Possibility of As-Cast Applications on $\beta$-Type Titanium Alloys Proposed in the Newly Expanded Area of $Bo_{\alpha}-Md_{\beta}$ Diagram

Xi-Long Ma, Kazuhiro Matsugi, Zhe-Feng Xu, Yong-Bum Choi, Ryohei Matsuzaki, Zi-Feng Lin, Xin-Gang Liu, and Hao Huang

1Department of Mechanical Materials Engineering, Hiroshima University, Higashi-Hiroshima 739-8527, Japan
2State Key Laboratory of Metastable Materials Science and Technology, Yanshan University, Hebei street 438#, Qinhuangdao 066004, China
3College of Mechanical Materials Engineering, Yanshan University, Hebei street 438#, Qinhuangdao 066004, China

Ten types $\beta$-type titanium alloys for as-cast applications were proposed by using mainly ubiquitous elements in the area greatly differ from conventional alloys in compositions, in the diagram consisting of bond order ($Bo$) and d-orbital energy level ($Md$). The object was to develop $\beta$-type titanium alloys with ultimate tensile strength value of 1000 MPa and fracture strain value of 10% in as-cast condition without the post-treatment after cold crucible levitation melting, and their microstructures were controlled by adjusting its process parameters. The same microstructure and mechanical properties were also indicated on both as-cast and solution treated alloys, which mean the unnecessary of solution treatment in proposed alloys. Ti-5.2Cr-5.5Mn-2.2Fe-5.5Zr, Ti-11Cr-6Mo-4.5Zr-0.5Al and Ti-13Zr-6Mo-6Cr-5V alloys with a $\beta$ mono phase achieved objective values of mechanical properties in as-cast condition, which lead to development of alternative materials to the conventional $\beta$-type titanium alloys, since they reduce energy consumption and 25% production costs by omitting complex post processing procedures. Moreover, the phase boundary between the mono $\beta$ phase and dual $\beta$ plus intermetallic compound phases were predicted for the first time in $\beta$-type titanium alloys, according to the ten proposed alloys in newly expanded compositional area of the $Bo_{\alpha}-Md_{\beta}$ diagram.

Keywords: titanium alloy design, DV-Xa method, cold crucible levitation melting, energy-saving materials, segregation in solidification

1. Introduction

Titanium based alloys have been extensively investigated for a variety of applications due to their excellent material properties, such as its biocompatibility, excellent combination of high-temperature strength, and lightweight.1-5 In particular, $\beta$-type titanium ($\beta$-Ti) alloys with high strength, excellent corrosion resistance, shape memory ability, and high specific strength are widely used in aerospace, bio-implant, and industrial applications.6-9 However, the higher cost of $\beta$-Ti alloys compared to other common structural alloys have limited their usage fields due to the high cost of raw materials, the term length of the development process and its complex post-treatment.10,11 In addition, the relative complex deformation types of $\beta$-Ti alloys, including slip, twin, and martensite, make their mechanical control more difficult.12 Generally, the $\beta$-Ti alloys with single or combined deformation types show divergence in mechanical properties and deformation behaviors.13 Hence, the development of $\beta$-Ti alloys with low cost and controllable deformation types is important and meaningful.

In the past, repetitive experiments and empirical rules on the purpose of developing $\beta$-Ti alloys of reduced cost and controllable deformation types were implemented by researchers; these have been characterized by their high energy consumption and long development cycle.14,15 The proposal of the d-electrons concept can design $\beta$-Ti alloys and shorten the development cycle without trial and error experiments.16,17 The d-electrons concept based on the theoretical calculation of electronic structure theory has been applied to the design of high-performance materials such as Al, Bi, Ni, Zn, and Ti-based alloys.9,18-22 Two calculated parameters are utilized in the d-electrons concept, the bond order ($Bo$), which is a measure of the covalent bond strength between Ti and an alloying element, and the d-orbital energy level ($Md$), which correlates the electronegativity and metallic radius of elements.23,24 The d-electrons concept is easy and convenient to use in practical applications, compared with other alloy design methods such as the phase-field method and the thermodynamic modeling of ordered phases.19,25,26 The compositional average values of $Bo$ and $Md$ of Ti alloys are represented by $Bo_{\alpha}$ and $Md_{\beta}$, respectively.17 Ti alloys are classified into the $\alpha, \alpha + \beta, and \beta$ types according to the phases existing in alloys. Compositions of forty commercial alloys were plotted on the $Bo_{\alpha}$ and $Md_{\beta}$ coordinates; three types of titanium alloys were separated in the $Bo_{\alpha}-Md_{\beta}$ diagram.17,23 $\beta$-Ti alloys with slip dominant deformation universally possess high strength and a controllable deformation process compared with Ti alloys with twin and martensite deformation types.27 However, $\beta$-Ti alloys located in the new region of the $Bo_{\alpha}-Md_{\beta}$ diagram with a higher amount of $\beta$ stabilized elements and lower $Md_{\beta}$ values than conventional $\beta$-Ti alloys are rarely discussed in previous literature, because of the emergence possibility of inter-metallic compounds. Although this new region is a candidate area to develop $\beta$-Ti alloys with improved mechanical properties in as-cast condition, the superior solid solution hardening is foreseen for the $\beta$-Ti alloys located in the new region with the addition of sufficiently $\beta$ stabilized elements.

Titanium has a high affinity toward oxygen and hydrogen at elevated temperatures, which can greatly influence the properties of Ti alloys.28-30 These elements and other impurities are usually derived from the gas environment of the furnace and the contaminations of the crucible in the process of melting.9,17,31 The choice of appropriate melting
equipment is essential for the preparation of Ti alloys. Cold crucible levitation melting (CCLM) consists of a high-frequency induction furnace and two electric coils. Two electric coils are used for the heating and levitation of the metals in the crucible, respectively.32 The materials will be melted and suspended by the induction current without contact between the materials and copper crucible during the melting process. Furthermore, uniform composition and the high purity of Ti alloys can be obtained by the effect of the electromagnetic stirring force and higher vacuum performance of the furnace.17,31,33

The reported β-Ti alloys, TUT 1A (Ti–13V–3Al–3Cr–2Nb) and 15-3-3-3 (Ti–15V–3Cr–3Sn–3Al), have never been used in as-cast condition without post-treatments as structural materials, because of the resulting undesirable mechanical properties, according to previous reports.34-36 In contrast, the 15-3-3-3 alloy, which was treated by solution treatment and aging was commonly used as sheet, plate, and airframe materials, and showed the ultimate tensile strength (σUTS) of approximately 1000 MPa and a fracture strain (εf) of 10%.35,36 However, when calculating the cost of the Ti alloy for aircraft applications, if the raw material cost is set as unit 1, the cost of the casting process is approximately 0.5, the post-treatment cost is approximately 1.5, and the cost of secondary processing is approximately 2.37 The post-treatment cost is remarkably expensive compared with that of casting, because of its high energy consumption. The cost reduction trend of Ti alloys is focused on the following methods:37-40 The first approach is the choice of cheaper raw materials. The second method is the development of new Ti alloys with improved mechanical properties, which can simplify or omit the post-treatment processes. The third way is to improve the efficiency of manufacturing and post-treatment equipment. Finally, the fourth method is the expansion of the production scale to reduce fringe costs. The high performance of titanium alloys with the σUTS of 1000 MPa and εf of 10% just as in as-cast condition is a landmark alloy-development for energy-saving measures, compared with conventional alloys such as 15-3-3-3 with high performance manufactured by complex post-processing. The development of light alloys applied in as-cast condition, such as aluminum and magnesium alloys, has proven to be an effective way to reduce their cost and energy consumption.22,38,39

In the present study, ten types of β-Ti alloys for as-cast applications were proposed, on the basis of the d-electrons concept, by using the BoT-Md diagram. To develop β-Ti alloys with an σUTS value of 1000 MPa and εf value of 10% in as-cast condition, the new compositions of ten types of β-Ti alloys were chosen using mainly ubiquitous elements in the newly expanded area, greatly differing from conventional alloys. This implies the choice of cheaper raw materials and the design of new β-Ti alloys with improved mechanical properties as cost reduction measures occur at the same time. Ingots of experimental alloys were produced by the CCLM technique as a single manufacturing process for saving energy; their microstructures were controlled by adjusting its cooling process parameters. The microstructure and mechanical properties of the ten types of β-Ti alloys were discussed in as-cast and solution treated conditions.


The nominal compositions of ten types of β-Ti alloys were designed on the basis of the d-electrons concept using mainly ubiquitous elements. The BoT and Md values of these β-Ti alloys were calculated using the discrete-variational Xα (DV-Xα) cluster calculation method on the MTi4 cluster model in the case of bcc Ti.41,42 The BoT and Md values of each alloy were calculated by the following eqs. (1) and (2).

\[
BoT = \sum X_i(BoT)_i \\
Md = \sum X_i(Md)_i
\]

Where \(X_i\) is the molar fraction of component i in Ti alloy, \((BoT)_i\) and \((Md)_i\) were the numerical values of \(BoT_i\) and \(Md_i\) for each component i, respectively.9,40 By using eqs. (1) and (2), the BoT and Md values of the 15-3-3-3 alloy were also calculated conveniently. Firstly, the chemical composition unit of Ti–15V–3Cr–3Sn–3Al in mass% was converted to Ti–14.18V–2.78Cr–1.22Sn–5.35Al in mol\%. In this condition, the \(X_i\) values of Ti, V, Cr, Sn, and Al were 0.7647, 0.1418, 0.0278, 0.0122, and 0.0535, respectively. The \((BoT)_i\) and \((Md)_i\) values of Ti, V, Cr, Sn, and Al were 2.79 and 2.45; 2.81 and 1.87; 2.78 and 1.48; 2.28 and 2.10; and 2.43 and 2.20, respectively.23 The molar fraction of each element in the alloy is multiplied by its respective BoT or Md value, then the values of all the elements are summated to obtain the BoT and Md values of this alloy, as shown as follows:

\[
BoT = X_Ti(0.7647) \times BoT_Ti(2.79) + X_V(0.1418) \times BoT_V(2.81) + X_Cr(0.0278) \times BoT_Cr(2.78) + X_Sn(0.0122) \times BoT_Sn(2.28) + X_Al(0.0535) \times BoT_Al(2.43) = 2.77
\]

\[
Md = X_Ti(0.7647) \times Md_Ti(2.45) + X_V(0.1418) \times Md_V(1.87) + X_Cr(0.0278) \times Md_Cr(1.48) + X_Sn(0.0122) \times Md_Sn(2.10) + X_Al(0.0535) \times Md_Al(2.20) = 2.32
\]

The 2.77 and 2.32 were the BoT and Md values of the 15-3-3-3 alloy calculated by taking its average chemical composition, diagram 741 shows the compositional locations of ninety-three commercial and reported β-Ti alloys. There are the indications of deformation modes consisting of slip, twin, and martensite types and excellent mechanical properties have been produced by combinations of both compositional and post-manufacturing process approaches, such as TUT 1A (σUTS: 1400 MPa, εf: 6%).35,36 The positions of TUT 1A and 15-3-3-3 alloys in the BoT-Md diagram are also shown in Fig. 1. The β stabilized area in lower Md values is a candidate, or the “target area”, indicated by solid black arrows in the newly expanded area, for as-cast applications of β-Ti alloys without post-treatment compared with conventional alloys. The promising mono β phase alloys with high strength and elongation can be proposed in this target area showing the expanded compositional area where it is greatly different from ninety-three commercial and reported alloys. The BoT value of 2.79 which is equal to that of pure Ti and five Md values of 2.16, 2.20, 2.24, 2.28 and 2.32 were selected to investigate the mono phase region. The other
The value of 2.81 was chosen as the high Bo value for improvement of strength properties. According to the principle of the Bo and Md values, the newly proposed ß-Ti alloys were named from HU-01 to HU-10, as shown in Fig. 1. The compositions of the ten newly proposed ß-Ti alloys in mol% or mass% and their respective Bo and Md values are listed in Table 1. The chemical compositions of the ten alloys in Table 1 are determined by considering the Bo and Md values to propose alloys in the target area where they greatly differ from ninety-three commercial and reported alloys in the Bo-Md diagram. Furthermore, the usage of ubiquitous elements facilitates the reduction of alloy cost, and the easy disposal of an abandoned alloy. In addition, the vectors pointing from pure Ti that represent the location of Ti-10 mass%M (M is an additional alloying element) are shown in Fig. 2(a). The elements circled by a square correspond to the alloying elements selected in the present study from the viewpoints of the Bo and Md values to propose alloys in the target area where they greatly differ from ninety-three commercial and reported alloys in the Bo-Md diagram. Furthermore, the usage of ubiquitous elements facilitates the reduction of alloy cost, and the easy disposal of an abandoned alloy. The ubiquitous Cr and Mn elements were chosen as the major additional elements, which had the high ability to shift the positions of ß-Ti alloys to the target area with low Md values in the Bo-Md diagram. The Fe and V elements were helpful in moving the ß-Ti alloys to a lower Md area in the Bo-Md diagram. The Zr, Mo, Al, and Ta elements were chosen to adjust the Bo values of ß-Ti alloys. The MTi14 cluster model which was used for the calculation of bcc Ti is shown in Fig. 2(b).

3. Experimental Procedures

3.1 Materials and manufacturing process

The purity of raw materials for preparing ten newly proposed ß-Ti alloys were Ti, Cr, Mn, Fe, V, Zr, Mo, Al, and Ta with 99.8, 99.9, 99.9, 99.9, 99.9, 99.0, 99.9, and 99.8 mass%, respectively. Hereafter, the compositions of ten newly proposed ß-Ti alloys were given in mass% in this study. All ingots of ten proposed ß-Ti alloys were prepared by CCLM (capacity of 1 kg in Fe melt/100 + 60 kW) and their microstructures were controlled by adjusting its process parameters. 100 and 60 kW are the rated power of the upper and lower electric coils of the CCLM, respectively. The maximum temperature and holding temperature of the CCLM depend on the melting point of alloying elements. In the HU-01 alloy, for example, to completely melt the raw materials and fully stir the molten metals, the molten metal with 150 cubic centimeters was heated to 2350 K in the heating process. Then, for its complete stirring, the molten metal was held for 300 s at the constant temperature of approximately 2180 K. Subsequently, the molten metal was heated to 2350 K, as a solidification pretreatment. Finally, the molten
metal was cooled and solidified in the copper crucible after switching off the electric power in the upper and lower coils after the melting process. The detailed parameters of CCLM equipment during the melting process are shown in Fig. 3. The profiles of temperature in molten metal, electric power in upper and lower coils, and pressure in the Ar atmosphere of the levitation melting and cooling process are shown in Fig. 3 (a), (b), and (c), respectively. The upper and lower electric coils were utilized for heating by high-frequency induction and levitation by the eddy current for molten metals. These functions were successfully carried out, which led to the achievement of a homogeneous mono-β phase (mentioned in 4.1 section) and the low contents of gaseous impurities. The different grain sizes of alloys were obtained by both cooling methods of molten metals, that is, the solidification of the melting Cu crucible and split-cold mold placed below the hole of the melting Cu crucible in the bottom part of the melting furnace. In contrast, the different grain sizes could also be influenced by the different Ar gas purity. These Ti ingots were prepared in the solidification of the melting Cu crucible under the purity of 99.99% Ar atmosphere in the present study. The contents of gaseous impurities of oxygen and nitrogen were lower than those (oxygen and nitrogen: 0.069 and 0.006%, respectively) in the raw materials. This is because the high vacuum level of \(3 \times 10^{-3}\) Pa was obtained by using a rotary pump (RP) and diffusion pump (DP) as shown in Fig. 3.17,31)

The schematic illustrations of the ingots produced by CCLM and tensile specimen showing both the equiaxed and columnar grain distribution and cutting position for a tensile specimen in an ingot are shown in Fig. 4. The dimensions of the ingots and tensile specimens are given in millimeters (mm). The rectangle blocks were first cut by wire cutting from the ingot. Then, the tensile specimens were also prepared in these rectangle blocks. The edge lengths of rectangle blocks were \(a\bar{b}, \bar{c}d, \bar{e}f, \) and \(g\bar{h}\) of 30 mm, \(a\bar{d}, \bar{b}c, \) \(e\bar{h}, \) and \(g\bar{f}\) of 10 mm, and \(a\bar{e}, \bar{b}f, \bar{c}g, \) and \(d\bar{h}\) of 35 mm, respectively. The equiaxed and columnar grains in the ingot were further observed by the optical microscope (OM) images. The columnar grains with larger and various sizes were observed at the bottom and close to the lower part (tip part) of the ingot compared with those of equiaxed grains part with the uniform sizes in the upper part of ingot. Therefore, the positions with equiaxed grains were chosen to cut the tensile specimens. The sizes of equiaxed grains were approximately 200 µm in diameter as shown in the OM images in Fig. 4 and discussed in detail in Figs. 5 and 6, respectively. The as-cast specimens were cut directly from the ingot. Whereas the solution treatment was carried out at 1173 K for 3.6 ks, the specimens cut from the ingot were sealed in a quartz tube under an argon atmosphere following by quenching in cold water.

### 3.2 Microstructural characterization

The specimens were ground, polished and etched using sandpaper of 80 to 2500 mesh, different grades of polishing...
paper and a mixed solution of distilled water, nitric acid, and hydrofluoric acid (95:3:2 in volume ratio), respectively. The microstructural observation of as-cast and solution treated specimens was carried out using OM imaging analysis. The constituent phases and lattice constants of ten experimental alloys were identified by X-ray diffraction (XRD) with Cu-Kα radiation generated at 40 kV and 30 mA at ambient temperature. The chemical compositions of HU-01 and HU-05 alloys were measured by point analysis via an electron probe micro-analyzer (EPMA). For the preparation of the solidification paths, the point analysis, which thoroughly crossed two grains of each specimen was measured with an interval of 25 µm between every two points.

3.3 Tensile tests

The gauge sizes of tensile specimens were 6 mm in diameter and 20 mm in length with grips of 10 mm in diameter as shown in Fig. 4. The tensile tests were carried out at an initial strain rate of $1.9 \times 10^{-4} \text{s}^{-1}$ under room temperature, the fracture strain values of tensile specimens were measured using an extensometer and the stress-strain curves were obtained by a mechanical testing machine during the tensile process. The Vickers hardness measurements were tested with a load of 300 N for 10 s.

4. Results and Discussion

4.1 Microstructures

The OM images of ten types of β-Ti alloys in as-cast and solution treated conditions are presented in Figs. 5 and 6 and the area fraction of the constructed phases of the ten types of β-Ti alloys are presented in Fig. 7. For the HU-01 to HU-05 alloys with the constant $B_0$ value of 2.79 in both as-cast and solution treated conditions, the mono β phase of the HU-01 and HU-02 alloys were observed in both as-cast and solution treated conditions as shown in Fig. 5(a) and (b), (c) and (d), (e) and (f), (g) and (h), (i) and (j), respectively. In contrast, the presence of dual β plus intermetallic compound phases was observed in Fig. 5(e) and (f), (g) and (h), (i) and (j), (k) and (l), corresponding to the HU-03 to HU-05 alloys in both as-cast and solution treated conditions, respectively. The average grain sizes of the HU-01 to HU-05 alloys in both as-cast and solution treated conditions were measured to be, on the basis of the microstructure results, 290 and 305, 235 and 242, 210 and 215, 186 and 198, and 175 and 185 µm, respectively. The decrease of the $M_d$ value or higher alloying led to the decrease of grain sizes, regardless of the post-treatments. It would be due to the fact that the additional alloying elements will provide more nucleation opportunities for the titanium alloys. The increased amount of nucleation will lead to the refinement of grain size. For the HU-06 to HU-10 alloys with the constant $B_0$ value of 2.81, the mono β phase was...
observed in HU-06 alloy in both as-cast and solution treated conditions as shown in Fig. 6(a) and (b). In contrast, the presence of dual $\beta$ plus intermetallic compound phases was observed in Fig. 6(c) and (d), (e) and (f), (g) and (h), and (i) and (j), corresponding to the HU-07 to HU-10 alloys in both as-cast and solution treated conditions, respectively. The average grain sizes of HU-06 to HU-10 alloys in both as-cast and solution treated conditions were 280 and 295; 230 and 245; 193 and 205; 191 and 205; and 180 and 195 µm, respectively. The same relationship between the $M_{dt}$ values and grain sizes existed regardless of the $B_{ov}$ values. The 3 to 8% increment in the grain sizes was measured by the solution treatment, regardless of the $B_{ov}$ values.

Moreover, the occurrence positions of the intermetallic compounds expanding from the grain boundaries inward toward the grains were more clearly observed with the increasing content of additional elements in the alloys. The contents of intermetallic compounds were evaluated by measuring the area fractions in the ten types of $\beta$-Ti alloys in both as-cast and solution treated conditions, according to their OM results. The increment in intermetallic compound content was observed and measured from HU-03 to HU-05 $\beta$-Ti alloys, as shown in Fig. 7(a). Simultaneously, the increased tendency in contents of intermetallic compounds occurred in the HU-07 to HU-10 alloys, as shown in Fig. 7(b). The area fractions of intermetallic compounds in the HU-03 to HU-05 alloys in as-cast and solution treated conditions were 18.4% and 16.1; 26.1 and 22.5; and 36.2 and 32.3%, respectively. Meanwhile, the area fractions of intermetallic compounds in HU-07 to HU-10 alloys in as-cast and solution treated conditions were 5.3 and 3.3; 8.6 and 6.2; 16.3 and 12.4; and 26.2 and 22.3%, respectively. In contrast, the absences of intermetallic compounds were observed in the HU-01, HU-02, and HU-06 alloys. The TiCr$_2$ and TiCrMn phases were detected by XRD as shown in Figs. 8 and 9, and these intermetallic compounds were known as brittle phases.45,46) The ternary intermetallic TiCrMn is a partial manganese substituted derivative of the TiCr$_2$ and the substitution of the Cr by Mn in the lattice of TiCr$_2$ made the atomic stacking closer.47)

According to the microstructures of ten types of $\beta$-Ti alloys, the phase boundary between the mono $\beta$ phase and the dual $\beta$ plus intermetallic compound phases were roughly identified in the newly expanded area of the $B_{ov}$-$M_{dt}$ diagram for the first time. The lattice constants of the ten types of $\beta$-Ti alloys were calculated from the interatomic layer distances of the primary (110) reflections, using the results of Figs. 8 and 9. The higher sensitive condition for the identification of TiCrMn and TiCr$_2$ in the 2$\theta$ value of 43 to 46° is also shown in Figs. 8 and 9(g), respectively. The XRD experiments of
each alloy were repeated and the data for the same alloy obtained from the repeated experiments were compared with each other. The results showed approximately the same value and tendency as shown in Fig. 10. The detailed values of lattice constants of the ten types of β-Ti alloys corresponding to the diffraction angle of (110) are shown in Fig. 10. The error bar from repeated experiments for the same alloy is shown even smaller than the symbol used in Fig. 10, which means that the invisible error bar was inside the symbol range. For the HU-01 to HU-05 β-Ti alloys with a Bo value of 2.79 in both as-cast and solution treated conditions, the values of lattice constants of HU-01 to HU-05 alloys were 0.328, 0.325, 0.323, 0.321, and 0.321 nm, as shown in Fig. 10(a), respectively. For the HU-06 to HU-10 β-Ti alloys with Bo value of 2.81 in both as-cast and solution treated conditions, as shown in Fig. 10(b), the values of lattice constants of HU-06 to HU-10 β-Ti alloys were 0.327, 0.323, 0.321, and 0.321 nm, respectively. In addition, the lattice constant of β-Ti metal with a value of 0.332 nm was also listed in Fig. 10(a) and (b) as a comparison. The decreased lattice constants with the decrease of Md values were measured in each of the five β-Ti alloys with constant Bo value, due to the increase of alloying elements with a smaller atomic radius that substituted the Ti in the crystal. The solid solution limits of ten types of β-Ti alloys were investigated by their respective values of lattice constants. For the two series of five β-Ti alloys with the same Bo value, the fitting lines of two adjacent values of lattice constants were obtained as shown in Fig. 10(a) and (b), respectively. The slope of the fitting lines changed dramatically between HU-02 and HU-03, and HU-06 and HU-07, respectively. In view of the above results, the solid solution limit appeared in interval between HU-02 and HU-03 for the β-Ti alloys with the Bo value of 2.79. In addition, the solid solution limit appeared in the interval between HU-06 and HU-07 for the β-Ti alloys with the Bo value of 2.81. The results of the OM, XRD patterns indicating the TiCr₂ and TiCrMn peaks and the lattice constant values were in agreement with each other and by their combination, the phase boundary in the newly expanded area of Bo-Md diagram was identified in the present study. The line among the HU-02, HU-03, HU-06, and HU-07 alloys as shown in Fig. 1, indicated the phase boundary between the mono β phase and the dual β plus intermetallic compound phases.

On the basis of the vectors that represent the location of Ti–10 mass%M as shown in Fig. 2, the changing in Md values was mainly influenced by the increase in Fe, Cr, and Mn contents. In addition, the intermetallic compounds, located in the grain boundary, consisted of TiCr₂ and TiCrMn. Therefore, the element distributions of Cr and Mn in one grain of the HU-01 and HU-05 alloys were investigated by their solidification paths. For the preparation of the solidification paths, the points analysis thoroughly crossing two grains of each specimen, was measured with the interval of 25 µm between every two points by EPMA. The segregation degree and composition scatters of the Cr and Mn elements in the HU-01 and HU-05 alloys in as-cast and after solution treated conditions are shown in Fig. 11. Heavier segregation in the HU-05 alloy was observed, compared with HU-01 alloy, regardless of the post-treatments. There was a little difference in compositional scatters between the as-cast and solution treated conditions in the HU-01 alloy. The segregation degree and composition scatters of Cr and Mn decreased by the solution treatment. The serious segregation and formation of intermetallic compounds in the HU-05 alloy were indicated by the widely distributed chemical composition scatters.
4.2 Tensile properties and fracture surface

The tensile curves of the HU-02 and HU-03, and HU-06 and HU-07 alloys in both the as-cast and solution treated conditions were chosen as typical specimens as shown in Fig. 12, respectively. The HU-02 and HU-06 alloys with the mono $\beta$ phase showed slip behavior consisting of a classical elastic-plastic tensile behavior, as mentioned in Fig. 1. They also showed high tensile strength and elongation values compared with those of HU-03 and HU-07 alloys with dual $\beta$ plus intermetallic compound phases. The fracture morphologies of the HU-02 and HU-06, and HU-03 and HU-07 alloys in as-cast condition were chosen as typical specimens, representing the alloys without or with the presence of intermetallic compounds, respectively. The precipitation of brittle intermetallic compounds TiCrMn and/or TiCr$_2$ located at the grain boundary, resulting in the fracture of specimens occurred during the elastic deformation stage in the tensile test process. The dimple fracture patterns that appeared in the HU-02 and HU-06 alloys in the as-cast condition corresponded to the relative satisfaction $\%$ values, as shown in Fig. 13(a) or (b), and (e) or (f), respectively. In contrast, the inter- and trans-granular deformations were observed in Fig. 13(c) or (d), and (g) or (h) and corresponded to the HU-03 and HU-07 alloy in as-cast condition.

The tensile properties of ten newly proposed $\beta$-Ti alloys with their respective $\sigma_{UTS}$ and $\varepsilon_f$ values in as-cast and solution treated conditions were shown in Fig. 14(a) and (b), corresponding to the $\beta$-Ti alloys with $B_0\varepsilon$ values of 2.79 and 2.81, respectively. The as-cast and solution treated alloys showed their respective $\sigma_{UTS}$ with $\varepsilon_f$ values, they were 1027 and 979 MPa with 10.12 and 10.21% for HU-01, 982 and 1002 MPa with 9.82 and 9.63% for HU-02, 531 and 406 MPa with 0.55 and 0.44% for HU-03, 279 and 155 MPa with 0.29 and 0.11% for HU-04, 329 and 232 MPa with 0.17 and
0.16% for HU-05, 984 and 1090 MPa with 10.32 and 10.63% for HU-06, 340 and 463 MPa with 0.40 and 0.50% for HU-07, 208 and 316 MPa with 0.30 and 0.26% for HU-08, 235 and 310 MPa with 0.23 and 0.27% for HU-09, 188 and 213 MPa with 0.20 and 0.21% for HU-10. HU-01 and HU-02 alloys with Md value of 2.32 and 2.28, respectively, showed the highest σUTS values among the five alloys with a Bo value of 2.79. In contrast, σUTS values decreased dramatically, which corresponded to the decrease of εf values. The alloys with an Md value less than 2.24 also showed the occurrence of TiCr2 and TiCrMn intermetallic compounds. The results showed that the presence of brittle intermetallic compounds in alloys caused a serious deterioration in their tensile properties. In addition, the HU-06 alloy with the Md value of 2.32 showed the highest σUTS value of 984 MPa and εf value of 10.32% in as-cast condition among the five alloys with a Bo value of 2.81. The alloys at the Bo value of 2.81 showed poor tensile properties with Md values less than 2.28, which was caused by the occurrence of TiCr2 and TiCrMn intermetallic compounds. The HU-01, HU-02 and HU-06 alloys performed satisfactorily in the objective values of their mechanical properties in as-cast and solution treated conditions, which led to the development of materials different from the conventional β-type Ti alloys, as they reduced energy consumption and production costs by omitting complex post-processing procedures.

4.3 Vickers hardness

The Vickers hardness of the ten types of β-Ti alloys in as-cast and solution treated conditions are shown in Fig. 15(a) and (b). The Vickers hardness values of the HU-01 to HU-10 alloys in as-cast and solution treated conditions were 325 and 332, 345 and 355, 366 and 372, 388 and 411, 422 and 466, 358 and 371, 410 and 433, 423 and 441, 436 and 446, and 440 and 467, respectively. All the alloys excepted for HU-01 showed a lower Vickers hardness value in as-cast condition than that of solution treated condition. The Vickers hardness values increased with the decrease of Md value by the solid solution hardening for the alloys with the same Bo value of either 2.79 or 2.81. Namely, the alloys with a lower Md value implied the higher addition amount of β stabilized elements, possessing superior solid solution hardening. The existence of a TiCr2 intermetallic compound led to an improvement in the hardness property of the reference 15-3-3-3 alloy, which was attributed to the higher hardness of TiCr2 intermetallic compound compared with that of its alloy matrix.48) The HU-05 alloy showed 29.8 and 40.7% improvements in Vickers hardness values compared with those of HU-01 alloy in as-cast and solution treated conditions. While the HU-10 alloy showed 22.9 and 25.6% improvements in Vickers hardness values compared with those of HU-06 alloy in as-cast and solution treated conditions, respectively. Moreover, the HU-06 alloy with a Bo value of 2.81 showed higher Vickers hardness values than that of HU-01 alloy with a Bo value of 2.79; this was attributed to the effect of the Bo value correlating with the mechanical properties.15) According to the chemical compositions of ten alloys and their respective Vickers hardness values, it was determined that the Vickers hardness of the five alloys with a Md value of 2.79 was dominantly influenced by the change in contents of intermetallic compounds, as shown in Figs. 7(a) and 15(a).

4.4 As-cast application possibility of proposed alloys in the newly expanded area in the Bo-Md diagram

There was agreement in the stress-strain curves and hardness values between the as-cast and solution treated samples for the mono β phase alloys of HU-01, HU-02, and HU-06. Their alloys even in the as-cast condition showed excellent values in the tensile properties, satisfying the initial objective values and confirming the possibility of as-cast applications. The exact prediction of the phase boundary between the mono β phase and dual β plus intermetallic compound phases could be proposed in the newly expanded area largely differing from compositional positions of conventional β alloys in the Bo-Md diagram.

5. Conclusions

(1) The ten newly proposed alloys which were produced by the CCLM technique as the single manufacturing process, and their microstructures were approximately controlled to the same level in both as-cast and after solution treated conditions. The distribution of equiaxed and columnar grains in ingots was evaluated by the rectangle blocks; the cutting positions for the tensile specimens were chosen in the upper part of an ingot with equiaxed grains.

(2) The line among the HU-02, HU-03, HU-06, and HU-07 alloys indicating the phase boundary between the mono β phase and dual β plus intermetallic compound phases, were successfully identified in the newly expanded area of Bo-Md diagram for the first time. The existence of brittle intermetallic compounds in proposed alloys caused a serious deterioration in their tensile properties. The HU-01, HU-02, and HU-06 alloys, with mono a β
Acknowledgements

This study was financially supported by JSPS KAKENHI C Grant Number JP18K11712. Simultaneously, this study was financially supported by the Japan Foundry Engineering Society. The Japanese version of the abstract and captions required for submission was kindly helped by Mr. Inoshita.

REFERENCES