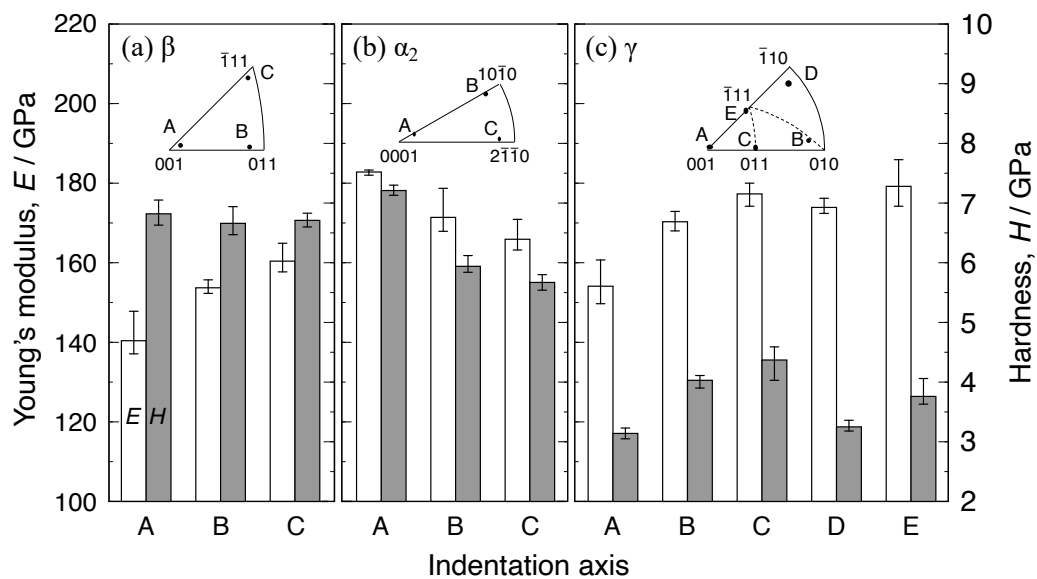
**Fig. 4-3** Isothermal section of Ti-Al-Cr ternary phase diagram at 1373 K. Note that the heat treatment temperature of alloy 40 is 1473 K.



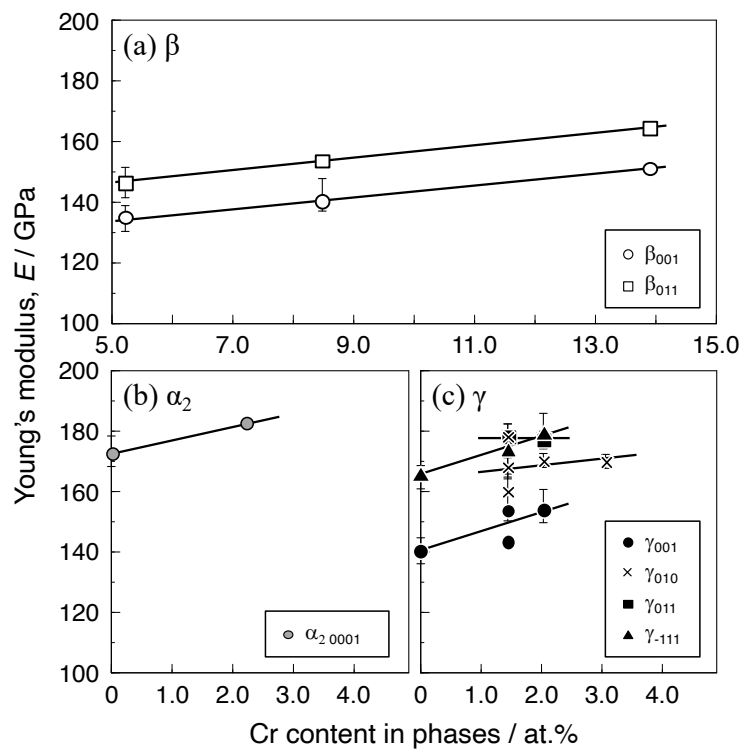
**Fig. 4-4** Indentation impressions in (a)  $\beta$ , (b)  $\alpha_2$ , and (c)  $\gamma$  phases in 43-3. Panels d–f are corresponding phase maps obtained by EBSD before the tests. Note that the maximum indentation load for  $\beta$  and  $\gamma$  phases is 30 mN, whereas that for  $\alpha_2$  phase is 25 mN.



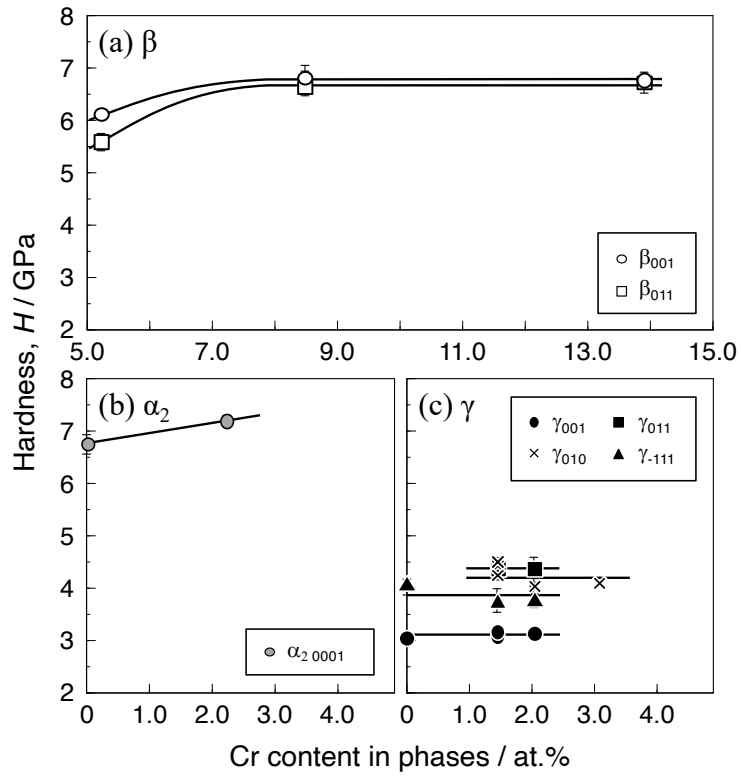
**Fig. 4-5** (a) Young's modulus and (b) hardness of representative points in each phase in 43-3 as a function of indentation depth. The red bands represent the depth range used for the averaging of properties.



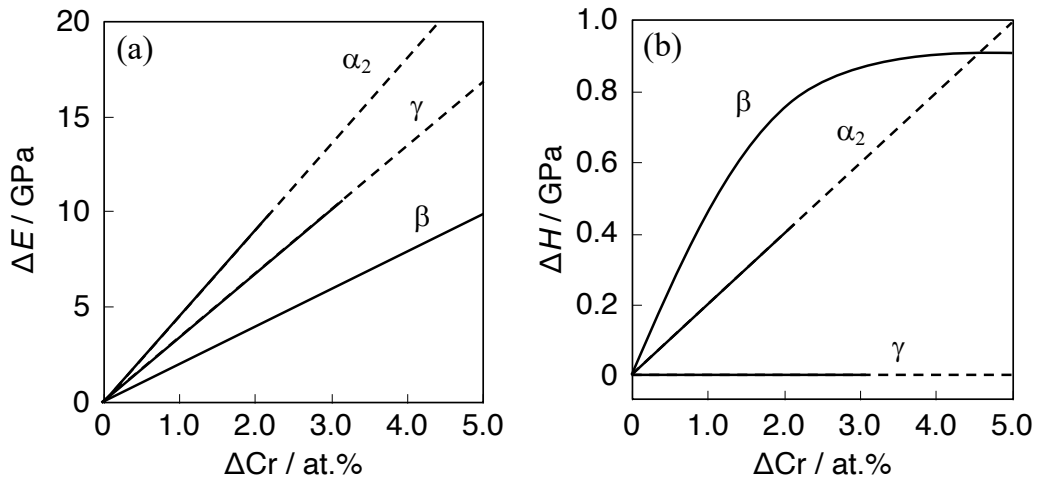
**Fig. 4-6** Young's modulus (white bar) and hardness (gray) of (a)  $\beta$ , (b)  $\alpha_2$ , and (c)  $\gamma$  phases with various orientations referred to the points in the standard stereographic triangle of each phase. Note that  $\beta$  and  $\gamma$  phases are from 44-4, whereas  $\alpha_2$  phase is from 43-3.



**Fig. 4-7** Cr content dependence of the Young's modulus in (a)  $\beta$ , (b)  $\alpha_2$ , and (c)  $\gamma$  phases.



**Fig. 4-8** Cr content dependence of the Hardness in (a)  $\beta$ , (b)  $\alpha_2$ , and (c)  $\gamma$  phases.



**Fig. 4-9** Change in the (a) Young's modulus and (b) hardness as a function of the increment of Cr content in each phase. The curves are drawn under the averaged values.



# Chapter 5

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Oxygen Effect on Young's Modulus and Hardness of the  
Constituent Phases Evaluated by Nano-indentation

## 5.1 Introduction

In chapter 4, the Young's modulus and the hardness of the  $\beta$ ,  $\alpha_2$  and  $\gamma$  phases and their chromium content dependence are evaluated. As mentioned in chapter 1, it is also needed to investigate the effect of oxygen on the mechanical properties since the oxygen is inevitably introduced in TiAl alloys, especially during the powder metallurgical processes.

It is known that the oxygen makes the alloys less ductile and more brittle [1–5]. In  $\alpha_2 + \gamma$  two-phase alloys, the oxygen is mainly partitioned into  $\alpha_2$  phase, and the solubility in  $\gamma$  phase is very limited, as reported by Menand et al. [6,7] and Nakashima et al. [8]. Thus, it is thought that the  $\alpha_2$  phase itself is closely related to deterioration of the properties. In most of the previous research, however, it should be noted that the microstructures of the alloys were also changed by the oxygen addition, indicating that the oxygen affects the phase equilibria among the three phases due to the difference in the amount of solute oxygen among the phase. Therefore, it is necessary to identify whether the change in mechanical properties is caused by the change in nature of the constituent phases due to the solute oxygen itself or by the microstructural changes associated with the change in phase equilibria among the phases concerned. Concerning the  $\beta$  phase, there is no report on the effect of oxygen addition on the chemical composition and the properties of  $\beta$  phase in equilibrium with the  $\alpha_2$  and  $\gamma$  phases, even though the mechanical properties are improved by introducing the  $\beta$  phase. In order to design an alloy having excellent mechanical properties even with a high amount of oxygen, it is necessary to evaluate how the oxygen affects the phase equilibria among the constituent phases and affects the mechanical properties of the phases.

In this chapter, the alloy with intentional oxygen addition was prepared. Then, the oxygen concentration as well as metal elements in the constituent phases were first evaluated. Secondly, the mechanical properties of the phases were measured by nano-indentation technique. Finally, the effect of solute oxygen on the properties of each phase was quantitatively evaluated from the obtained results.

## 5.2 Experimental procedure

### 5.2.1 Sample preparation

An alloy with a nominal composition of Ti-43Al-3Cr (at.%) was selected as a base alloy. It was confirmed that this alloy decomposes into the three phases of  $\beta$ ,  $\alpha_2$  and  $\gamma$  at 1373 K in the previous chapter. An oxygen-doped alloy of Ti-44Al-4Cr-1.0O was also used in this chapter. These two alloys are hereafter referred to as 43-3 and 44-4-O. The 43-3 alloy was fabricated using cold crucible induction melting and gravity casting followed by forging at 1573 K with a reduction rate of 80% by one stroke, and the 44-4-O was prepared by arc-melting under an argon atmosphere into a button ingot of approximately 120 g using high-purity metals and TiO<sub>2</sub> powder.

Although the preparation methods differ between alloys because of the different purposes such as the studies on the phase equilibria and creep behavior, these alloys were homogenized prior to the equilibrium heat treatment, so that the nano-indentation measurements to examine the mechanical properties of the constituent phases are independent of the alloy preparations. The alloy composition was analyzed with inductively coupled plasma optical emission spectroscopy for metal elements and inert gas fusion for oxygen. The nominal and analyzed composition of the alloys are summarized in **Table 5-1**. The oxygen content in 43-3 and 44-4-O is 0.12 at.% (0.05 wt.%) and 1.11 at.% (0.46 wt.%), respectively. In the heat treatments, the samples with a size of approximately  $6 \times 6 \times 10 \text{ mm}^3$  were wrapped with Ta foil and encapsulated in quartz tube evacuated and backfilled with Ar gas to minimize oxidation. The samples were first homogenized in the  $\beta$  single phase region at 1673 K for 30 min followed by water quenching, and then equilibrated at 1373 K for 672 h. The heat-treated samples were mechanically polished with SiC paper and diamond paste, and they were electrically polished using a solution of 90 vol.% ethanol containing 6 vol.% perchloric acid to remove surface damage.

### 5.2.2 Microstructure characterization and composition analysis

The microstructure of the specimens was observed with a field emission scanning electron microscope (FE-SEM). The crystallographic orientation was examined using electron backscatter diffraction (EBSD) technique prior to the nano-indentation tests, since the properties obtained with nano-indentation tests are dependent on the orientation, as described in chapter 4. For the EBSD analyses, the  $\beta$ ,  $\alpha_2$  and  $\gamma$  phases were indexed as bcc, ordered  $D0_{19}$  (hcp) and ordered  $L1_0$  (fct) structures, respectively. The chemical composition of the individual phases was determined using a field emission electron probe micro-analyzer, equipped with a wavelength-dispersive X-ray spectrometer (WDS) and a soft X-ray emission spectrometer (SXES). For the metal elements (Ti, Al, and Cr), WDS analyses were performed under an accelerating voltage of 20 kV and a probe current of 20 nA using pure metals as standards, and for the oxygen analyses, SXES was used under an accelerating voltage of 6 kV, a probe current of 200 nA, and dwell time of 300 s, as was described in elsewhere [8].

### 5.2.3 Nano-indentation testing

Young's modulus,  $E$ , and hardness,  $H$ , of the  $\beta$ ,  $\alpha_2$  and  $\gamma$  phases were measured by nano-indenter. The testing procedure is the same as chapter 4.

## 5.3 Results and discussion

### 5.3.1 Microstructures and phase analyses

**Figure 5-1** shows backscattered electron images and phase maps obtained by EBSD of

43-3 and 44-4-O after the equilibration at 1373 K. The phase with the brightest, intermediate and darkest contrast in the backscattered electron images is identified as  $\beta$ ,  $\alpha_2$  and  $\gamma$  phase, respectively by EBSD analysis. Both alloys consist of the three phases of the  $\beta$ ,  $\alpha_2$  and  $\gamma$ . In 43-3, the  $\beta$  and  $\gamma$  phases, mainly in granular morphology, are the predominant phases (**Fig. 5-1 (a, c)**), whereas in 44-4-O, the  $\alpha_2$  and  $\gamma$  phases, in lamellar morphology, are dominant (**Fig. 5-1 (b, d)**). It is obvious that the  $\alpha_2/\gamma$  lamellar microstructure is stabilized by the addition of oxygen to the alloy, as previously reported by Nishikiori et al. [3] and Lamirand et al. [4,5].

The analyzed chemical composition of each phase present in the alloys shown in **Fig. 5-1** are summarized in **Table 5-2** and plotted on the isothermal section in **Fig. 5-2**. The phase on the Ti-rich corner of the three-phase tie triangle is the disordered  $\alpha$  or ordered  $\alpha_2$  phase at the heat treatment temperature of 1373 K. Although we have not identified the ordering state, Shaaban et al. concluded that it is the  $\alpha$  phase in Ti-Al-Cr ternary system from the shape of tie triangle and the Al content of the phase [9]. In contrast, it is likely to be the  $\alpha_2$  phase in Ti-Al-Cr-O quaternary system, according to the shape of tie triangle. The oxygen contents analyzed in the three phases of 43-3 are higher than the oxygen content in the alloy. This is presumably due to the oxygen pickup during the heat treatment. Nakashima et al. reported that the oxygen concentration of TiAl alloys can increase by a few hundred wt. ppm during the heat treatment even if the treatment is conducted under argon atmosphere [8]. Our unpublished results also show the same tendency. The oxygen content in the alloys which is estimated from the analyzed oxygen content in the phases and the area fraction of the phases is 0.24 at.% for 43-3 and 1.14 at.% for 44-4-O. These values are reasonable when the oxygen pickup is taken into account. In both of the 43-3 and 44-4-O, the oxygen is enriched in the  $\alpha_2$  phase against the  $\beta$  and  $\gamma$  phases. Regardless of the oxygen levels in the alloys, the oxygen is poorly dissolved in the  $\gamma$  phase, and its concentration is nearly the same of less than 0.2 at.%. In contrast, the oxygen content increases slightly from 0.26 to 0.43 at.% in the  $\beta$  phase and increases drastically from 0.64 to 3.34 at.% in the  $\alpha_2$  phase with 1 at.% oxygen addition to the alloy. Consequently, the partition coefficient of oxygen between  $\alpha_2$  and  $\gamma$  phases,  $k_O^{\alpha_2/\gamma}$ , increases from 4.3 to 17.6, whereas that between  $\beta$  and  $\gamma$  phases,  $k_O^{\beta/\gamma}$ , increases from 1.7 to 2.3, where a partition coefficient was calculated as follows:  $k_O^{A/B} = X_O^A/X_O^B$  ( $X_O^A$  is the oxygen concentration in the A phase). In addition, the oxygen addition also changes the chromium concentration of each phase, especially in the  $\beta$  phase, although Al concentration of each phase remains almost unchanged; the chromium concentration in the  $\beta$  phase increases by 8 percentage points, whereas those in the  $\alpha_2$  and  $\gamma$  phases increase by only about 2 percentage points. The partition coefficients of chromium between each phase remains almost unchanged with the oxygen addition.

### 5.3.2 Change in Young's modulus and hardness with oxygen addition

The results of the nano-indentation in 43-3 and 44-4-O are summarized in **Table 5-3**. Since the Young's modulus,  $E$ , and hardness,  $H$ , of the three phases are dependent on the crystallographic orientation, the tests were performed with several indentation axes nearly parallel to low index orientations, based on the EBSD analysis. The  $E$  and  $H$  of each phase in the two alloys are compared at nearly the same orientation of [001], [0001] and [010] for the  $\beta$ ,  $\alpha_2$  and  $\gamma$  phases, respectively, as shown in **Fig. 5-3**. In the case where multiple tests were conducted for nearly the same orientation, e.g., [001] orientation of the  $\beta$  phase in 44-4-O, the value averaged over the multiple tests is used in **Fig. 5-3**. The  $E$  of  $\beta$  phase in equilibrium with the  $\alpha_2$  and  $\gamma$  phases increases tremendously from 135 to 162 GPa with 1 at.% of oxygen addition to the alloy, whereas that of the other two phases increases slightly from 183 to 189 GPa for the  $\alpha_2$  phase and from 169 to 173 GPa for the  $\gamma$  phase. In contrast, the  $H$  of  $\beta$  and  $\alpha_2$  phases increases from 6.1 to 7.1 GPa and from 7.2 to 8.2 GPa, respectively, whereas that of the  $\gamma$  phase remains almost unchanged at 4.4 GPa with oxygen addition to the alloy. Regardless of the oxygen level in the alloys, the  $\beta$  phase shows the smallest value of  $E$ , and the  $\gamma$  phase shows the smallest value of  $H$  among the three phases.

### 5.3.3 Separation of the oxygen effect and chromium effect

The present results clearly identified the change in the phase equilibria and the changes in the Young's modulus,  $E$ , and the hardness,  $H$ , of the  $\beta$ ,  $\alpha_2$  and  $\gamma$  phases in equilibrium each other with oxygen addition to the alloy in the Ti-Al-Cr ternary system. As mentioned earlier in section 5.3.1, the oxygen addition to the alloy changes not only the oxygen concentration, but also the chromium concentration in each phase. Therefore, the changes in properties of the phases with the oxygen addition should be affected both of the chromium and oxygen concentration, so that it is necessary to take the chromium effect into account in order to evaluate the effect of solute oxygen itself on the properties.

In the previous chapter, we investigated the effect of chromium on the  $E$  and  $H$  of the three phases of  $\beta$ ,  $\alpha_2$  and  $\gamma$ . Using the previous results, we separated the effect of oxygen and chromium, as schematically shown in **Fig. 5-4**. Here, we assumed that the oxygen content in each phase in the previous data is constant regardless of the alloy composition since the analyzed oxygen content in the alloys shows the same value of 0.12 at.%. In **Fig. 5-4**, "A" corresponds to the change in the mechanical property ( $E$  or  $H$ ) of the phases with the oxygen addition to the alloy in the present results shown in **Fig. 5-3**. From the interpolation (or extrapolation) line of the chromium effect in the alloys without oxygen-doping, obtained in chapter 4, we estimated the effect of oxygen on the mechanical properties (B). The calculated oxygen content dependence on the  $E$  and  $H$  in each phase is shown in **Fig 5-5**. The  $\beta$  phase shows the strongest oxygen content

dependence of the  $E$  and  $H$  among the three phases; the  $E$  and  $H$  in this phase increase by more than 10 GPa and 0.5 GPa, respectively, with the increase in oxygen content from 0.26 to 0.43 at.%. In contrast, the  $\alpha_2$  phase shows no or negative oxygen content dependence of the  $E$  and positive (but weaker) oxygen content dependence of  $H$ . Note that it is difficult to evaluate the oxygen content dependence of the  $E$  and  $H$  in the  $\gamma$  phase since the solute oxygen level in this phase is almost the same regardless of the oxygen concentration in the alloys. **Figure 5-6** shows the change in the measured properties against increment of oxygen content in each phase, together with those against increment of chromium content in each phase. In these figures, the oxygen content dependence in the  $\gamma$  phase is not shown since it is difficult to evaluate the dependence due to the limited solubility of oxygen in the  $\gamma$  phase, as mentioned earlier. In the  $\beta$  phase, the increasing rate of the  $E$  and  $H$  per at.% oxygen is 67 GPa/at.% and 2.7 GPa/at.%, respectively, much larger than that per at.% chromium (2.0 GPa/at.% and 0.4 GPa/at.%, respectively). In contrast, the  $E$  of  $\alpha_2$  phase does not depend on the oxygen content in the phase, and the increasing rate of the  $H$  in  $\alpha_2$  phase for oxygen is approximately 0.2 GPa/at.%, which is comparable to that for chromium.

#### 5.3.4 Effect of solute oxygen on the Young's modulus and hardness of each phase

The strongest oxygen content dependence of the  $E$  and  $H$  in the  $\beta$  phase would be associated with the size of the interstitial site. **Figure 5-7** shows the crystal structures of the phases in the present alloys and the interstitial sites in each phase. The lattice constants of the phases are referenced from [10]. The size of the octahedral sites is calculated using a hard-sphere model, but only approximate values are provided for  $\alpha_2$  and  $\gamma$  phases because it is difficult to determine the atomic radii in the two phases. The size of the interstitial octahedral site in the  $\beta$  phase, which exhibits A2 or B2 crystal structure, is less than half of that in the  $\alpha_2$  (D0<sub>19</sub>) and  $\gamma$  (L1<sub>0</sub>) phases, so that the lattice distortion around the interstitial oxygen in the  $\beta$  phase is the most significant among the three phases. Consequently, both of the  $E$  and  $H$ , which are related to chemical bonding between atoms and dislocation motion, respectively, increase the most with oxygen addition.

In the  $\alpha_2$  phase, the  $E$  does not increase, whereas the  $H$  increase with the oxygen addition. The former is associated with the chemical bonding, and the latter is associated with the dislocation motion. The no oxygen content dependence of  $E$  indicates that the interstitial oxygen atoms in  $\alpha_2$  phase does not affect the chemical bonding state between atoms. The difference between the  $\beta$  and  $\alpha_2$  phases would be caused by the relative size of the interstitial octahedral site to the size of oxygen atom. In contrast, the  $H$  of  $\alpha_2$  phase increases with the oxygen content due to the locking of dislocations. As mentioned earlier in section 3.1, the hcp phase is likely to be the  $\alpha$  phase (disordered) in 43-3 and the  $\alpha_2$  phase (ordered) in 44-4-O at the heat treatment temperature of 1373 K. Although the phases exist as an ordered phase at room temperature, the

size of anti-phase domain (APD) is much larger in the latter case than that in the former case. The smaller APDs in the  $\alpha_2$  phase makes the phase harder [11]. Therefore, the  $H$  of the  $\alpha_2$  phase may be larger than the measured value in the case where the phase exists as a disordered phase at the heat treatment temperature. This means that the effect of solute oxygen on the  $H$  of  $\alpha_2$  phase may be larger than the present result.

The mechanical properties of the  $\gamma$  phase are not affected by the oxygen addition since the oxygen concentration in the  $\gamma$  phase is extremely limited regardless of the oxygen level in the alloy. The limited solubility of oxygen in the  $\gamma$  phase would be associated with the type of atoms surrounding the octahedral site. There are some kinds of octahedral sites categorized by the surrounding atoms in  $\alpha_2$  ( $\alpha$ ) and  $\gamma$  phase as shown in **Fig. 5-7**. The octahedral site surrounded by six Ti atoms, namely  $Ti_6$  site, exists only in the  $\alpha_2$  (and  $\alpha$ ) phase, whereas the  $Ti_4Al_2$  and  $Ti_2Al_4$  sites exist in the  $\gamma$  phase. The size of these sites is not much different, but the Ti atoms generally have good affinity with oxygen atoms. Therefore, it can be deduced that the oxygen atoms preferentially occupy the  $Ti_6$  sites in the  $\alpha_2$  phase in comparison with the other sites, and they are poorly dissolved into the  $\gamma$  phase, which has only  $Ti_4Al_2$  and  $Ti_2Al_4$  sites. The fact that the  $\beta$  phase has the larger solubility than the  $\gamma$  phase despite the  $\beta$  phase has much smaller octahedral site would also be related to the affinity between atoms, but it is beyond the scope of this paper.

The fact that the oxygen is poorly dissolved into the  $\gamma$  phase and the mechanical properties of the  $\gamma$  phase remains unchanged with the addition of oxygen to the alloy provides a significant indication for alloy design. The  $\gamma$  phase is the softest and most deformable phase in TiAl alloys at room temperature as shown in chapter 2 and 4, and the present results indicate that the deformability of the  $\gamma$  phase remains unchanged with the oxygen addition to alloys. Therefore, it should be possible to design a microstructure without losing ductility and toughness even if the alloy contains high amount of oxygen, unlike the general belief. The authors concluded that the ductility worsening reported in literature [1–5] is due to the microstructure change with the addition of oxygen. On the contrary, the oxygen can be used as one of the alloying elements, not an impurity element. In fact, Larsen suggested that an oxygen concentration range from 800 to 1500 wt. ppm is effective for improvement of creep resistance [12]. In addition, the hard  $\beta$  and  $\alpha_2$  phase can enhance the deformability of  $\gamma$  phase by activating multiple deformation system as described in detail in the previous chapters. The oxygen mixed into alloys during powder processing can be useful for improvement of mechanical properties. It should be noted that the knowledge of phase equilibria is necessary to design an optimal microstructure for improved mechanical properties.

## 5.4 Summary

In order to identify the effect of oxygen on the Young's modulus and hardness of the  $\beta$ -Ti,

$\alpha_2$ -Ti<sub>3</sub>Al and  $\gamma$ -TiAl phases in equilibrium each other, Ti-Al-Cr ternary and Ti-Al-Cr-O quaternary alloys were intentionally prepared, and the properties of each phase were measured by nano-indentation method. The following conclusions were obtained:

1. Both of the oxygen-free and 1 at.% doped alloys used in this study decompose into the three phases of the  $\beta$ ,  $\alpha_2$  ( $\alpha$ ) and  $\gamma$ . The oxygen is preferentially dissolved into the  $\alpha_2$  ( $\alpha$ ) phase, and its concentration changes from 0.64 to 3.34 at.% with oxygen addition to the alloy, whereas that in the  $\gamma$  phase is limited below 0.2 at.% regardless of the oxygen content in the alloy. The oxygen concentration in the  $\beta$  phase changes from 0.26 to 0.43 at.%. The addition of the oxygen to the alloy also changes the chromium concentration of the phases, especially for the  $\beta$ , from 5.2 to 13.7 at.%.
2. The Young's modulus of the  $\beta$  phase in equilibrium with the  $\alpha_2$  and  $\gamma$  phases increases tremendously by nearly 30 GPa, whereas that of the other two phases increases by only a few GPa with 1 at.% of oxygen addition to the alloy. In contrast, the hardness of the  $\beta$  and  $\alpha_2$  phases increases by about 1 GPa, whereas that of the  $\gamma$  phase remains almost unchanged with oxygen addition to the alloy.
3. When the chromium effect is excluded, the  $\beta$  phase shows the strongest oxygen content dependence of the  $E$  and  $H$  among the three phases. The increasing rate of the  $E$  and  $H$  per at.% oxygen in the phase is 67 GPa/at.% and 2.7 GPa/at.%, respectively, much larger than that per at.% chromium. In contrast, the  $\alpha_2$  phase shows no or negative oxygen content dependence of the  $E$  and positive (but weaker) oxygen content dependence of  $H$  (0.2 GPa/at.%). Note that it is difficult to evaluate the oxygen content dependence of the  $E$  and  $H$  in the  $\gamma$  phase since the solute oxygen level in this phase is almost the same regardless of the oxygen concentration in the alloys.
4. The unchanged mechanical properties of the  $\gamma$  phase due to the limited solubility provides a significant indication for alloy design. Even if the alloy contains high amount of oxygen, the deformability of the  $\gamma$  phase would remain unchanged, and it should be possible to design a microstructure without losing ductility.



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**Table 5-1** Nominal and analyzed composition of the alloys studied.

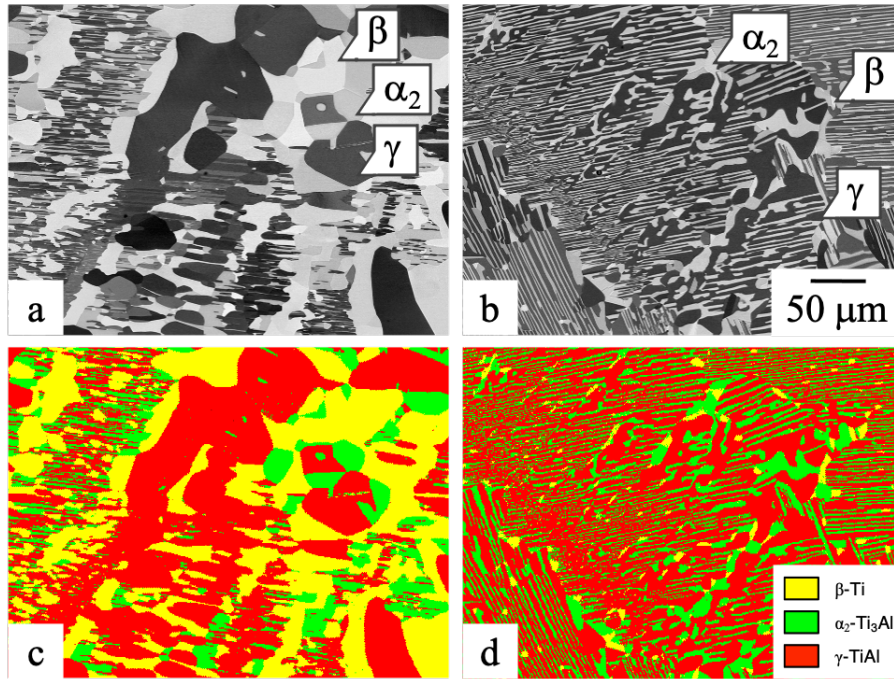
| Mark   | Nominal Composition / at.% |    |     |      | Analyzed Composition / at.% |     |      |      |
|--------|----------------------------|----|-----|------|-----------------------------|-----|------|------|
|        | Al                         | Cr | O   | Ti   | Al                          | Cr  | O    | Ti   |
| 43-3   | 43                         | 3  | 0   | Bal. | 42.5                        | 2.9 | 0.12 | Bal. |
| 44-4-O | 44                         | 4  | 1.0 | Bal. | 44.2                        | 4.1 | 1.11 | Bal. |

**Table 5-2** Analyzed compositions of each phase in the alloys studied.

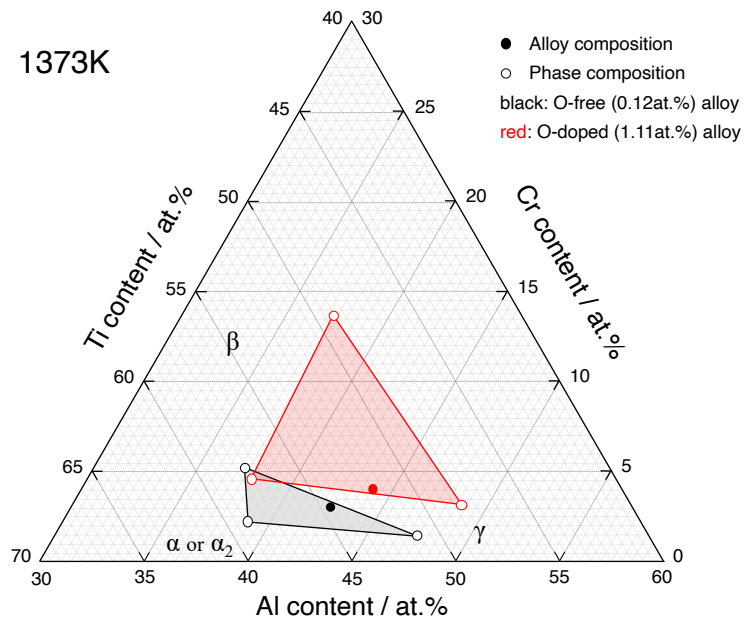
| Alloy  | Phase present      | Composition / at.% |      |      |      | Partition coefficient of Cr |                   | Partition coefficient of O |                   |
|--------|--------------------|--------------------|------|------|------|-----------------------------|-------------------|----------------------------|-------------------|
|        |                    | Al                 | Cr   | O    | Ti   | $\beta/\gamma$              | $\alpha_2/\gamma$ | $\beta/\gamma$             | $\alpha_2/\gamma$ |
| 43-3   | $\beta$            | 37.2               | 5.2  | 0.26 | Bal. | 3.7                         | 1.6               | 1.7                        | 4.3               |
|        | $\alpha_2(\alpha)$ | 38.9               | 2.2  | 0.64 | Bal. |                             |                   |                            |                   |
|        | $\gamma$           | 47.4               | 1.4  | 0.15 | Bal. |                             |                   |                            |                   |
| 44-4-O | $\beta$            | 37.3               | 13.7 | 0.43 | Bal. | 4.3                         | 1.4               | 2.3                        | 17.6              |
|        | $\alpha_2$         | 37.8               | 4.6  | 3.34 | Bal. |                             |                   |                            |                   |
|        | $\gamma$           | 48.7               | 3.2  | 0.19 | Bal. |                             |                   |                            |                   |

**Table 5-3** Nano-indentation test results of the three phases in each alloy.

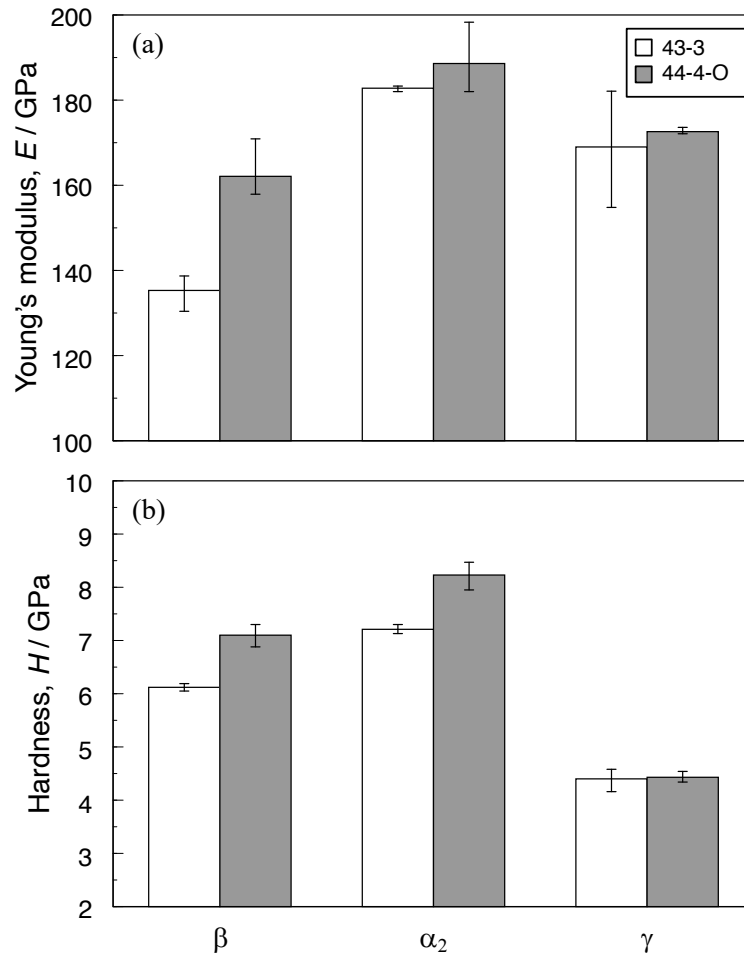
| Alloy  | Phase      | Orientation   | Number of measurements | Young's modulus / GPa |         |         | Hardness / GPa |         |         |
|--------|------------|---------------|------------------------|-----------------------|---------|---------|----------------|---------|---------|
|        |            | Approximation |                        | Average               | Maximum | Minimum | Average        | Maximum | Minimum |
| 43-3   | $\beta$    | 001           | 4                      | 135.3                 | 138.9   | 130.4   | 6.12           | 6.19    | 6.05    |
|        |            | 011           | 10                     | 146.5                 | 154.8   | 141.5   | 5.60           | 5.75    | 5.42    |
|        | $\alpha^2$ | 0001          | 3                      | 182.8                 | 183.3   | 182.0   | 7.21           | 7.30    | 7.13    |
|        |            | 10-10         | 7                      | 171.4                 | 178.7   | 167.9   | 5.94           | 6.12    | 5.84    |
|        |            | 2-1-10        | 9                      | 165.9                 | 170.9   | 163.2   | 5.67           | 5.80    | 5.54    |
|        | $\gamma$   | 001           | 3                      | 153.9                 | 154.1   | 150.3   | 3.07           | 3.09    | 3.04    |
|        |            | 001           | 3                      | 143.6                 | 143.9   | 143.3   | 3.17           | 3.19    | 3.13    |
|        |            | 010           | 3                      | 178.6                 | 182.1   | 174.8   | 4.26           | 4.36    | 4.16    |
|        |            | 010           | 4                      | 168.0                 | 171.5   | 164.8   | 4.44           | 4.52    | 4.36    |
|        |            | 010           | 7                      | 160.3                 | 165.1   | 154.8   | 4.50           | 4.58    | 4.36    |
|        |            | 011           | 4                      | 178.7                 | 182.4   | 174.5   | 4.38           | 4.49    | 4.22    |
|        |            | -111          | 13                     | 173.4                 | 179.3   | 164.2   | 3.72           | 3.99    | 3.54    |
| 44-4-O | $\beta$    | 001           | 3                      | 160.5                 | 163.5   | 157.9   | 7.10           | 7.28    | 6.92    |
|        |            | 001           | 3                      | 161.0                 | 164.7   | 158.3   | 7.12           | 7.18    | 7.07    |
|        |            | 001           | 4                      | 162.1                 | 165.2   | 160.1   | 7.09           | 7.30    | 6.88    |
|        |            | 001           | 4                      | 164.8                 | 170.9   | 160.3   | 7.09           | 7.12    | 7.05    |
|        |            | -111          | 4                      | 172.3                 | 173.9   | 171.0   | 6.78           | 6.82    | 6.72    |
|        | $\alpha^2$ | 0001          | 1                      | 186.6                 | 186.6   | 186.6   | 8.39           | 8.39    | 8.39    |
|        |            | 0001          | 2                      | 186.4                 | 187.3   | 185.6   | 8.12           | 8.24    | 7.99    |
|        |            | 0001          | 1                      | 188.2                 | 188.2   | 188.2   | 8.15           | 8.15    | 8.15    |
|        |            | 0001          | 2                      | 183.1                 | 184.3   | 182.0   | 8.04           | 8.14    | 7.95    |
|        |            | 0001          | 1                      | 198.3                 | 198.3   | 198.3   | 8.46           | 8.46    | 8.46    |
|        |            | 0001          | 6                      | 188.6                 | 191.0   | 183.9   | 8.23           | 8.47    | 8.13    |
|        |            | 2-1-10        | 2                      | 160.4                 | 162.7   | 158.1   | 8.10           | 8.16    | 8.04    |
|        |            | 2-1-10        | 5                      | 170.5                 | 174.8   | 165.3   | 7.41           | 7.58    | 7.29    |
|        | $\gamma$   | 010           | 3                      | 172.6                 | 173.6   | 172.1   | 4.43           | 4.54    | 4.34    |
|        |            | 011           | 5                      | 175.3                 | 176.7   | 173.3   | 4.28           | 4.44    | 4.18    |
|        |            | 011           | 2                      | 176.8                 | 177.0   | 176.5   | 4.24           | 4.24    | 4.23    |
|        |            | 011           | 2                      | 180.5                 | 181.2   | 179.8   | 4.13           | 4.15    | 4.11    |
|        |            | -111          | 2                      | 180.7                 | 181.0   | 180.4   | 4.68           | 4.71    | 4.66    |
|        |            | -111          | 7                      | 177.0                 | 178.3   | 174.9   | 4.05           | 4.13    | 3.99    |
|        |            | -111          | 1                      | 170.6                 | 170.6   | 170.6   | 3.96           | 3.96    | 3.96    |



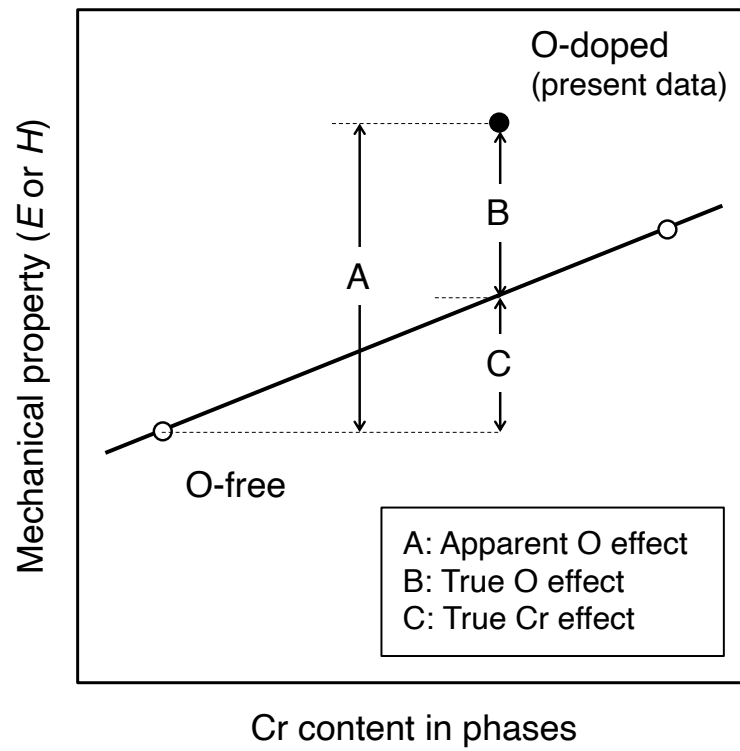
**Fig. 5-1** Backscattered electron images and phase maps obtained by EBSD of (a, c) 43-3 and (b, d) 44-4-O after the heat treatments.



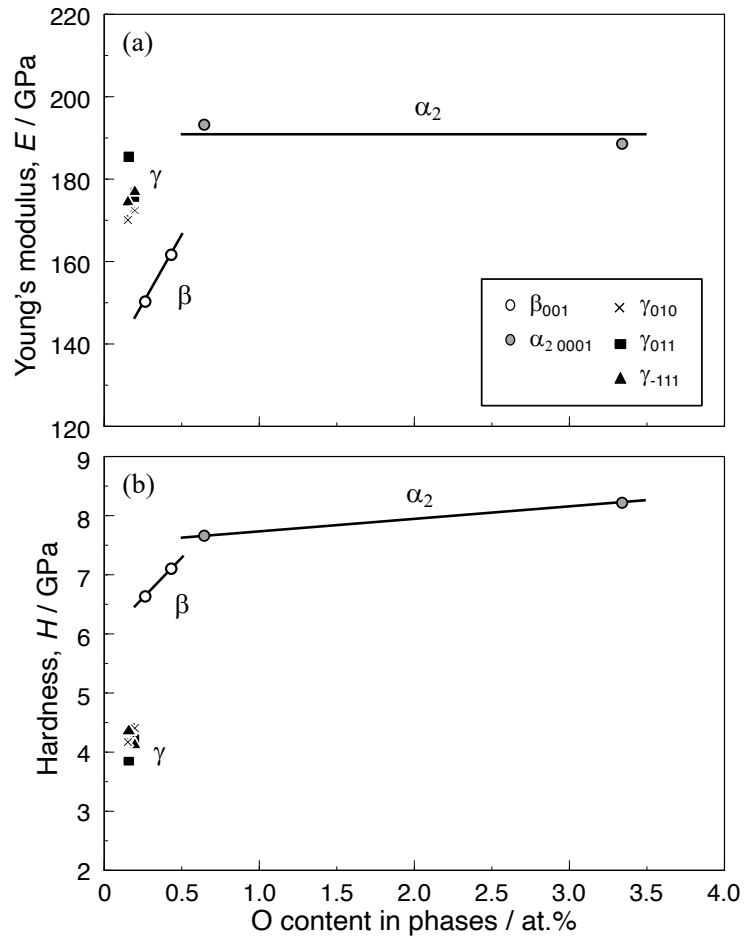
**Fig. 5-2**  $\beta/\alpha(\alpha_2)/\gamma$  three-phase tie triangle at 1373 K in oxygen-free (black) and -doped (red) alloys.



**Fig. 5-3** (a) Young's modulus and (b) hardness of the  $\beta$ ,  $\alpha_2$  and  $\gamma$  phases of the oxygen-free (43-3) and -doped (44-4-O) alloys.

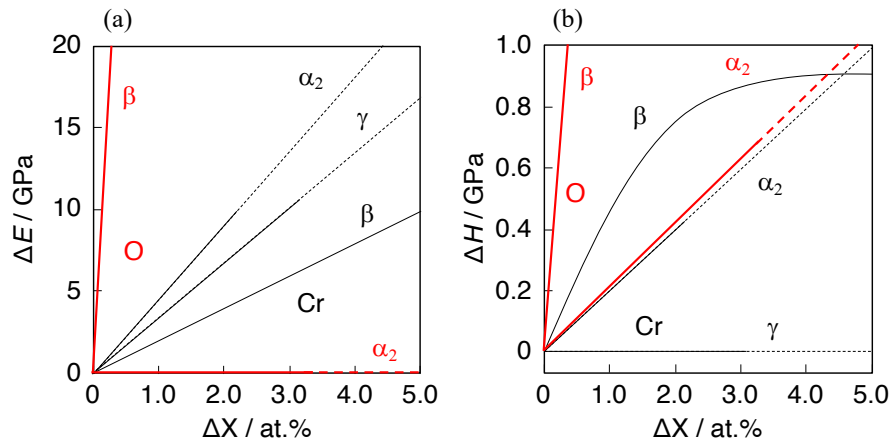


**Fig. 5-4** Schematic illustration of the separation of oxygen effect and chromium effect on the mechanical properties.

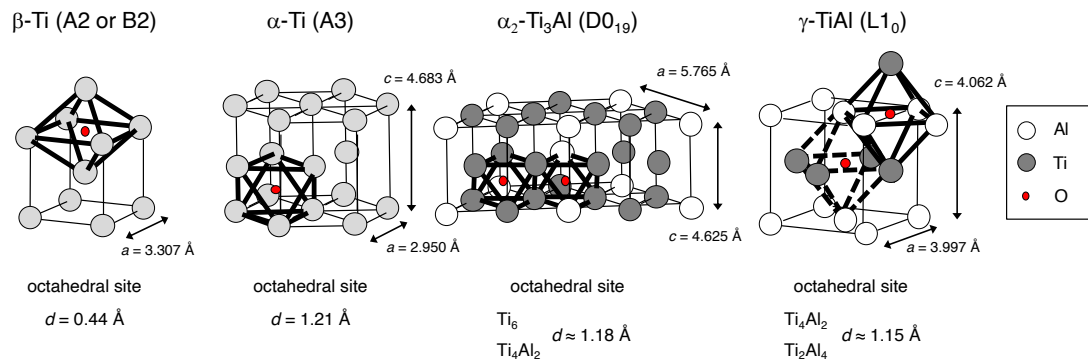


**Fig. 5-5** Oxygen content dependence of (a) Young's modulus and (b) hardness of each phase. The plot of the phase with less oxygen content was calculated in the way shown in Fig. 5-4.





**Fig. 5-6** Change in the (a) Young's modulus and (b) hardness as a function of the increment of oxygen (red) or chromium (black) content in each phase.



**Fig. 5-7** Size of interstitial sites in each phase.

# Chapter 6

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Temperature Effect on Young's Modulus  
and Hardness of the Constituent Phases  
Evaluated by Nano-indentation

## 6.1 Introduction

In **Chapters 4 and 5**, the Young's modulus and hardness of the constituent phases in TiAl alloys were investigated. However, the target service temperature of the LPT blades of TiAl alloys is around 1073 K, so that the properties of each phase at elevated temperatures also have to be evaluated. There are some reports on the mechanical properties of the  $\alpha_2$  and  $\gamma$  single phase alloys at elevated temperatures [1,2]. However, the composition of the  $\gamma$  single phase alloys is usually Al-rich or stoichiometric composition, so that their mechanical behaviors are different from those of the  $\gamma$  phase in equilibrium with  $\alpha_2$  and  $\beta$  phase.

Recently, nano-indenters for high temperature measurements have been developed [3]. It allows to evaluate mechanical properties of constituent phases in multi-phase alloys at high temperatures up to about 1373 K. In this chapter, the Young's modulus and hardness of the phases were measured by nano-indentation at elevated temperatures up to 1073 K, and the effect of temperature on the properties was evaluated.

## 6.2 Experimental procedure

### 6.2.1 Sample preparation

An alloy with nominal composition of Ti-43-3Cr (at.%) was investigated in this chapter. This alloy is hereafter referred to as 43-3. The 43-3 alloy was fabricated using cold crucible induction melting and gravity casting followed by forging at 1573 K with a reduction rate of 80% by one stroke. In the heat treatments, the samples with a size of approximately  $6 \times 6 \times 10 \text{ mm}^3$  were wrapped with Ta foil and encapsulated in quartz tube evacuated and backfilled with Ar gas to minimize oxidation. The samples were first homogenized in the  $\beta$  single phase region at 1673 K for 30 min followed by water quenching, and then equilibrated at 1373 K for 672 h. The heat-treated samples were mechanically polished with SiC paper and diamond paste, and they were electrically polished using a solution of 90 vol.% ethanol containing 6 vol.% perchloric acid to remove surface damage.

### 6.2.2 Microstructure characterization

The microstructure characterization procedure is the same as that in chapter 4.

### 6.2.3 Heating of nano-indenter

The nano-indenter used in this chapter can perform the measurement at elevated temperatures up to about 1073 K by heating both sample and tip separately. In order to obtain accurate results, we have to avoid the thermal drifts caused by the temperature difference between the sample and tip. In order to match the temperatures of the sample and tip, the temperature difference was estimated by repeating contact and non-contact between the sample and tip and

observing the change in displacement due to thermal expansion or contraction. Then, the temperature of the sample was adjusted until the temperature difference disappeared. Finally, the measurements can be conducted at the target temperature.

#### 6.2.4 Nano-indentation testing

Young's modulus,  $E$ , and hardness,  $H$ , of the  $\beta$  and  $\gamma$  phases were measured by nano-indenter at room temperature, 673 K, 873 K and 1073 K. A Berkovich tip made of sapphire was used in this chapter since diamond tips are not suitable for high-temperature measurements [ref]. The Poisson's ratio and the Young's modulus of the sapphire tip were set to 0.3 and 450 GPa, respectively. Other testing conditions are the same as those in **Chapter 4**.

**Figure 6-1** is a schematic illustration showing the thermal history applied to the sample used in this chapter. After the heat treatment at 1373 K, nano-indentation tests were performed at room temperature. Subsequently, the sample (and tip) were heated at a rate of about 10 K/min, and the temperature matching procedure and the tests were done at the temperature. After each measurement set at high temperatures, the sample was cooled to room temperature and heated again for the next temperature.

### 6.3 Results and discussion

**Figure 6-2** shows backscattered electron (BSE) image of 43-3 after the equilibrium heat treatment at 1373 K. As shown in **Chapter 4**, the alloy consists of the three phases of  $\beta$ ,  $\alpha_2$  and  $\gamma$ . Due to the small fraction of the  $\alpha_2$  phase, the nano-indentation tests were conducted to only  $\beta$  and  $\gamma$  phases.

**Figure 6-3** shows *in situ* secondary electron (SE) images taken at room and high temperatures. The sample was set on the indenter, and its surface was inclined at an angle of 75°. Note that these images were taken with low resolution to check the test position. The microstructure can be clearly observed at room-temperature, although the phases cannot be identified with SE images. At temperatures of 673 and 873 K, the SEM images are noisy, but the microstructure can be observed. The contrast between phases became clear with temperature probably due to the oxidation of the surface. At 1073 K, the microstructure cannot be identified anymore due to the noise. **Figure 6-4** shows a post mortem SE image of the tested area together with a BSE image of the corresponding area before testing. The sample surface is oxidized, but the phase boundaries and indentation impressions can be identified.

After the nano-indentation tests at high temperatures and post mortem observation, the sample was polished again, and the microstructure was observed by FE-SEM as shown in **Fig. 6-5**. Fine precipitates with a size of about 1  $\mu\text{m}$  are observed in the  $\beta$  grains, and fine  $\gamma$  lamellae are observed in the  $\alpha_2$  phase. However, the phase of the precipitates observed in the  $\beta$  phase, as well

as the timing of their formation, remain unclear. Further experiments are needed to identify the phase of precipitates and their formation timing.

**Figure 6-6** shows indentation load–depth curves of each phase region at various temperatures. At each temperature, the tests were performed on the phase having the same crystallographic orientation since the properties depend on the orientation. The tests at 673 K were unsuccessful, so that the results at 673 K are not included in this figure. For both of the  $\gamma$  phase and the  $\beta$  phase region, pop-in behavior was often observed at 873 K, whereas no or few clear pop-ins were observed at the other temperatures.

**Figure 6-7** shows the change in  $E$  and  $H$  of the  $\gamma$  phase and  $\beta$  phase region with temperature. Both of the  $E$  and  $H$  of the  $\gamma$  phase decrease with temperature. In contrast, the  $E$  and  $H$  of the  $\beta$  phase region increase at temperatures from room temperature to 873 K, and they decrease at temperatures from 873 to 1073 K. The  $E$  of  $\gamma$  phase is larger than that of the  $\beta$  phase region below a temperature of 873 K, but becomes smaller than that of the  $\beta$  phase region at around 900 K. On the other hand, the  $H$  of  $\gamma$  phase is smaller than that of the  $\beta$  phase region at all temperatures below 1073 K. Note that the  $E$  and  $H$  of  $\beta$  phase region measured in the present study may be larger than those of the  $\beta$  phase itself without precipitates.

#### 6.4 Summary

In order to identify the effect of temperature on the Young's modulus and hardness of the  $\beta$ -T and  $\gamma$ -TiAl phases in equilibrium each other, the properties of the phases were measured at room temperature and elevated temperatures by nano-indentation method. The following conclusions were obtained:

1. The  $\beta$  phase with a composition of Ti-37.2Al-5.2Cr produces precipitation during a few hours of heating at a temperature below 1073 K. The precipitates exhibit a plate- or needle-like morphology and a size of about 1  $\mu\text{m}$ .
2. The Young's modulus of the  $\gamma$  phase shows stronger temperature dependence than that of the  $\beta$  phase (+ precipitates) region, and it is larger than that of the  $\beta$  phase region below 873 K but becomes smaller at 1073 K. In contrast, the hardness of the  $\beta$  phase (+ precipitates) region shows stronger temperature dependence than that of the  $\gamma$  phase, whereas it is larger than that of the  $\gamma$  phase at temperatures below 1073 K.

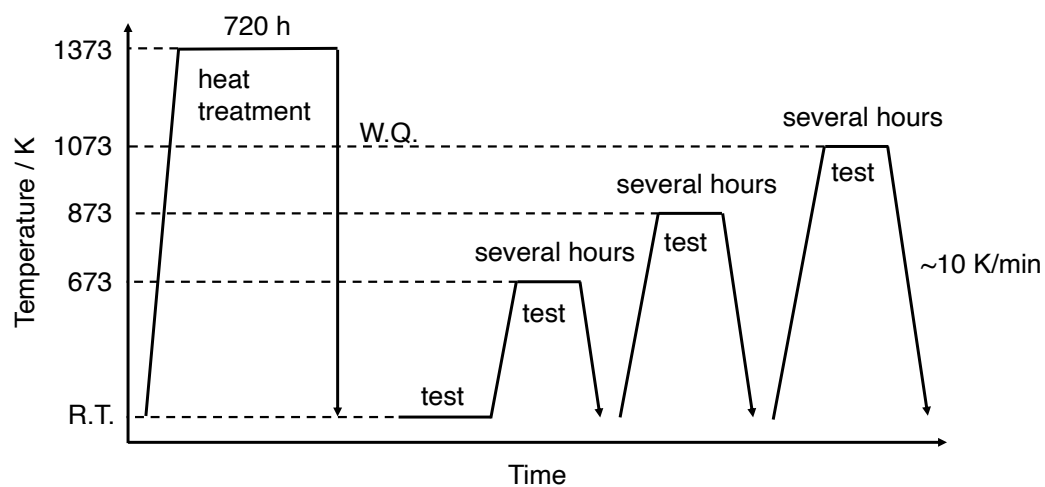
As future work, the following problems should be addressed:

- when the precipitates in  $\beta$  phase are produced
- what phase the precipitate is

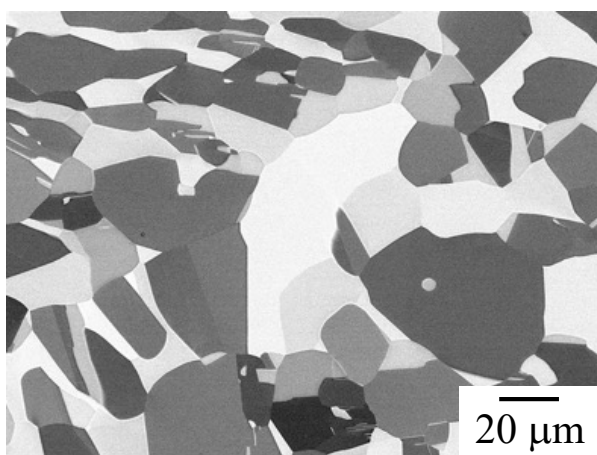
- how the precipitates affect the properties
- the temperature dependence of the properties of  $\alpha_2$  phase
- what material of the tip is the best for the indentation on TiAl alloys at elevated temperatures
- the reproducibility of the measurements at elevated temperatures

## References

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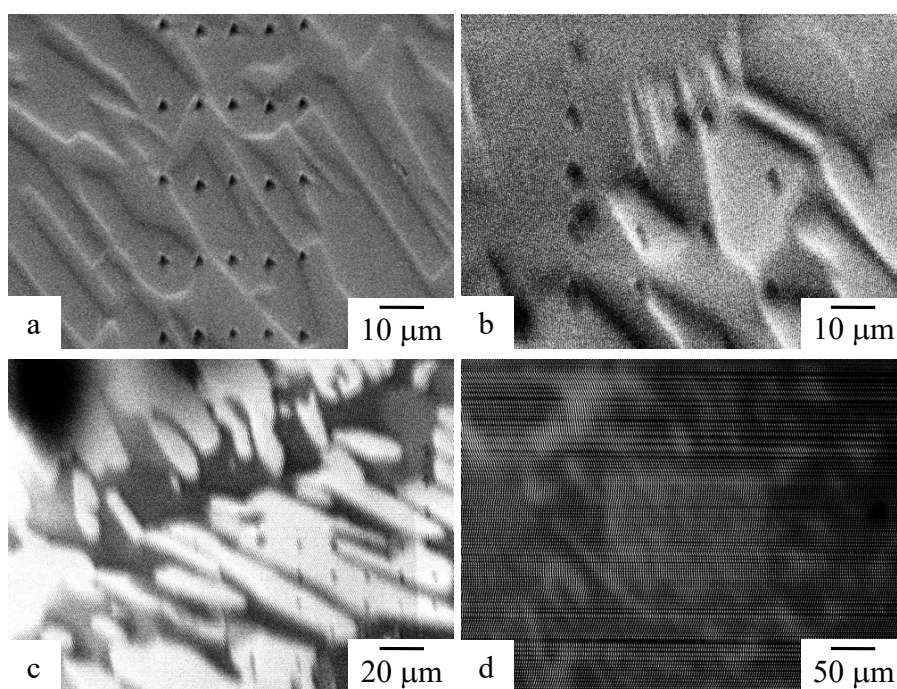


**Fig. 6-1** Schematic illustration of thermal history applied to the sample used in this chapter.

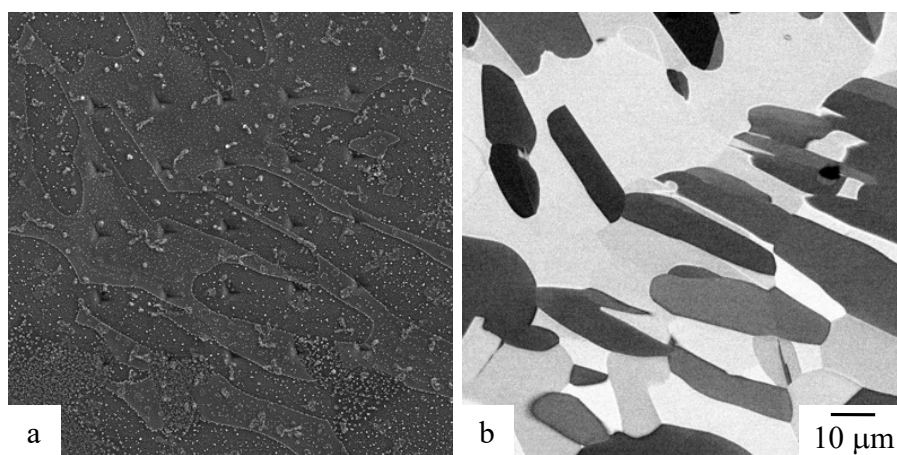


**Fig. 6-2** Backscattered electron image of 43-3 after the equilibrium heat treatment at 1373 K.

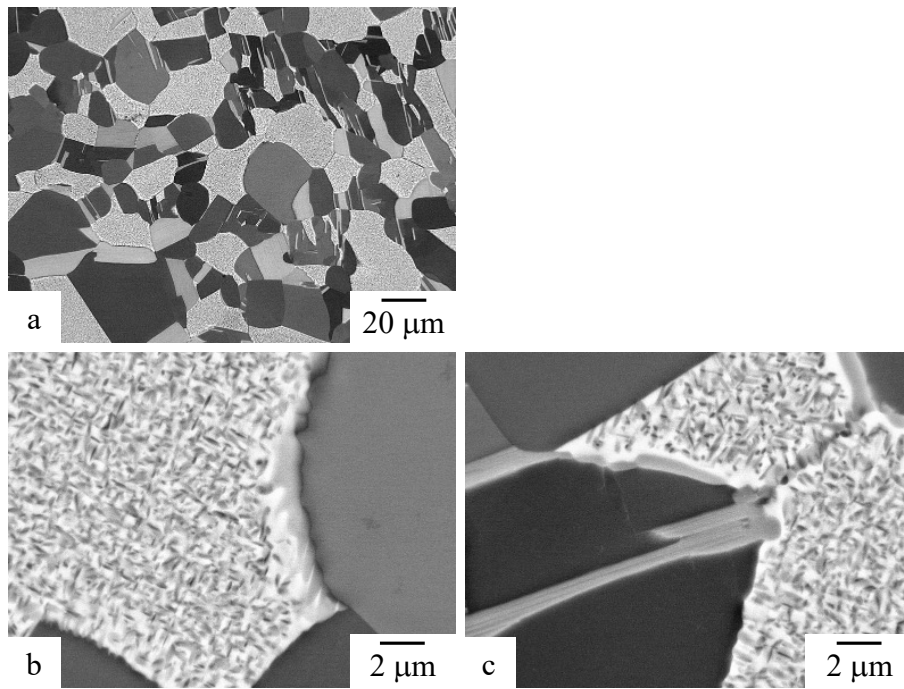




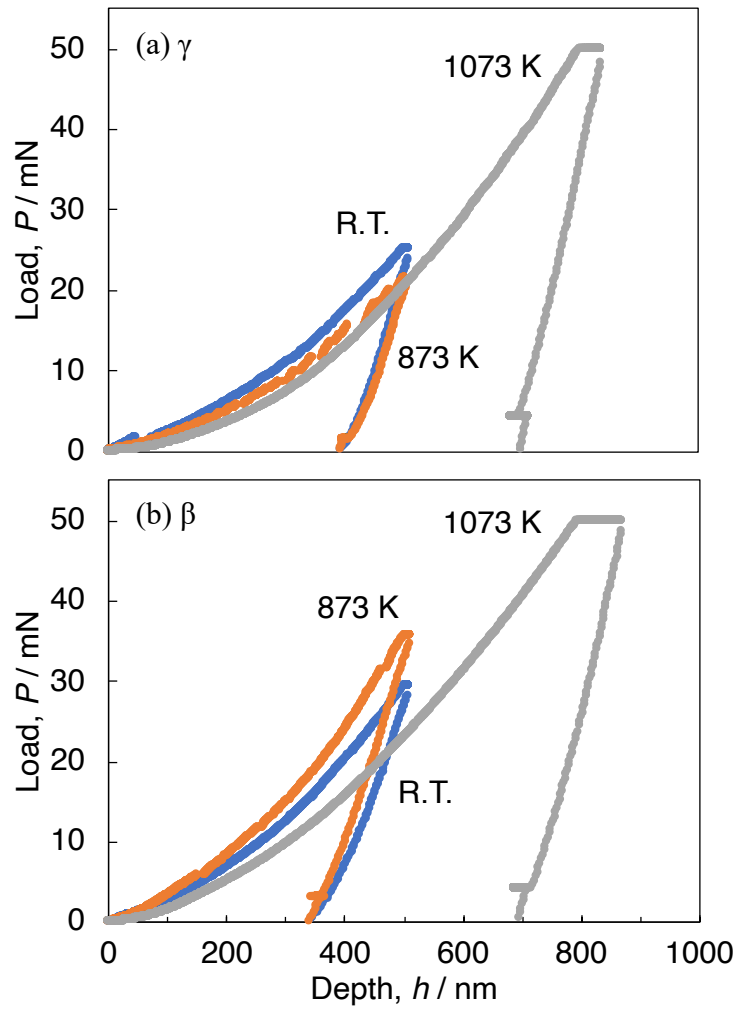
**Fig. 6-3** *In situ* secondary electron images taken at (a) room temperature, (b) 673 K, (c) 873 K and (d) 1073 K.



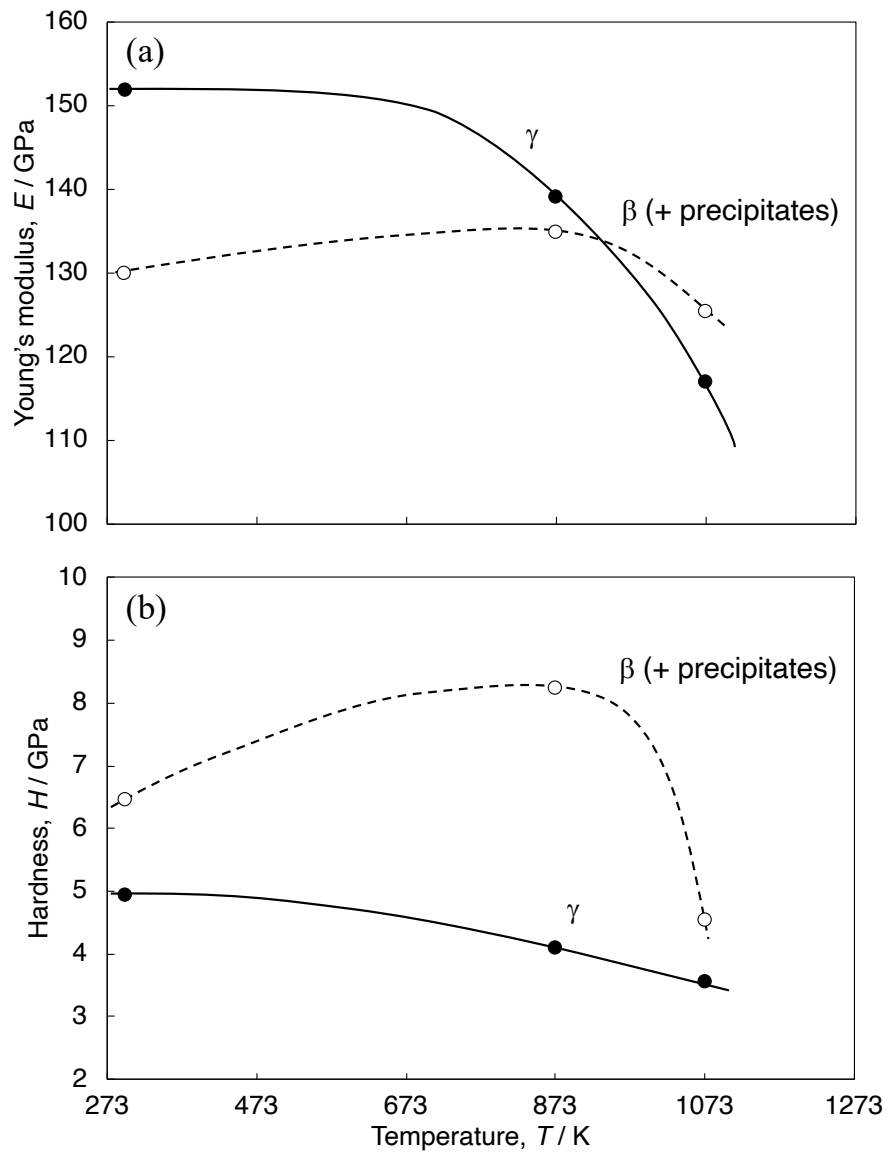
**Fig. 6-4** (a) Secondary electron image of the tested area and (b) backscattered electron image of corresponding area before testing.



**Fig. 6-5** Backscattered electron images of the polished surface after the high temperature tests: (a) low and (b) high magnification.



**Fig. 6-5** Load-depth curves of (a)  $\gamma$  phase and (b)  $\beta$  phase region at room temperature, 873 K and 1073 K.



**Fig. 6-7** Change in (a) Young's modulus and (b) hardness of  $\gamma$  phase and  $\beta$  phase region with temperature.

# **Chapter 7**

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Utilization of Mechanical Properties of  
the Constituent Phases for Alloy Design

## 7.1 Introduction

In Japan, the development of an advanced TiAl alloy which can be applied to both metal injection molding (MIM) and additive manufacturing (AM) processes has been engaged as a part of Cross-ministerial Strategic Innovation Promotion Program (SIP), “Materials Integration for revolutionary design system of structural materials” [1]. Part of the findings in this thesis also contributed to the project. In this project, target required mechanical properties of ultimate tensile strength at 1023 K and fracture toughness at room temperature were set although the concrete values cannot be given in this thesis. In this chapter, the approach to achieve the development of new alloy with required properties is introduced, making use of the findings of this thesis.

## 7.2 Effect of $\beta/\gamma$ cellular microstructure on the mechanical properties

In the previous researches [2,3] and this thesis, it was demonstrated that the  $\beta/\gamma$  cellular microstructure on the  $\alpha_2/\gamma$  lamellar grain boundaries is effective for mechanical properties due to the combination of hard and strong nature of the  $\beta$  phase and soft and deformable nature of the  $\gamma$  phase. In this chapter, the effect of  $\beta/\gamma$  cellular microstructure on the tensile strength and fracture toughness at room temperature is also verified using a model alloy.

**Figure 7-1** shows the controlled microstructure of a model alloy of Ti-43Al-3Cr (at.%). The volume fraction of the  $\beta/\gamma$  cellular microstructure ( $V_{\text{cell}}$ ) was controlled in a wide range. Tensile test and three-point bending tests were performed on the  $V_{\text{cell}}$ -controlled alloys at room temperature. **Figure 7-2** shows stress-strain curves of the samples with various  $V_{\text{cell}}$ . Both tensile strength and ductility increase with  $V_{\text{cell}}$ . The ultimate tensile strength and fracture toughness at room temperature are presented as a function of  $V_{\text{cell}}$  in **Fig. 7-3**. The fracture toughness is enhanced by introduction of a certain amount of  $\beta/\gamma$  cellular microstructure, whereas too much introduction gives rise to a negative effect. **Figure 7-4** shows a graph with the tensile strength on the vertical axis and fracture toughness on the horizontal axis. The introduction of an appropriate amount of  $\beta/\gamma$  cellular microstructure results in the superior balance of the properties, and it is beyond the rule of mixture that is derived from the results of  $V_{\text{cell}} = 0\%$  and  $100\%$ . Depending on the required mechanical properties, we can select the optimal volume fraction of the  $\beta/\gamma$  cellular microstructure.

**Figure 7-5** shows the microstructure near the crack pathway after the bending tests. In the case where no  $\beta/\gamma$  cellular microstructure is introduced, crack easily propagates if the adjacent lamellar grains have similar lamellar orientations (**Fig. 7-5 (a)**). In contrast, by decorating the lamellar grain boundaries with  $\beta/\gamma$  cellular microstructure, the crack can be stopped at the interface between lamellar grain and cellular region, regardless of the adjacent lamellar grain orientation (**Fig. 7-5 (b)**). In polycrystalline TiAl alloys, the orientation of each lamellar grain is not controllable, so that there necessarily exist weak points against the crack propagation as

schematically shown in **Fig. 7-6**. However, we can control the  $\beta/\gamma$  cellular precipitation reaction along the grain boundaries. The author believes this can be a key to enhance the mechanical properties of TiAl alloys.

### 7.3 Role of oxygen as an alloying element for alloy design

As mentioned in chapter 5, the oxygen can be used as one of the alloying elements, not just an impurity element, since it does not affect the deformable nature of the  $\gamma$  phase but harden the other phases of  $\beta$  and  $\alpha_2$ . Also, the oxygen makes the control range of the  $\beta/\gamma$  cellular microstructure expand due to the retardation effect of cellular precipitation reaction (chapter 3). This retardation effect could be effective for the improvement of creep resistance since the dynamic transformation during creep deformation can deteriorate the creep properties [4]. However, the oxygen addition to TiAl alloys significantly changes the phase equilibria. In Ti-Al-Cr ternary system, the Cr concentration of the phases, especially  $\beta$ , drastically increases as described in chapter 5. In the case of Ti-Al-Nb system, it was reported that the  $\beta + \alpha + \gamma$  three-phase tie triangle shifts toward high Nb side as shown in **Fig. 7-7**, and the equilibrium phases of Ti-45Al-15Nb alloy at 1473 K changes from  $\beta + \gamma$  to  $\alpha + \gamma$  by the addition of 1 at.% of oxygen as shown in **Fig. 7-8**. The selection of alloy compositions becomes difficult due to these change in phase equilibria. We need to select different alloy compositions depending on the oxygen level in the alloys, which differs from process conditions. Therefore, we have tried to reduce the effect of oxygen on the phase equilibria change and successfully found that the combined addition of certain M elements (M:  $\beta$  phase stabilizer element) is effective as shown in **Fig. 7-9**.

### 7.4 Inverse approach for alloy design based on mechanical property database

For the alloy development in SIP program, the “inverse” approach shown in **Fig. 7-10** was tried to be applied. In this approach, the required properties are used as input and the process conditions for satisfying them are output. **Figure 7-11** shows the schematic flowchart of our material design system using the inverse approach. The system basically consists of Mechanical Properties prediction Module (MPM), Microstructure Design Module (MDM) and Process Design Module (PDM). We first estimate the microstructural factors, such as volume fractions of microstructure component, to achieve the requirement in MPM. Then, the alloy compositions and heat treatment conditions are proposed to control the optimal microstructure in MDM. Finally, the manufacturers can consider the fabrication conditions for the final products in PDM. Each module requires the large amount of experimental database, such as microstructure, mechanical properties, phase equilibria and kinetics. The obtained findings in this thesis can be used for MPM.

As a consequence of the efforts in SIP program, a new alloy that satisfy the target required mechanical properties of tensile strength at 1023 K and fracture toughness was successfully

developed by MIM process as shown in **Fig. 7-12**. This alloy contains approximately 0.75 at.% of oxygen, and the microstructure consist of the combination of the  $\alpha_2/\gamma$  lamellar grains and the  $\beta/\gamma$  cellular microstructure around them, although the exact alloy composition and microstructure cannot be given in this thesis. The mechanical properties balance is beyond the existing alloys of high strength TNM and high toughness GE 48-2-2. The fabrication of low-pressure turbine blade with large size over 200 mm in length was also succeeded.

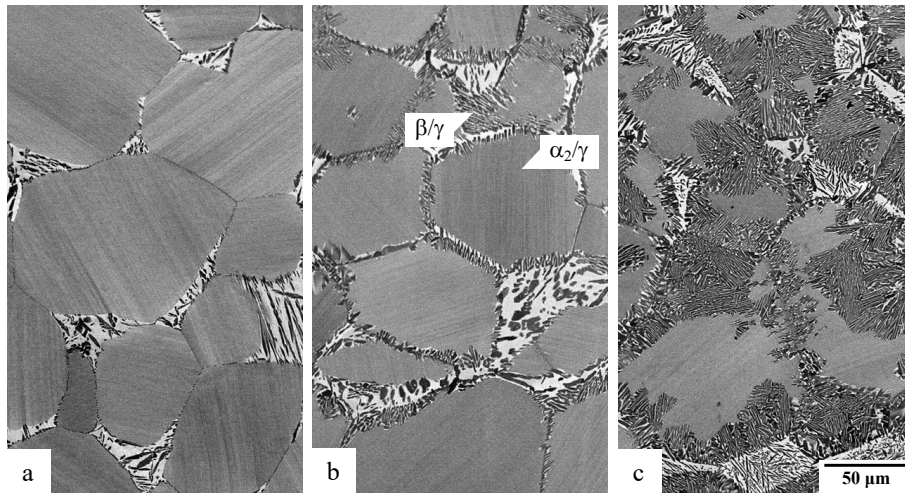
## **7.5 Summary**

In this chapter, the approach of alloy development for satisfying the required mechanical properties in SIP program was introduced, by utilizing the findings obtained in this thesis. The  $\beta/\gamma$  cellular microstructure around the  $\alpha_2/\gamma$  lamellar grains was verified to be effective for various mechanical properties, due to the combination of hard and strong nature of the  $\beta$  phase and soft and deformable nature of the  $\gamma$  phase. The possibility of oxygen as an alloying element was presented, and actually, a new alloy containing a certain amount of oxygen was successfully developed. This alloy exhibits the required mechanical properties of high strength and high fracture toughness.

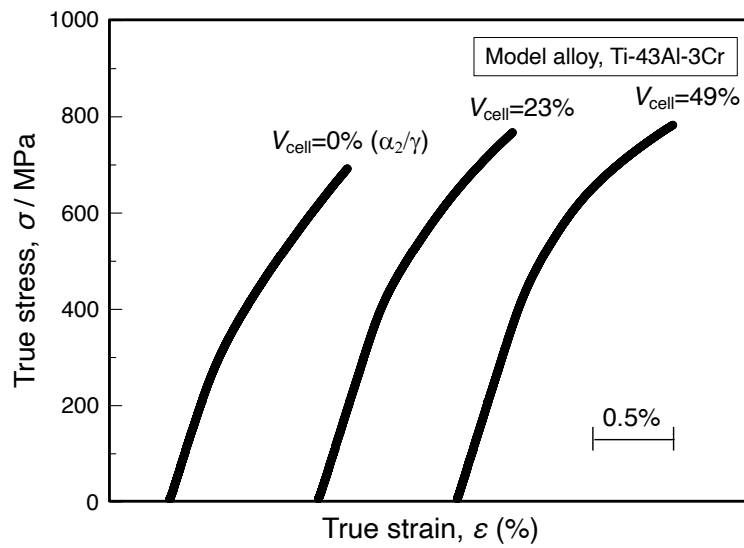


## References

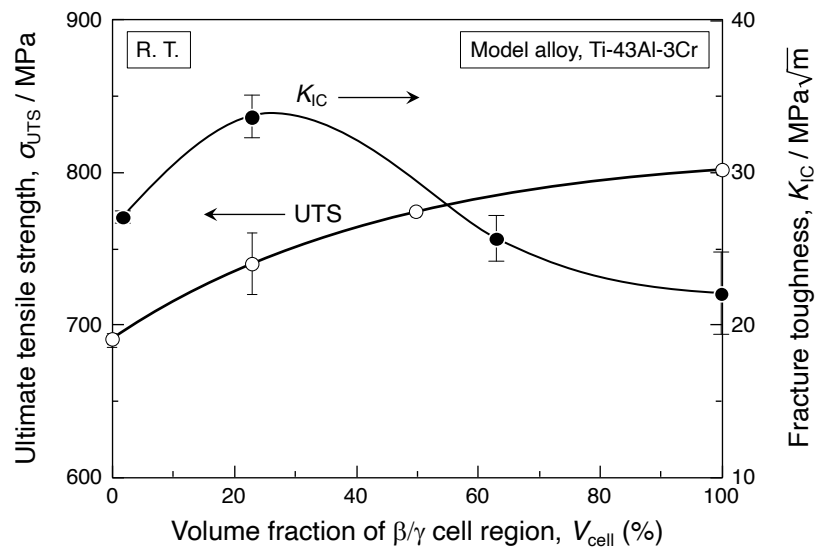
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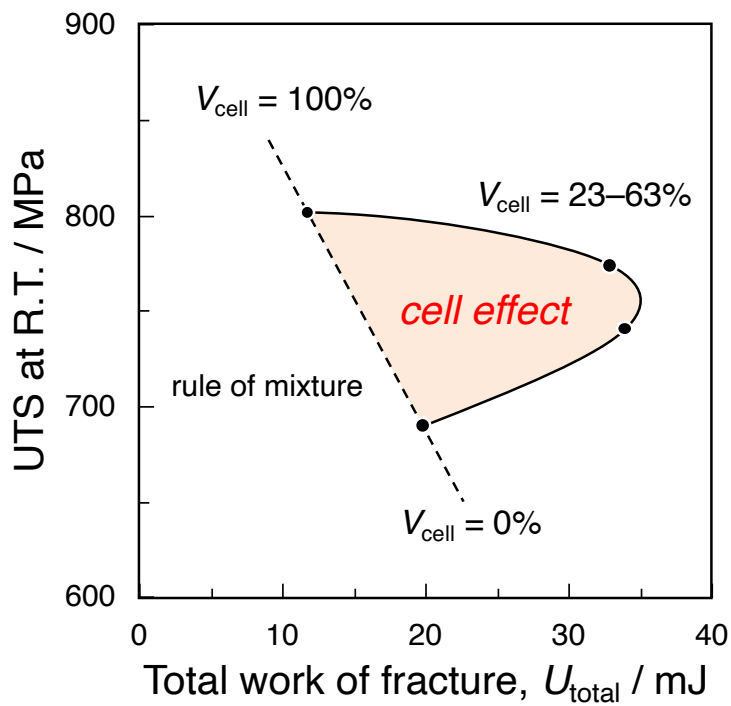
**Fig. 7-1** Controlled microstructures of a model alloy of Ti-43Al-3Cr with  $\beta/\gamma$  cell fraction of (a) 0%, (b) 23% and (c) 49%.



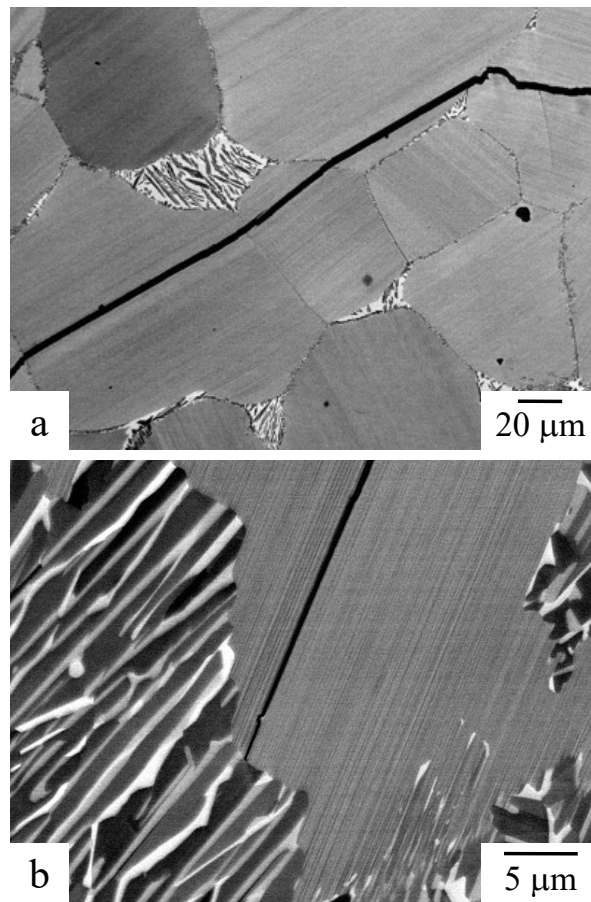
**Fig. 7-2** True stress-strain curves of the model alloy with the various volume fraction of  $\beta/\gamma$  cellular microstructure at room temperature.



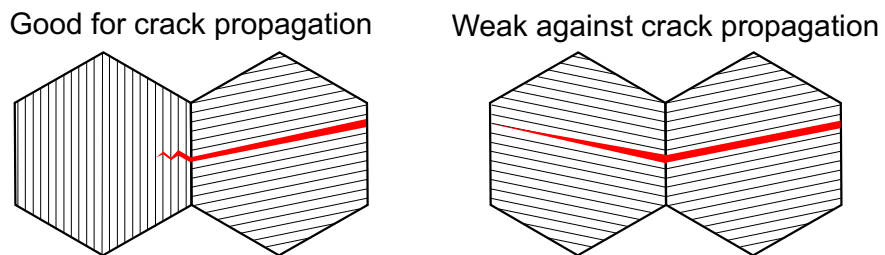
**Fig. 7-3** Ultimate tensile strength and fracture toughness as a function of the volume fraction of  $\beta/\gamma$  cellular microstructure region.



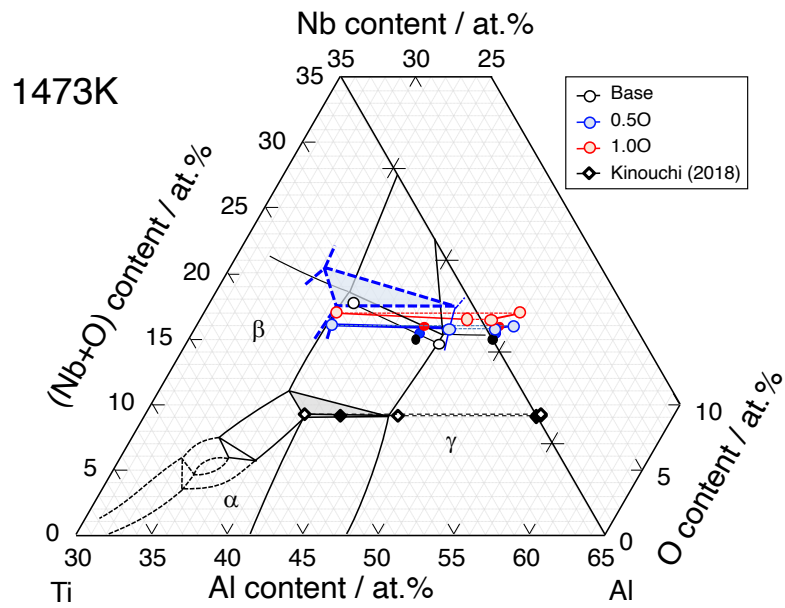
**Fig. 7-4** Relationship between tensile strength and total work of fracture as a function of the volume fraction of  $\beta/\gamma$  cellular microstructure region.



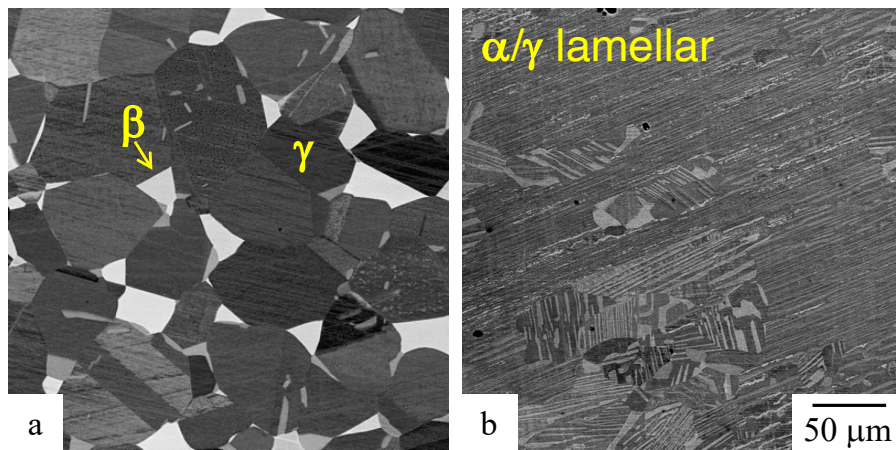
**Fig. 7-5** Microstructures near the cracks after the bending tests: (a) No  $\beta/\gamma$  cell on the lamellar grain boundaries and (b)  $\beta/\gamma$  cell introduced on the lamellar grain boundaries.



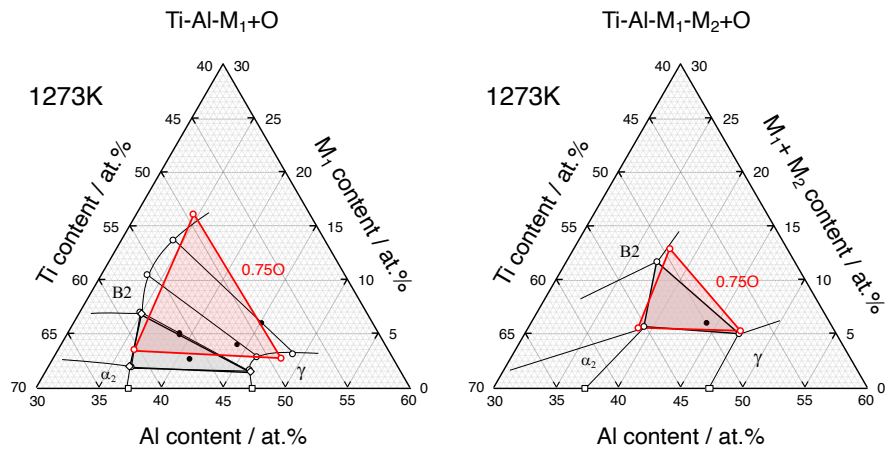
**Fig. 7-6** Schematic illustration of crack propagation in fully lamellar microstructure without  $\beta/\gamma$  cell. The crack propagation behavior changes depending on the orientation of adjacent lamellar grains.



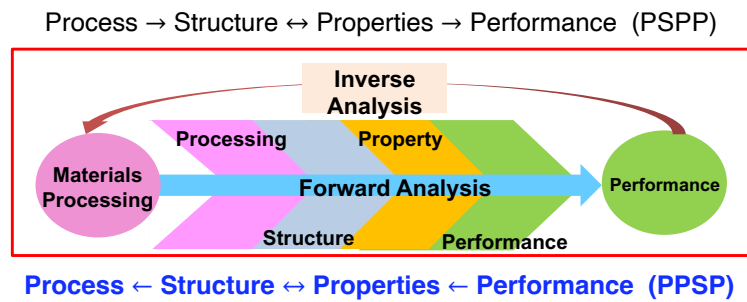
**Fig. 7-7** Parallel projection of the terminal compositions present in Ti-45Al-15Nb-(0, 0.5 and 1.0)O alloys equilibrated at 1473 K.



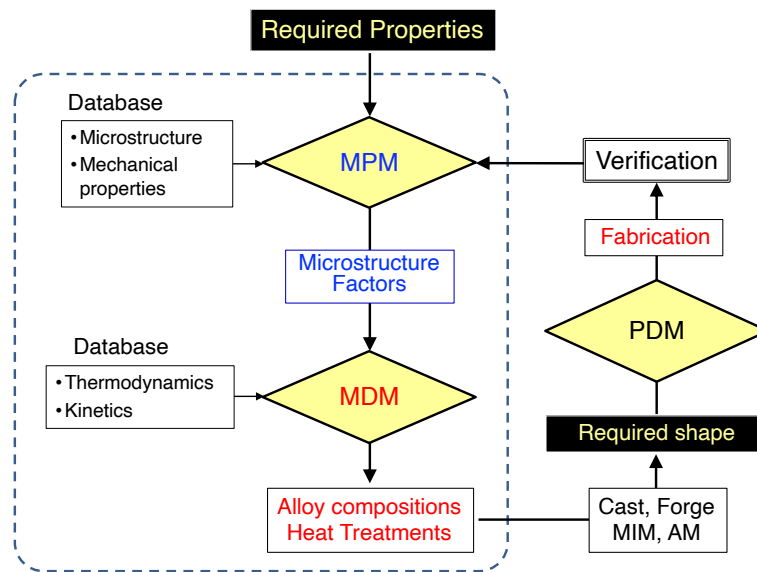
**Fig. 7-8** Microstructures of (a) Ti-45Al-15Nb and (b) Ti-45Al-15Nb-1.0O after equilibration at 1473 K.



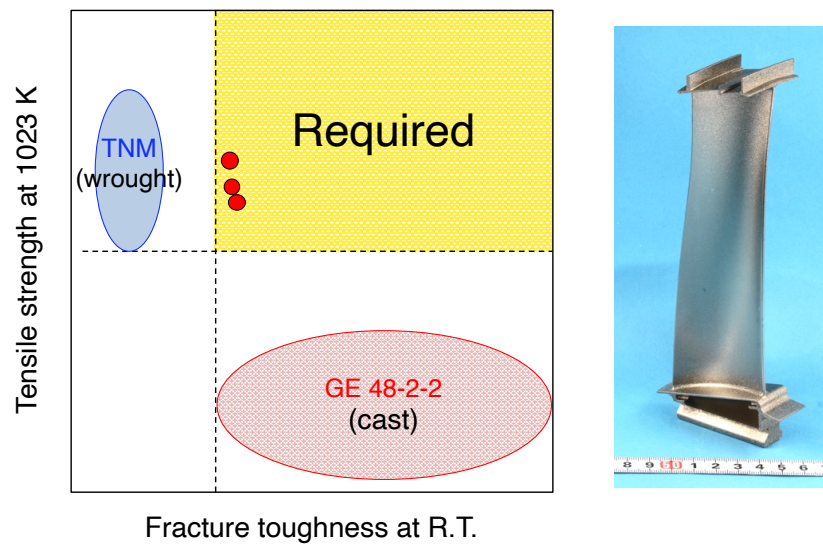
**Fig. 7-9** Change in  $\beta + \alpha_2 + \gamma$  three-phase tie triangle with oxygen addition in the systems with single addition and combined addition of M elements (M:  $\beta$  stabilizer V or VI group element).



**Fig. 7-10** Schematic illustration showing procedure of alloy development.



**Fig. 7-11** Schematic flowchart of our material design system using inverse approach. MPM, MDM and PDM represent Mechanical Properties prediction Module, Microstructure Design Module and Process Design Module, respectively.



**Fig. 7-12** Tensile strength at 1023 K and fracture toughness at room temperature of the newly developed alloy through MIM process and a large scale product of LPT blade. This alloy contains approximately 0.75 at.% of oxygen.

# Chapter 8

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## Conclusions



## 8.1 Summary of this thesis

This thesis investigated on the mechanical properties of the microstructural constituents ( $\beta$ -Ti,  $\alpha_2$ -Ti<sub>3</sub>Al and  $\gamma$ -TiAl phases and the  $\alpha_2/\gamma$  lamellae), which is important for understanding the effect and role of each constituent and designing advanced microstructures, in oxygen doped and undoped TiAl base alloys containing  $\beta$ -Ti phase. The role of the  $\beta$  phase and the effect of the oxygen, both of which are often or sometimes considered to be detrimental factor for TiAl alloys, were especially focused. Based on the obtained findings, the advanced microstructure design principle was proposed. Followings are conclusions obtained in this thesis:

In chapter 1, “General Introduction”, the necessity of the improvement in fuel efficiency of aircraft was described from the viewpoint of carbon neutrality and fuel cost reduction, and  $\gamma$ -TiAl alloys were introduced as a promising material for the improved fuel efficiency because of their light weight and high strength at high temperatures. The current progress and problems regarding the microstructure and the mechanical properties of TiAl alloys were reported, specifically focused on the  $\beta$  phase and the oxygen. Finally, the objective and outline of this thesis were given.

In chapter 2, “Local Deformation Behavior of TiAl Base Alloys under Tensile Loading”, the deformation behavior during tensile loading were investigated, focusing on the  $\alpha_2/\gamma$  lamellar microstructure,  $\beta$  grains and  $\gamma$  grains as microstructure constituents. It was found that the deformation in the  $\alpha_2/\gamma$  lamellar microstructure mainly occurs in the  $\gamma$  plates in the vicinities of the  $\alpha_2/\gamma$  and  $\gamma/\gamma$  lamellar interfaces, and the deformation the  $\beta/\gamma$  duplex microstructure occurs mainly along  $\{111\}$  planes with high Schmid factor of the  $\gamma$  grains. Also, it was identified that the high stress concentration takes place near the  $\beta/\gamma$  phase boundary regions. Finally, an alloy with high room temperature ductility was developed by controlling the microstructure with high volume fraction of the  $\gamma$  phase and high density of the  $\beta/\gamma$  phase boundaries.

In chapter 3, “Microstructure Formation in Oxygen-containing TiAl Alloy and Three-dimensional Characterization of the Microstructure”, the microstructure formation in an oxygen-containing TiAl alloy was investigated, especially focusing on the  $\beta$  phase on lamellar grain boundaries and along lamellar interfaces. The microstructure control using the  $\beta/\gamma$  cellular precipitation and the  $\beta$  phase precipitation along lamellar interfaces was proved to be possible even in the TiAl alloys containing certain amount of oxygen, although it has been reported that the oxygen destabilizes the  $\beta$  phase. It was found that the cellular precipitation reaction is kinetically suppressed by the addition of oxygen, and the author suggested that the control range of volume fraction of the cellular microstructure is expanded due to this suppression. Moreover, the  $\alpha_2/\gamma$  lamellar microstructure with the  $\beta$  precipitates on lamellar interfaces was three-dimensionally observed, and the characteristic of the precipitated  $\beta$  phase was identified.

In chapter 4, “Young’s Modulus and Hardness of  $\beta$ ,  $\alpha_2$  and  $\gamma$  Phases in Ti-Al-Cr Ternary

Alloys and Their Chromium Content Dependence”, the Young’s modulus and the hardness of the  $\beta$ ,  $\alpha_2$  and  $\gamma$  phases in Ti-Al-Cr ternary alloys are measured using nano-indentation technique, and the effect of chromium content on the properties is evaluated. The author identified that the  $\beta$  phase shows the lowest Young’s modulus of 141 GPa among the three phases in equilibrium each other, 173 GPa for the  $\alpha_2$  phase and 167 GPa for the  $\gamma$  phase, and the hardness of the  $\beta$  phase is 5.9 GPa, comparable to that of the  $\alpha_2$  phase (6.3 GPa) and much harder than that of the  $\gamma$  phase (3.9 GPa). With the Cr addition, the increasing rate of the Young’s modulus per atomic percent Cr in the  $\beta$  phase is the smallest (2.0 GPa/at.%) among the three phases, whereas that of the hardness becomes the highest (0.4 GPa/at.%) in a range of 5 to 8 at.% Cr. It was found that the hardness of the  $\gamma$  phase remains unchanged regardless of the Cr content.

In chapter 5, “Effect of Solute Oxygen on Young’s Modulus and Hardness of  $\beta$ ,  $\alpha_2$  and  $\gamma$  Phases”, the effect of the solute oxygen on the Young’s modulus and the hardness of the phases is evaluated by preparing an alloy with intentional oxygen addition. It was found that the  $\beta$  phase shows the strongest oxygen content dependence of the Young’s modulus and the hardness among the three phases, and the increasing rate per atomic percent oxygen in this phase is much larger than that per atomic percent chromium. The  $\gamma$  phase dissolve the oxygen very limitedly, the mechanical properties of this phase remain almost unchanged with oxygen addition to the alloy. The author suggested that the unchanged mechanical properties of the  $\gamma$  phase provides a significant indication for alloy design, i.e., even if the alloy contains high amount of oxygen, the deformability of the  $\gamma$  phase would remain unchanged, and it should be possible to design a microstructure without losing ductility.

In chapter 6, “Effect of Temperature on Young’ Modulus and Hardness of  $\beta$  and  $\gamma$  Phases”, the Young’s modulus and hardness of the  $\beta$ -T and  $\gamma$ -TiAl phases in equilibrium each other were measured at room temperature and elevated temperatures to identify the effect of temperature on the properties. The  $\beta$  phase with a composition of Ti-37.2Al-5.2Cr produces precipitation during a few hours of heating at a temperature below 1073 K, and the properties of the  $\beta$  phase itself could not be measured in the investigated alloy. Although further investigation is needed on this topic, the following results were obtained: The Young’s modulus of the  $\gamma$  phase shows stronger temperature dependence than that of the  $\beta$  phase (+ precipitates) region, whereas the hardness of the  $\beta$  phase (+ precipitates) region shows stronger temperature dependence than that of the  $\gamma$  phase.

In chapter 7, “Utilization of Mechanical Properties of the Constituent Phases for Alloy Design”, from the obtained findings in this research, the concept for alloy and microstructure design to satisfy required properties was considered. First, using a model alloy, the effectiveness of the  $\beta/\gamma$  cellular microstructure for the mechanical properties was verified. Then, the possibility of the oxygen as one of the alloying elements was reviewed, based on the findings obtained in chapter 3 and 5. Finally, a newly developed alloy containing a certain amount of oxygen and

having a microstructure of the  $\alpha_2/\gamma$  lamellar grains and the  $\beta/\gamma$  cellular microstructure around them was introduced. This alloy exhibits an excellent balance of the mechanical properties of tensile strength at 1023 K and fracture toughness.

In chapter 8, “Conclusions”, the obtained findings in this thesis are summarized.

As a conclusion of this thesis, the author emphasizes that the  $\beta$  phase or  $\beta/\gamma$  cellular microstructure is effective for improvement in various mechanical properties, and the oxygen does not necessarily deteriorate the properties of TiAl alloys if the appropriate microstructure control is employed. On the contrary, the oxygen can be an alloying element, not an impurity element if we know the effect of oxygen precisely. Finally, it should be noted that reliable phase equilibria database is necessary for the alloy and microstructure design.

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岡田 陽太郎