Technical Report

“Metallurgy” of Structural Titanium Alloys: Past-Current-Future

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Abstract

Regarding the trends in research and development of structural titanium (Ti) alloys in Japan, this manuscript reviews the past and current situation and presents our thoughts on future strategy. As a basic research policy for deformation processing and microstructural control, it is necessary to promote “the reviewing” of research and development thanks to a data-science approach in order to identify the optimum process condition and microstructural formation that do not depend on empirical rules. In addition, the optimal design of alloy/microstructure/mechanical properties as “a game-changing approach,” for example focusing on the non-equilibrium phases (martensite, omega phase) or the impurity addition in Ti alloys that have not been developed for the application of structural components, is given as an innovative research direction. The history of titanium is extremely short compared to that of steel, and therefore it still has major potential.

1. Introduction

Titanium is a light practical industrial metal next to magnesium and aluminum. Titanium and titanium alloys exhibit good corrosion resistance, room temperature strength (tensile strength of 300 to 1 300 MPa), and high-temperature strength. For these properties, they are used mainly in aircraft and also in a wide range of other applications, such as general consumer products and medical equipment. Titanium alloys are roughly classified into the alpha (α) (HCP) type, alpha-beta ($\alpha+\beta$) type, and beta (β) type (BCC) in equilibrium phases, depending on the constituent phases and crystal structures. The practical use of titanium started to increase with the development of the Ti-6Al-4V alloy in 1951. Since then, various other titanium alloys have been developed and commercialized based on the Ti-6Al-4V alloy. The construction of technologies for smelting and plastically working titanium and titanium alloys and the basic understanding of their physical properties had mostly been completed by the 1990s. After various research and development booms as described below, we now seem to be at a crossroads for the next strategy regarding titanium and titanium alloys.

In this report, we investigate the past and present of titanium research activities in Japan. For the future of titanium research activities, we introduce our theories as examples of our research results and examine the future direction of titanium research in Japan.

2. Past and Present

Titanium is a metal whose commercial production was established by the Kroll process in 1946. It has made great progress as a practical material since then. The report titled “Advancement of Titanium Research Activities in Japan” was published by the Iron and Steel Institute of Japan in 1993.[1] It reviews the titanium research and development situations in Japan about 30 years ago.[1] The Iron and Steel Institute of Japan established the Titanium Research Committee in 1986 and the Heat-Resistant High-Strength Titanium Research Group (chaired by Teruo Kishi) in 1990. The report summarizes the study results of the research group. The contents are diverse from processes (refining, melting, casting, plastic working) through microstructures and properties (strength, toughness, high temperature properties, surface properties, diffusion, and phase transformation), and new alloys. Many industry, government, and academic institutions contributed their research results. The report is full of the titanium production technologies established and of the practical targets achieved. We can see that the period covered by the report was the heyday of titanium research activities in Japan. At present, we seem to be standing at a new crossroads after the booms described later.

In and after the 1990s, many low-priced titanium alloys were developed and commercialized in the world and in Japan.[2,3] Our understanding of $\alpha+\beta$ alloys has deepened. The research and development of β alloys had been thriving since the 1980s and especially in the 1990s. The research and development of β titanium alloys began in the 1950s, mainly for aircraft applications. Typical aircraft β alloys include the Ti-10V-2Fe-3Al (Ti-10-2-3) alloy and Ti-5Al-5V-

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5Mo-3Cr (Ti-5553) alloy. These titanium alloys have excellent strength and are commercialized for use in landing gears. The Ti-5553 alloy is a relatively new alloy developed mainly in Russia in the 1990s. As a β alloy trend in Japan after the 1980s, research and development flourished on omega (ω) transformation in metastable β alloys and the resulting {332} twins. Many β alloys and metastable β alloys were developed in industry. After the 1990s, Japan began vigorous research and development on biomedical low elastic modulus β titanium alloys and biomedical shape memory and superelastic titanium alloys by utilizing the softening of phonons in a peculiar phase transformation in metastable β alloys and resulting ω transformation and thermoelastic alpha double prime (α") martensite transformation. At present, many basic principles are published mainly by academia.[4,5] This is one of Japan's strengths from a global perspective.

At present, the aircraft industry is weaker in Japan than in Europe and the United States. Commercially pure titanium accounts for most of the wrought titanium materials produced in Japan. The chemical, electric power, electrolysis, and plate heat exchanger industries account for most of the titanium applications in Japan. Since 2010, the global aircraft demand has been markedly increasing.[6] Following this trend, Japan's titanium alloy and heavy industry companies have been striving to establish aircraft titanium alloy manufacturing technologies. (We are now under the influence of COVID-19 but will rebound once the pandemic ends.) In this way, we are now faced with critical challenges to develop new titanium materials for aircraft applications. In the research and development efforts by industry and academia as described later, it is important that industry and academia can develop and propose Japan's original titanium technologies.

3. From Now On (from both basic and innovative aspects)

Japan is particularly strong in the practical deployment of commercially pure titanium and in the research and development (trends of academia) of biomedical β titanium alloys. We must maintain these trends in the future. It is also necessary to strongly promote Japan's technological and research and development capabilities in aircraft titanium alloy applications. Therefore, for example, it is necessary to solve the issues from both basic and innovative aspects as described later in "technical establishment of titanium alloys for aircraft". In the sections that follow, citing our research results as examples, we introduce and examine the basic direction of structural titanium alloy manufacturing and the innovative direction of significantly improving the mechanical properties of titanium alloys.

3.1 Simultaneous achievement of both mechanical property enhancement and fabrication ease of structural titanium alloys

Figure 1 summarizes the strength-ductility balance (tensile strength-total tensile elongation balance)[7] and strength-fracture toughness balance[8] of titanium alloys. There are trade-off relationships or so-called "banana curve" relationships in which gaps exist. For example, in the strength-fracture toughness relationship, β alloys show higher toughness. This is because the β phase contributes more to toughness as a constituent phase. Gaps are also seen in each constitutive phase. Under the strong influence of microstructural factors, the lamellar morphology exhibits higher fracture toughness. The microstructural factors also greatly influence the strength-ductility balance. The equiaxed morphology shows good room temperature ductility in contrast to toughness. These relationships are also strongly influenced not only by the microstructural morphology, but also by the phase fraction, particle size, and crystal orientation. Precise microstructural control is required to optimally coordinate and enhance the mechanical properties. When aiming for balance between further cooperative advancement of mechanical property and good fabricability, it is necessary to advance research and development from both basic and innovative aspects. Specifically, to break away from the conventional "empirical rules" as a basic aspect, it is necessary to deepen the understanding of the working mechanisms that connect the current practical processes (casting and plastic working), microstructural evolution, and performance (mechanical properties) and to select the microstructures and process conditions that optimize the performance. On the innovative side, on the other hand, it is desirable to create game changing titanium alloy design concepts, for instance. An example of a specific research approach in the basic phase is the construction of process, microstructure, and material property prediction models fused with phenomenological interpretation by making full use of data science as represented by "materials informatics". As an innovative example, we can expect new developments based on "metastability" in a broad sense of the term, such as non-equilibrium phases (martensite and ω phase), addition of impurities, and multi-scale inhomogeneous microstructure evolution. In the following sections, we introduce our cases, centering on our research results of the Ti-6Al-4V alloy.

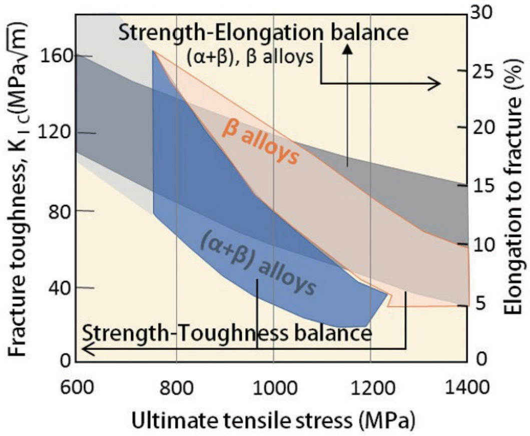

Fig. 1 Ultimate tensile strength and ductility/fracture toughness balance in Ti alloys[7,8]

3.1.1 Basic: Hot working of titanium alloys and prediction of microstructure and properties

In the general manufacturing flow of titanium alloys, an ingot is hot worked (or broken down) and homogenized into multiple passes in the high-temperature β phase region (ingot breakdown) and then in the β phase region or $\alpha+\beta$ phase region, depending on the application. After that, the ingot is aging and statically heat treated to relieve stress, adjust the β phase content, control alpha phase precipitation, and adjust the particle size and crystal orientation. The resulting product is placed on the market. It is important to optimize the microstructure while maintaining sound workability (uniform crack-free deformation) in this series of complicated steps or to establish a precise prediction technology that does not depend on the past empirical rules. For sound workability, it is necessary to optimally convert the working energy into the energy required for the microstructural change while maintaining the plastically stable state. The processing map method is used to evaluate this energy conversion quantitatively.[9] A detailed explanation is omitted for lack of space. **Figure 2** is a processing map for forging the Ti-6Al-4V alloy (50%

reduction of area) with the equiaxed morphology as a starting microstructure.[10] From this, we can see that the power dispersion efficiency or microstructural change conversion rate and the plastically stable region change, depending on the working temperature and strain rate. It is clear that the low-rate deformation range corresponds to the optimum machining conditions at any working temperature. This is because the recrystallization processes of α grains and β grains proceed in a continuous manner in titanium alloys unlike steel, as described later. When the equiaxed microstructure is a starting state in the hot working process of the Ti-6Al-4V alloy, superplasticity occurs predominantly in an extremely low rate region of $10^{-3}\,s^{-1}$ or less. Dynamic recovery (DRV) or continuous dynamic recrystallization (CDRX) occurs predominantly in the low-rate to medium-rate regions. When the lamellar microstructure is a starting state, the kinking phenomenon and dynamic globularization occur in the α lamellae. In the low temperature region, brittle fracture originates from the grain boundary α phase. Working in the low temperature and high-rate region in both the starting microstructures is likely to cause plastic instability due to adiabatic shear banding. There is a risk of sudden brittle fracture in the working process. Regarding this CDRX activity, **Fig. 3** shows the densities of low-angle grain boundaries (subgrains) and high-angle grain boundaries in the 700°C isothermal forging process of the Ti-6Al-4V alloy (equiaxed starting microstructure).[11] This figure shows that the low-angle grain boundaries and high-angle grain boundaries both increase in the grain boundary density with a slope equivalent to that of the true strain. The increase in the density of the low-angle grain boundaries reflects the formation of subgrains where grain boundaries evolve from dislocations. The density of high-angle grain boundaries also increases with a similar slope. It is clear that the subgrains continuously rotate and increase in angle (CDRX activation). Titanium alloys essentially have higher stacking fault energy than steel. DRV and CDRX appear more predominantly without exhibiting nucleation and growth-type discontinuous recrystallization behavior (DDRX). There are a variety of microstructure change mechanisms in the hot working process of titanium alloys. Strong effects are produced by the working conditions, alloy type, and starting microstructure.

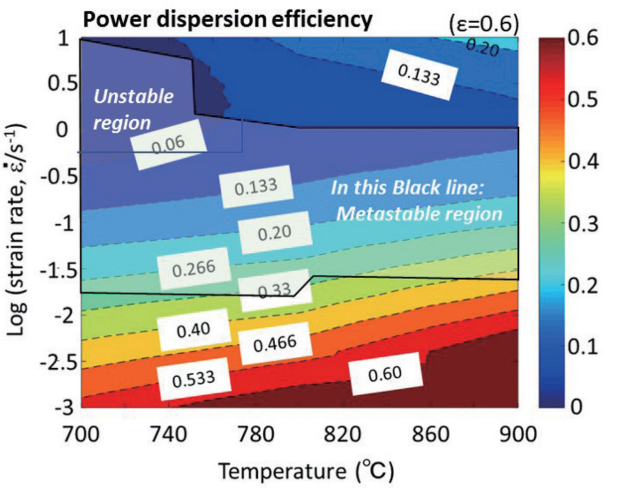

Fig. 2 Process map of Ti-6Al-4V alloy with equiaxed microstructure (referred and modified from reference 10))

Macroscale and mesoscale models for precisely predicting various microstructure changes are introduced below. Various scale-dependent models are reported for predicting microstructures on the nanomicron scale, on the mesoscale, and on the macroscale or product scale.[12] Microstructures of micro-regions are predicted by the Monte Carlo (MC) method, the cellular automaton (CA) method, and the phase field (PF) method, among other methods. These models derive microstructures from diffusion equations or total free energy evolution equations. They predict the microstructures from a physical standpoint and are advantageous in that they can precisely express microstructural changes in the metal working and heat treatment processes. When these microstructure predictions are applied in macro areas such as parts manufacturing, on the other hand, there are still many problems with generalization from the viewpoint of calculation time. The physical metallurgical (PM) model and the internal state variable (ISV) models are available as typical examples of models for predicting microstructures and properties in macro regions.[12] The PM model has a strong empirical element. It optimizes

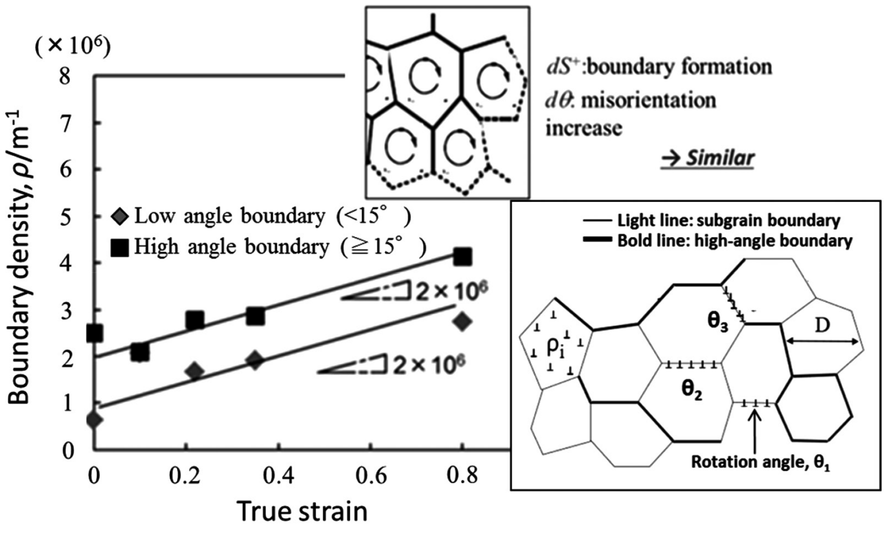

Fig. 3 Change in boundary densities under isothermal forging (at 700°C) of Ti-6Al-4V alloy with equiaxed starting microstructures and schematic illustration showing CDRX behavior (referred and modified from reference 11))

and derives many material constants from experimental results by constitutive equations expressing physical phenomena. Such a model can reflect highly accurate results in specific ranges (prediction conditions) but the prediction condition ranges are limited. The ISV model has a mathematical model built centered on the dislocation density evolution for microstructural changes and plastic flow characteristics and can reflect more physically based prediction results than the PM model. The coupling of many constitutive equations, however, makes it necessary to derive many material constants. In this way, there are various scale-dependent constitutive models for microstructure prediction. Their characteristics have advantages and disadvantages. Below are reported the results of the microstructure prediction made by applying the PM model and ISV model in the semi-enclosed and closed die forging processes of Ti-6Al-4V alloy turbine disks. Simplified PM and ISV models are applied and outlined. For the details, refer to Reference 13). The constitutive equations described below include many material constants. The description of the material constants is omitted for lack of space. For their details, also refer to Reference 13).

The dislocation density evolution (ρ) in the working process was predicted from the Kocks-Mecking relation[14] expressed by Equation (1). Here, it is simply shown by the dislocation hardening term ($k_1\sqrt{\rho}$) and the recovery term ($k_2\rho$). The effect of recrystallization is incorporated into the recovery term and is not considered here. The terms k_1 and k_2 are the reaction rate terms.

The term k_2 is expressed by the Arrhenius equation (Equation (2)) with the strain rate and temperature as variables.

$$\frac{d\rho}{d\varepsilon} = k_1\sqrt{\rho} - k_2\rho \tag{1}$$

$$k_2 = k_0\dot{\varepsilon}^{m_2-1}\exp\left(-\frac{Q_{CL}}{RT}\right) \tag{2}$$

The dynamic recrystallization rate X_{DRX} is given by the Johnson-Mehl-Avrami-Kolmogorov (JMAK) equation (Equation (3)). This equation expresses a recrystallization process involving discontinuous nucleation and growth but is reported to also be applicable to continuous recrystallization. The JMAK equation is simply adopted here. In the equation, β_d is the reaction rate term, k_d is the Avrami index, and ε_{C2} is the strain at which recrystallization starts. To incorporate these constitutive equations into the finite element analysis method (FEM) and to accommodate unsteady condition changes (temperature and strain rate) in the working process, the recrystallization rate is calculated by iteratively adding total derivatives with the FEM as given by Equations (4) and (5).

$$X_{DRX} = 1 - \exp\left[-\beta_d \times \left(\frac{\varepsilon - \varepsilon_{C2}}{\varepsilon_{0.5}}\right)^{k_d}\right] \tag{3}$$

$$d\left(X_{DRX}\right)^{n} = \frac{\partial X_{DRX}}{\partial \varepsilon}d\varepsilon + \frac{\partial X_{DRX}}{\partial \varepsilon_{0.5}}d\varepsilon_{0.5} + \frac{\partial X_{DRX}}{\partial \varepsilon_{C2}}d\varepsilon_{C2} + \frac{\partial X_{DRX}}{\partial \beta_d}d\beta_d \tag{4}$$

$$X_{DRX}{}^{n+1} = X_{DRX}{}^{n} + dX_{DRX}{}^{n} \tag{5}$$

Figure 4 shows the results of FEM calculations performed by introducing these constitutive equations as subroutines into a general-purpose FEM code (DEFORM-3D, v12). Columnar specimens of the Ti-6Al-4V alloy (equiaxed microstructure) as shown in Fig. 4 (a) were isothermally forged at 850°C into turbine disk shapes (strain rate: 0.05 s^{-1} and reduction of thickness: 72 mm). The effective strain is shown in Fig. 4 (b), the dislocation density is shown in Fig. 4 (c), and the dynamic recrystallization fraction is shown in Fig. 4 (d). Each reveals an inhomogeneous distribution pattern. The dislocation density and dynamic recrystallization fraction distributions roughly correlate with the effective strain distribution. More specifically, on the other hand, the dynamic recrystallization fraction exhibits a more inhomogeneous distribution behavior. This is probably the effect of the forging temperature and speed that changed in an unsteady state during the forging process. These inhomogeneous distribution patterns also strongly affect the mechanical properties of the forged product. In a simple equiaxed microstructure, for example, the results of prediction by classical strengthening laws (Hall-Petch formula, Bailey-Hirsch formula, compound law) correlated well with the experimental results to some extent.[10] At present, a recrystallization and grain growth model suitable for titanium alloys is constructed centered on the dislocation density evolution that incorporates the CDRX phenomenon in a more advanced manner.[15]

In recent years, physical phenomenon prediction technologies have remarkably progressed by making full use of machine learning, deep learning, and reinforcement learning on the basis of data science. In the field of materials science as well, the development of materials by making full use of data science under the concept of materials informatics has drawn strong attention.[16] We performed

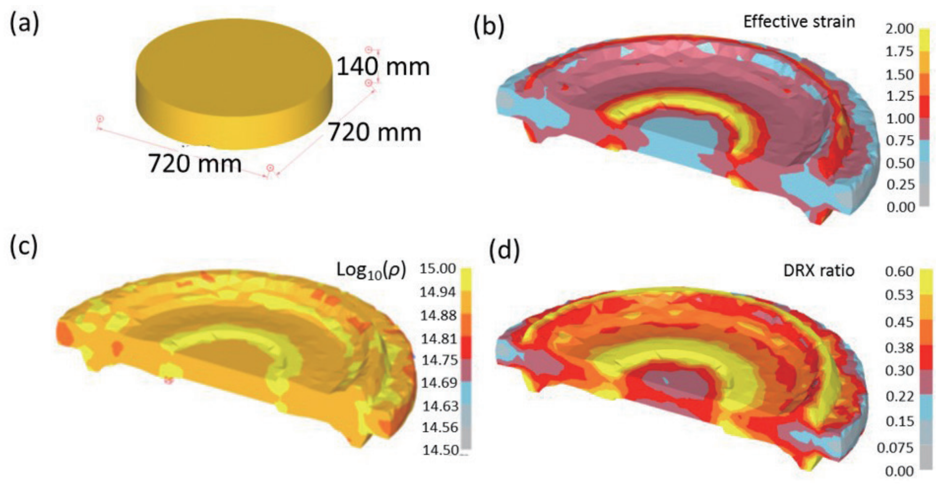

Fig. 4 FEM distribution for turbine-disk-forging (in process condition of 850°C - 0.05 s^{-1} and height reduction of 50%)
(a) Initial shape and dimension, (b) Effective strain, (c) Dislocation density, (d) Fraction of dynamic recrystallization

the computational analysis of the above-mentioned microstructure prediction with the aid of machine learning. Among various machine learning algorithms, the neural network (NN) was adopted in our study. Many books have been published about machine learning. We studied various Python-Scikit-learn algorithms using Reference 17). As shown in **Fig. 5**(a), the NN arranges nonlinear operators called units (or neurons) in input, middle, and output layers, and optimizes weighting factors (w_{ij}) between the units. The NN is a method for representing and predicting complexly linked phenomena. The meanings of the optimized values are black boxes. It is difficult to consider the physical meanings of the optimized values, but it is possible to consider the linkage (importance analysis) of the values. Hints are given about the relationship of the main factors in the physical phenomena involved. In this study, for example, supervised learning (regression) was performed by the NN with the working conditions, or temperature, strain rate, and strain amount, as input factors and with the post-working microstructural changes, like dynamic recrystallization, dislocation density, grain growth, and dynamic spheroidization, as output factors. As a result, a good correlation was obtained between the working conditions and the microstructural factors. Figure 5(b) shows the results of predicting the dynamic recrystallization rate by introducing the NN algorithm and the obtained weighting factor into FEM subroutines. Compared with the calculation results of Fig. 4(d), the NN results show a similar distribution behavior but exhibit a more uniform distribution pattern. The NN results provide a better correlation with the experimental results than the FEM results.[18] With the more physically based PM and ISV models, errors are accumulated at each calculation step with respect to the changes in unsteady working conditions (dynamic changes in temperature and strain rate in the working process). When the deformation is large, the gaps with the experimental results consequently increase. When we try to build a more elaborate PM or ISV model, we must consider many material constant terms. This causes the risk of approximate elements becoming stronger. We must accommodate other intricately involved phenomena and unsteady states while retaining the physical meanings of the PM and ISV models. We will have to optimally use machine learning to make elaborate predictions and to deepen the understanding of physical phenomena in an inversely analytical manner. In the study about the Ti-6Al-2Sn-4Zr-6Mo alloy,[18] we found by using machine learning or the combination of the NN and clustering that the mechanism of the dynamic recovery process varies with the working conditions (temperature and strain rate) and is divided into three regions. We also found quantitatively that the strain acts as the strongest influencing factor especially under the working conditions where the dynamic globularization of the α phase is activated. For future titanium alloy production, it will be important to understand the empirical rules-based phenomenology and to conduct research and development by adopting digital transformation (DX). These endeavors may lead to new discoveries.

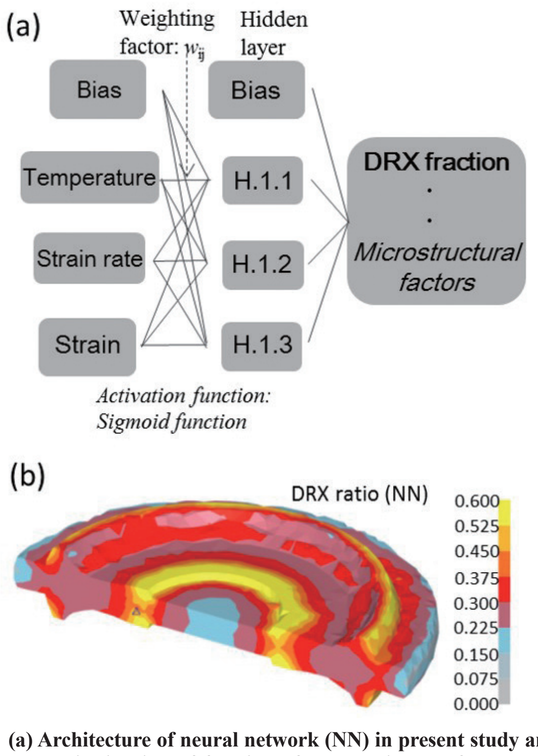

Fig. 5 (a) Architecture of neural network (NN) in present study and (b) FEM distribution of fraction of DRX estimated from NN algorithm

3.1.2 Innovative: Microstructure control of titanium alloys utilizing metastable phase, and room temperature deformation and working characteristics

As described above, the limits of the design concept that dramatically enhance the mechanical properties of structural metal materials are now becoming apparent. The creation of innovative and game-changing titanium alloy design guidelines that transcend these limits is required worldwide. Among such examples are design based on the metastable phases (martensite (α', α") and ω) and design guidelines utilizing impurity elements (O, N, etc.). From shape memory, superelasticity, and low modulus design functionality perspectives with the metastable β titanium composition, many basic principles have been elucidated and disseminated from Japan. These are the strengths of Japan's titanium research. We expect these concepts to be applied to the development of structural titanium. Our research results are reported below, indicating the possibility of applying α' martensite in titanium alloys to structural materials. Here the properties of α' martensite in the Ti-6Al-4V alloy, a typical titanium alloy, are presented.

Figures 6(a1) and (a2) show the microstructures of Ti-6Al-4V alloy specimens solution treated at 1 100°C (a1) and 950°C (a2), respectively, and then quenched in ice water. We hereinafter refer to these specimens as the 1100STQ and 950STQ specimens, respectively. The β transus temperature (Tβ) of the Ti-6Al-4V alloy is about 995°C. The 1100STQ specimens exhibit an acicular α' martensite microstructure. In the 950STQ specimens solution treated at 950°C or below the Tβ temperature, a black equiaxed α phase is formed. The 950STQ specimens exhibit an ($\alpha + \alpha$') duplex microstructure in which acicular α' martensite is formed by quenching from the surrounding residual β. Figure 6(b) shows the room temperature stress-strain curves of the STQ specimens and of the ST-FC specimens solution treated in the same way as the STQ specimens and then furnace cooled. The 1100ST-FC specimens exhibit a lamellar morphology and the 950ST-FC specimens exhibit an ($\alpha + \beta$) bimodal morphology. The results of the specimens that exhibit an equiaxed morphology are also shown in Fig. 6(b). From these results, we can see that the 1100STQ specimens with a single α' martensite microstructure are high in strength as recognized so far but fracture due to brittleness immediately after yielding. On the other hand, the 950STQ specimens are observed to exhibit high strength and good room temperature ductility. These results suggest that an α'

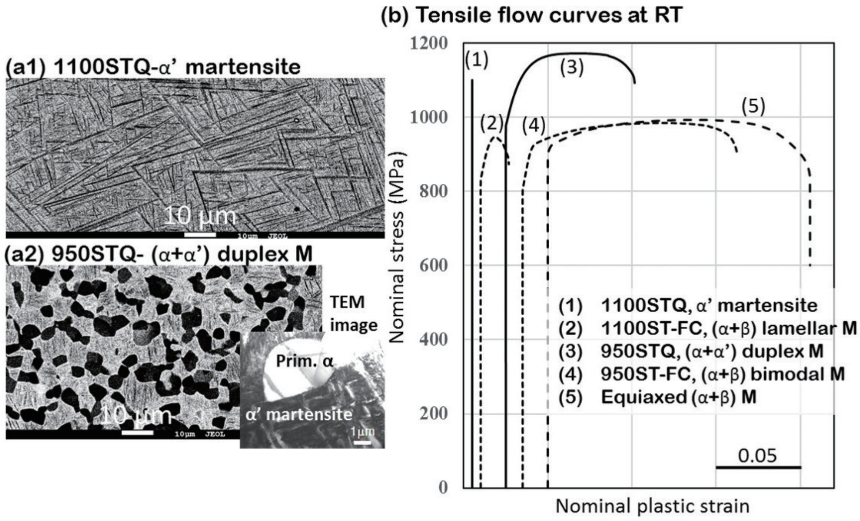

Fig. 6 Quenching microstructures of Ti-6Al-4V alloy of (a1) 1100STQ and (a2) 950STQ specimens, and (b) stress-plastic strain curves (at RT) of heat treated Ti-6Al-4V alloys

martensite microstructure exhibits good room temperature ductility and plastic behavior by the formation of an appropriate duplex microstructure. Regarding this, we found that the ($\alpha+\alpha$') duplex microstructure shows an excellent critical rolling ratio in cold rollability.[19] Major deformation mechanisms of the α phase are presented here. In a dislocation slip, the $(01\bar{1}0)[\bar{2}110]$ slip (<a> prismatic slip) activates. In addition, the $\{0001\}$<$11\bar{2}0$> slip (<a> basal slip), $\{10\bar{1}1\}$ $\{\bar{1}\bar{1}23\}$ slip, and $\{11\bar{2}2\}$<$\bar{1}\bar{1}23$> slip (<c + a> pyramidal slip) activate as minor modes. Another major deformation mechanism is deformation twinning. The $\{1\bar{1}02\}$ and $\{\bar{1}2\bar{1}2\}$ twinning systems mainly activate.[20] Deformation twins are frequently active in commercially pure titanium and low-alloy near α titanium alloys but are rarely observed in aluminum-titanium alloys. How to activate twinning in the plastic process while maintaining high strength is required as a development guideline. Why did the 1100STQ specimens (α' martensite microstructure) exhibit brittle behavior and the 950STQ specimens (($\alpha+\alpha$') duplex microstructure) exhibit ductile behavior as shown in Fig. 6(b)? The effect of morphology may be considered but the difference in the crystal plasticity mechanism is considered to exert a greater effect. Analysis of the deformation microstructure observed many <a> basal dislocations and $\{10\bar{1}1\}$ twins in both the 1100STQ and 950STQ specimens. The $\{10\bar{1}1\}$ twins are also formed after quenching. It is difficult to distinguish these $\{10\bar{1}1\}$ twins. It is reported that the area fraction of twins increases particularly in the 950TQ specimens after deformation and that the deformation activates the $\{10\bar{1}1\}$ twins mainly.[19, 21] Manero et al.[22] reported similar findings. In the plasticity mechanism of the Ti-6Al-4V alloy, the <a> basal slip is likely to activate and especially the $\{10\bar{1}1\}$ twins are activated. Compared to the conventional $\{11\bar{2}1\}$ twins that frequently activate in the equilibrium α phase, the $\{10\bar{1}1\}$ twins are high in the critical resolved shear stress (CRSS) and are recognized as a twinning mode that does not readily activate. The $\{10\bar{1}1\}$ twins are twins that are caused by the lattice invariant deformation to relieve strain during the α' martensite transformation. They correspond to the twins that form in correspondence to the softening of β phonons on the (011) plane at high temperature and to the lattices. This supports the high mobility of the $\{10\bar{1}1\}$ twins in the metastable state of α' martensite. Thus, α' martensite itself seems to exhibit higher ductility than the equilibrium α martensite that exhibits a similar hexagonal close-packed (HCP) microstructure. So why did the 1100STQ specimens (α' martensite) exhibit brittle behavior as shown in Fig. 6(b)?

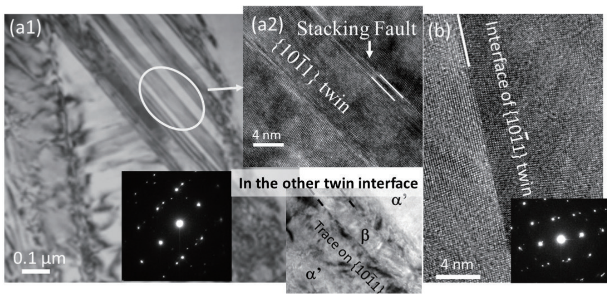

Fig. 7 High resolution TEM images of (a1)(a2) 1100STQ and (b) 950STQ specimens (herein, images were taken in the vicinity of $\{10\bar{1}1\}$ twin) (referred and modified from reference 19))

Figure 7 shows high-resolution electron microscope (HREM) micrographs focusing on the $\{10\bar{1}1\}$ twin interface inside the α' variants generated by self-adjustment in the lattice invariant deformation of the 1100STQ specimens ((a1) and (a2)) and 950STQ specimens (b). From these micrographs, a stacking fault or fine β phase is observed at the twin interface in the 1100STQ specimen, and a clear twin interface is observed in the 950STQ specimen. From a hardenability viewpoint, it is inferred that diffusion transformations competed with one another in the late cooling process of the 1100STQ specimens and that a fine diffusion β phase or stacking fault as its precursor was consequently formed at the $\{10\bar{1}1\}$ twin interface. For the 950STQ specimen, on the other hand, it is inferred that vanadium was enriched in the β phase during the heat treatment in the ($\alpha+\beta$) two-phase region to increase hardenability and that the twin interface was clearly revealed without the formation of a fine diffusion β phase at the twin interface during the quenching process. This strongly affected the plastic mechanism. For the 1100STQ specimen, it is considered that the stacking fault or diffusion β phase at the twin interface initiated a sudden fracture and caused brittle behavior. For the 950STQ specimen, it is considered that the mobility of the $\{10\bar{1}1\}$ twin interface was not hampered and that twinning-induced plasticity (TWIP) was activated to exhibit high ductil-

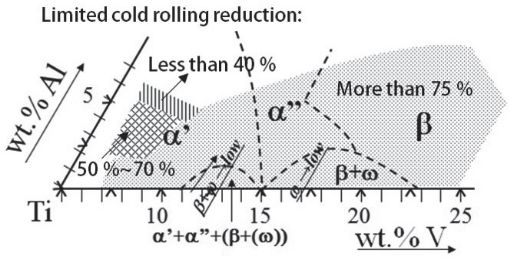

Fig. 8 Phase constituent and limited cold rolling reduction of quenched Ti-Al-V alloys (solution treated and quenched from above 1 000°C) (referred and modified from reference 21))

ity. This phenomenon is observed not only in the Ti-6Al-4V alloy, but also in other titanium alloys. **Figure 8** is a ternary phase diagram that summarizes the constituent phases and limited cold rolling reduction ratios at room temperature (maximum rolling ratios at which the sheet being rolled is cracked) of Ti-Al-V alloys solution treated at or above 1 000°C and quenched.[21] Like the Ti-6Al-4V alloy, a near-α high-Al titanium alloy is extremely low in the critical rolling reduction ratio in a single α' martensite microstructure. A low-Al or high-V titanium alloy, on the other hand, is high in hardenability and exhibits excellent cold rollability in spite of the single HCP α' martensite state. In these titanium alloy systems superior in workability at room temperature, many <a> basal dislocation traces and $\{10\bar{1}1\}$ twin traces are observed in the α' martensite deformation microstructure as in the Ti-6Al-4V alloy. These activities are mainly responsible for high cold rollability.

Under the worldwide recognition that "the α' martensite is brittle", no practical research and development have been conducted on the α' martensite. Appropriate microstructure control of the α' martensite can increase both the strength and ductility of the α' martensite at the same time. This approach is strongly expected to open up the new possibility of microstructure control. In addition, as described above, we can expect development centered on the aforementioned metastable α' martensite and ω phases and on the game changing initiatives utilizing impurity additions. We earnestly hope that Japan's strengths will be demonstrated in the field of structural titanium alloys and that its design concepts will be developed and deployed in these areas.

4. Conclusions

Our report is audaciously titled "'Metallurgy' of Structural Titanium Alloys: Past-Current-Future." While reviewing the history of titanium research in Japan, we have stated that we are currently in an important phase and have presented our thoughts on the "future" of titanium research in Japan. We will have to push ahead with our "reviewing" of basic research on process and alloy design by employing materials informatics and DX approaches, to realize true "optimization" based on those results, and to create Japan's originally innovative challenges and design guidelines at the same time. In particular, it is no exaggeration to say that current titanium research in the world revolves around "3D printers." When we surveyed titanium research papers published by Elsevier in and after 2010, we found that nearly 30% are related to additive manufacturing and 3D printers. (The actual number is much more when we count the papers published in and after 2018.) In 2019, a world conference on titanium was held in Nantes, France. A total of 88 sessions were organized at the conference. Of these sessions, 13 addressed additive manufacturing (3D-AM). Additive manufacturing is currently the most noted research field in the world. This attests to the fact that the metallurgy-based design guidelines that have dramatically enhanced the mechanical properties of structural titanium alloys are reaching their limits. We hope for the creation of new innovative microstructure control concepts of Japanese origin to lead the world. We sincerely desire that titanium research and development will make great progress with close industry-academia collaboration.

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