Microstructural and mechanical properties of α-titanium sintered material via thermal decomposition of additive chromium oxide particles

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A R T I C L E   I N F O

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A B S T R A C T

The pre-mixed pure Ti and Cr₂O₃ powder was consolidated by spark plasma sintering (SPS) and hot extrusion to fabricate α-titanium (Ti) materials with oxygen (O) and chromium (Cr) elements by powder metallurgy (PM) process. The Cr₂O₃ particles were completely decomposed during SPS, and then O and Cr atoms were dissolved in α-Ti matrix. Oxygen atoms were remarkably improved the mechanical strength of PM Ti-O-Cr alloys by their solid solution hardening effect. The Cr solution and Ti₄Cr precipitates had important roles to obstruct the grains coarsening behavior by the solute drag and Zener pinning effects, respectively. The solid solution strengthening effect by Cr atoms, however, was very limited due to a small Cr solubility of about 0.35 at% in α-Ti phase of Ti-O-Cr alloys. Since Ti₄Cr precipitates with 10–20 μm diameters were not so fine, they hardly contributed to the precipitation hardening of Ti-O-Cr alloys.

1. Introduction

Titanium (Ti) and its alloys are widely used as aircraft components, chemical products plant and medical devices due to their high specific strength, excellent corrosion resistance and biocompatibility [1–3]. For the further improvement of their mechanical properties, the alloying design by using the expensive rare metals was mainly discussed in the previous studies. From a viewpoint of the sustainable use of rare metals, however, a long-term strategy in the novel materials design and processing must be established [4]. For example, carbon (C), oxygen (O), nitrogen (N), hydrogen (H) and silicon (Si), which are ubiquitous resources, are employed as the alloying elements to improve the mechanical properties of Ti materials by PM process [5–12]. In particular, O and N atoms are representative α-Ti phase stabilizer, and effectively improve the mechanical strength of Ti materials by their solid solution hardening behaviors because of a large solubility of both elements in α-Ti phase shown in Ti-O and Ti-N binary phase diagrams [13]. At the same time, it is well known that the ductility significantly decreases with increase in their contents. In the recent studies, however, PM Ti-O and Ti-N materials revealed a good balance between high strength and excellent ductility. In preparation of these Ti materials, the pre-mixed pure Ti and TiO₂ or TiN powder was used as the starting materials. The additive TiO₂ or TiN particles were decomposed during sintering, and O or N atoms originated from them were dissolved into α-Ti matrix. In this study, the elemental mixture of pure Ti powder and chromium oxide (Cr₂O₃) particles was employed to fabricate PM Ti-O-Cr alloys. In SPS process [14], the additive Cr₂O₃ particle was decomposed, and O and Cr elements were dissolved in α-Ti phase. The lattice constant changes by these solution atoms were quantitatively evaluated by using XRD (X-ray Diffraction) profiles of PM Ti-O-Cr and Ti-O alloys. Increasing in the Cr₂O₃ content, not only Cr solution, but also Ti-Cr precipitates at α-Ti grain boundaries were effective to obstruct the grain coarsening. Microstructures changes were investigated through SEM (Scanning Electron Microscope) with EBSD (Electron Back Scattering Diffraction), EPMA (Electron Probe Microanalysis) and TEM (Transmission Electron Microscope) with EDS (Energy Dispersive X-ray Spectrometry) analysis. Tensile properties of PM Ti-O-Cr alloys were evaluated, and the strengthening mechanism was discussed by using their microstructures analysis results.

2. Experimental procedure

A mean particle size of pure Ti powders (TC-450, Toho Technical Service Co.) and Cr₂O₃ particles (KOJUNDO Chemical Laboratory Co.) are 27.8 μm and 2.5 μm, respectively. Both raw powder materials have a purity of 99.9%. The elemental mixture powder of them was prepared by ball milling process for 3.6 ks, where the mixing ratio of Cr₂O₃ particles to the pre-mixed powder was 0–5 mass%. They were
3. Results and discussion

3.1. Oxygen and chromium distribution in Ti sintered materials

Ellingham diagram [15] shows the TiO$_2$ formation free energy, $\Delta G[\text{TiO}_2]$ is much small compared to $\Delta G[\text{Cr}_2\text{O}_3]$ in a wide temperature range from 300 K to 1500 K. It means Cr$_2$O$_3$ particles of the pre-mixed raw powder are completely reduced during SPS at 873 K ~ 1273 K. When using the pre-mixed Ti-5mass% Cr$_2$O$_3$ powder, Fig. 1 shows XRD profiles of Cr$_2$O$_3$ raw particle, the mixture powder, the sintered materials at 873 K ~ 1273 K and pure Ti material sintered at 1273 K. The analysis results of Cr$_2$O$_3$ peak at $2\theta = 33.2$–34.0 degree and that of Ti (0 0 0 2) peak at 37.0–39.0° are (a) and (b), respectively. A very small diffraction peak of Cr$_2$O$_3$ was detected in the profiles of Ti materials sintered at 873 K and 973 K as shown in Fig. 1(a), while the same peak was never detected in Ti materials sintered at 1073 K or more. Regarding Ti (0 0 0 2) diffraction peak in Fig. 1(b), increasing in the sintering temperature up to 1073 K, the peak gradually shifted to the lower diffraction angle. It means a distance between the basal planes of α-Ti crystal, having a hexagonal close-packed (hcp) structure, increased, and the lattice expansion of α-Ti crystal in c-axis direction occurred. Fig. 2 reveals the dependence of the lattice values in c-axis direction of Ti-5mass% Cr$_2$O$_3$ and pure Ti sintered materials on sintering temperature. They were calculated from the XRD profiles shown in Fig. 1(b) by using Bragg law [16]. Pure Ti sintered materials have a constant lattice value ($\sim 4.685$ Å) when the sintering temperature changed from 873 K to 1273 K. On the other hand, in the case of Ti-5.0 mass% Cr$_2$O$_3$ sintered materials, the lattice constant remarkably increased and reached 4.716 Å with increasing the temperature up to 1073 K. Furthermore, a very small lattice constant difference in sintering at between 1073 K and 1273 K was detected. The previous studies suggest that O atoms solution into α-Ti crystal occurred after decomposition of Cr$_2$O$_3$ particles in SPS and resulted in the increment of the lattice constant in c-axis when the sintering temperature increased from 873 K to 1273 K. Therefore, the SPS temperature of 1273 K was employed to consolidate the pre-mixed Ti-Cr$_2$O$_3$ powder in this study.

XRD analysis was applied to Ti-X mass% Cr$_2$O$_3$ (X = 0–3) sintered materials after the homogenization heat treatment at 1273 K for 3.6 ks in vacuum. Fig. 3 shows a dependence of the lattice constants of α-Ti in c-axis (a) and a-axis (b) direction on the oxygen content of Ti-X% Cr$_2$O$_3$ sintered materials. At the same time, those of Ti-Ymass%TiO$_2$ (Y = 0–1.5) materials prepared in the previous study [7] were also used as comparison data. These lattice constants were calculated from the diffraction peaks of (1 0 − 1 3) and (1 1 − 2 2) planes in α-Ti crystals of each material. As shown in (a), in the case of Ti-Cr$_2$O$_3$ sintered materials, the lattice constant in c-axis direction proportionally increased with increase in the oxygen content. An increasing ratio (a gradient of the approximation straight line) is $5.6 \times 10^{-3}$ Å/O atom), and has a good agreement with that of Ti-TiO$_2$ materials ($5.7 \times 10^{-3}$ Å/O atom). This is because Ti-Cr binary phase diagram [13] reveals a Cr solubility limit inα-Ti phase is about 0.6 at%, and then Cr solution effect on the lattice expansion of α-Ti crystal is very small. That is, the lattice

![Fig. 1. XRD profiles of Cr$_2$O$_3$ particle, Ti-5.0 mass% Cr$_2$O$_3$ raw mixture powder, their sintered materials at 873 K~1273 K and pure Ti sintered material at 1273 K: 2θ = 33.2°–34.0° (a) and 37.0°–39.0° (b).](image)

![Fig. 2. Dependence of lattice constants in c-axis direction of Ti-5.0 mass% Cr$_2$O$_3$ and pure Ti sintered materials on sintering temperature.](image)
The constant increment is mainly due to O solid solution in the case of Ti-Cr$_2$O$_3$ sintered materials as well as Ti-TiO$_2$ materials. As for the lattice constant change in a-axis direction shown in (b), it shows a constant value and independent of the oxygen content. This tendency is similar to the results in the previous studies on Ti materials with O solid solution [7,18,19].

3.2. Grains refining behavior of Ti extruded materials

Fig. 4 shows inverse pole figure (IPF) maps in the cross-section of extruded Ti-Cr$_2$O$_3$ materials, where the Cr$_2$O$_3$ content is 0 mass% (a), 0.25 mass% (b), 0.5 mass% (c), 1.0 mass% (d) and 3.0 mass% (e). The α-Ti mean grain size calculated from EBSD results significantly decreased with increase in the Cr$_2$O$_3$ content. All specimens mainly consist of equiaxed grains and a texture with (0 0 0 1) basal planes parallel to the extrusion direction. When the grains are refined, the crystal rotation easily occurs by plastic deformation during extrusion. Therefore, the extruded Ti-Cr$_2$O$_3$ materials with fine grains revealed the randomized orientation as shown in Fig. 4(c)~(e).

Fig. 5 reveals a dependence of mean grain size of Ti-Cr$_2$O$_3$ and Ti-TiO$_2$ extruded materials on the oxygen content. The mean grain size of each specimen was calculated by using IPF maps in EBSD analysis. In both, the grain size becomes constant when O content reaches about 1.5 at%. Ti-Cr$_2$O$_3$ materials, however, indicate a remarkable grain refinement compared to Ti-TiO$_2$ materials. It is obvious that Cr distribution in the Ti matrix is significantly effective for the grain refining behavior, and the role of Cr elements on α-Ti grains refinement will be discussed in later.

Fig. 6 shows EMPA and TEM-EDS analysis results of Ti-5.0 mass %Cr$_2$O$_3$ extruded material. The point analysis by TEM-EDS reveals that about 3.0 at% O atoms uniformly exist inside of α-Ti grains and their boundaries. On the other hand, Cr elements are locally detected at the
grain boundaries, and their average content of 16.1 at% is much large compared to the inside of α-Ti grains with 0.35 at% Cr. By considering the Ti-Cr binary phase diagram showing that Cr solid solubility limit in α-Ti phase is about 0.6 at%, Cr solution content of 0.35 at% in α-Ti grains is smaller than this solubility in the phase diagram. The previous study reported that an experimental solubility of Cr elements in α-Ti phase significantly decreases compared to that in the Ti-Cr phase diagram when both Cr and N atoms dissolve in α-Ti at the same time [20]. Therefore, this material also shows a smaller Cr solubility of about 0.35 at% due to the solid solution of both Cr and N atoms in α-Ti. On the other hand, as mentioned above, Cr content of 16.1 at% at grain boundaries extremely exceeds Cr solubility limit, and then Cr elements locally precipitate as Ti-Cr compounds after sintering. An electron diffraction analysis by TEM was conducted for phase identification of these Cr elements shown in Fig. 6(e). The diffraction pattern successfully detected the above precipitates as Ti$_4$Cr intermetallic compounds as shown in Fig. 7(b), and α-Ti structures were observed inside the grains in (c). In addition, as shown in Fig. 6(e), TEM-EDS analysis on Cr elements segregated at the grain boundary (No.6-13) indicates Ti: Cr = 80:16 (at%), and this atomic ratio is almost equivalent to the composition ratio of Ti$_4$Cr compounds. It is concluded that a small amount of Cr atoms uniformly dissolved in α-Ti phase and most of them precipitated as Ti$_4$Cr compounds at the grain boundaries of Ti-5.0 mass%Cr$_2$O$_3$ material.

In order to investigate the effect of Cr elements on the grain refining behavior of Ti-Cr$_2$O$_3$ extruded materials shown in Fig. 5, the microstructural analysis by EBSD was conducted on Ti-X mass% Cr$_2$O$_3$ (X = 0, 0.25, 1.0) materials before and after heat treatment (H.T) in vacuum. The H.T condition at 823 K for 86.4 ks was employed in consideration of α-Ti recrystallization temperature of 723 K. Fig. 8 shows the changes in IPF maps and a mean grain size of Ti-Cr$_2$O$_3$ materials before and after H.T, where the Cr$_2$O$_3$ content is 0 mass% (a), 0.25 mass% (b) and 1.0 mass% (c). In the case of as-extruded Ti-0.25 mass%Cr$_2$O$_3$ material before H.T shown in (b), it has fine equiaxed α-Ti grains (2.91 µm) compared to pure Ti material (5.82 µm) shown in (a). The addition of 0.25 mass%Cr$_2$O$_3$ particle means 0.15 at% Cr elements contained in the material, which is smaller than Cr solubility in α-Ti (0.35 at%) as mentioned above. That is, most of Cr elements are dissolved as the solution atoms in the grains, and their solute drag was active to obstruct the grains coarsening. This is because the extruded rods were rapidly cooled in the atmosphere after hot extrusion, and there was not enough time for their coarsening behavior in cooling. On the other hand, pure Ti material with no Cr$_2$O$_3$ addition shows a remarkable grain growth after H.T (9.63 µm) as shown in (a). When 0.25 mass%Cr$_2$O$_3$ particle was contained, its specimen also revealed a large increment of the mean grain size from 2.91 µm to 7.20 µm via H.T in (b). Furthermore, in the case of Ti-1.0 mass%Cr$_2$O$_3$ material in (c), the grain coarsening behavior was completely stopped, and no change in α-Ti grain size was observed in the specimen after H.T at 823 K. Fig. 9 indicates Cr mapping results and backscattered electron (BSE) images by EDS of Ti-X mass% Cr$_2$O$_3$ extruded materials, where X is 0.25% in (a) and 1.0% in (b), respectively. As mentioned above, most of Cr elements are dissolved in the matrix, and a very few Cr precipitates locally exist at the grain boundaries of (a) Ti-0.25 mass%Cr$_2$O$_3$ material. It means that both Cr solute drag [21,22] and Zener pinning [23–25] by the precipitates are limited to obstruct the grains growth during a long-time H.T at 823 K for 3.6 ks. On the other hand, a lot of Ti$_4$Cr precipitates uniformly dispersed along the grain boundaries of (b) Ti-1.0 mass%Cr$_2$O$_3$ material, and resulted in the complete control of grains coarsening behavior by Zener pinning in the specimen after H.T at 823 K shown in Fig. 8(c). When Zener pinning effect is active to obstruct the grain growth, its growing force (σ) balances the dragging force by the...
Fig. 7. Electron diffraction patterns of extruded Ti-5.0 mass% Cr₂O₃ material, TEM image (a), diffraction patterns of Ti₄Cr near grain boundary (b) and α-Ti (c) in grain.

Fig. 8. Changes in IPF maps and mean grain size of extruded Ti-Cr₂O₃ materials before and after heat treatment at 823 K for 86.4 ks in vacuum, where Cr₂O₃ content is 0 mass% (a), 0.25 mass% (b) and 1.0 mass% (c).
Precipitates at the boundaries \((\Delta G_{\text{p}})\), which is express as Eq. (1) by Zener-Smith model [23].

\[
\Delta G_{\text{p}} = \frac{\pi d n V}{2}
\]

where, \(d\), \(n\) and \(V\) is a diameter, a number density per unit area, and molar volume of precipitates, respectively. As mentioned above in Fig. 9, a number density of Ti-Cr precipitates of Ti-1.0 mass%Cr \(_2\)O\(_3\) material is much larger than that of Ti-0.25 mass%Cr \(_2\)O\(_3\) one. Therefore, according the above Eq. (1), it is concluded that Zener drag effect by Ti-Cr compounds at the grain boundaries is dominant to obstruct \(\alpha\)-Ti grains coarsening behavior of Ti-1.0 mass%Cr \(_2\)O\(_3\) material.

3.3. Tensile properties of Ti-Cr\(_2\)O\(_3\) materials and their strengthening mechanism

Fig. 10 shows a dependence of yield stress (a) and elongation to failure (b) of Ti-Cr\(_2\)O\(_3\) and Ti-TiO\(_2\) extruded materials on the O content.
at the ambient temperature. The yield stress (YS) of the former remarkably increases with increase in O content as well as Ti-TiO$_2$ materials, which are strengthened by O solid solution mechanism [26]. As shown in (b), a high enough elongation more than 20% is obtained until the addition of 1.0 mass% Cr$_2$O$_3$ particles (oxygen content; 1.90 at%). In the case of Ti-3.0 mass% Cr$_2$O$_3$ O material (O content; 3.53 at%), however, it is remarkably reduced to about 2%, and the specimen is very brittle due to a lot of Ti$_4$Cr compounds dispersed in the matrix. On the other hand, focusing on the gradient of YS line of each specimen shown in Fig. 10(a), Ti-Cr$_2$O$_3$ material has two different slopes in the relationship between YS and oxygen content even though the gradient of Ti-TiO$_2$ material is constant (276.2 MPa/at% O). In particular, the slope of Ti-Cr$_2$O$_3$ materials with 1.90 at% O or less (512.9 MPa/at% O) is significantly large. It means these materials are strengthened by both O and Cr elements originated from Cr$_2$O$_3$ particles. On the other hand, when O content is over 1.90 at%, the slope of Ti-Cr$_2$O$_3$ materials (272.5 MPa/at% O) is almost equal to that of Ti-TiO$_2$ materials. It indicates the main strengthening factor is O solid solution hardening when Ti-Cr$_2$O$_3$ materials contain more than 1.90 at% O elements.

In consideration of both α-Ti grains refinement and solid solution behaviors of the extruded Ti-Cr$_2$O$_3$ materials with O content less than 1.90 at% shown in Fig. 5, the strengthening factors by the grain refinement, O and Cr solid solution are effective. The quantitative evaluation of each factor of Ti-Cr$_2$O$_3$ materials is carried out as follows:

First of all, the grain refining effect (σ$_{gr}$) can be estimated by using Hall-Petch equation as shown below [27,28];

$$\sigma_{gr} = \sigma_{0} + Kd^{-\frac{1}{2}} \tag{2}$$

where, $K$ is Hall-Petch constant (18.6 MPa/mm$^{-\frac{1}{2}}$ [17]) and $d$ is a mean grain size of the specimen. Table 1 shows the oxygen content, a meanα-Ti grain size, and YS increment (Δσ$_{gr}$) calculated by Eq. (2) of Ti-Cr$_2$O$_3$ and Ti-TiO$_2$ extruded materials. The YS increment (94–232 MPa) by grains refining of Ti-Cr$_2$O$_3$ materials is much larger than that (20–32 MPa) of Ti-TiO$_2$ materials due to the remarkable grain refinement by Zener pinning effect of the former as shown in Fig. 5.

With regard to the solid solution strengthening effect (Δσ$_{sss}$), sss; solid solution strengthening, O and Cr elements are active as the dissolved atoms to increase the lattice constant in c-axis of hcp α-Ti crystals of Ti-Cr$_2$O$_3$ materials. At first,Δσ$_{sss}$ by oxygen solution is calculated by using Labusch limit shown as follows [29];

$$\Delta\sigma_{sss} = \frac{\sigma_{0}}{\alpha} + \frac{1}{5\phi} \left( \frac{F_{m}^{c}c^{\frac{2}{3}}w}{4Gb^2} \right)^{\frac{1}{2}} \tag{3}$$

where, Schmid factor ($\phi$) of 0.44–0.45 is measured by SEM-EBSD analysis on each specimen. A maximum attractive force ($F_m$) of 6.22 × 10$^{-10}$ [30], which was experimentally and theoretically determined in the previous study regarding Ti extruded materials with O solution, is employed. The O solution concentration (c), four parabolic arcs of width ($w$), shear modulus ($G$), and Burger’s vector (b) of each specimen employed in the previous works [9] are used in this study. Fig. 11 shows Δσ$_{sss}$ by O solution using the above Eq. (3) shown as “Theoretical” and the revised experimental as function of O content of Ti-Cr$_2$O$_3$ extruded materials, where “revised experimental” means the YS increment after removing the grain refining effect (Δσ$_{gr}$) from the original experimental values. The theoretical and revised experimental results increase with increasing the O content, and the theoretical results are also generally consistent with the experimental values. The strict analysis, however, indicates that the revised experimental is 40 MPa larger than the theoretical. Fig. 12 reveals a difference between the above theoretical and experimental results (Δσ$_{d}$; difference) as function of the Cr content of Ti-Cr$_2$O$_3$ extruded materials. Δσ$_{d}$ is constant in the Cr content more than about 0.35 at%, which means an experimental solid solubility of Cr atoms in α-Ti shown in Fig. 6(e). As mentioned above, the grains refining behavior, O and Cr elements solid solution are the main strengthening factors of Ti-Cr$_2$O$_3$ extruded materials. In addition, when Ti$_4$Cr precipitation hardening is active to improve their mechanical property, the estimated diameter of such effective precipitates is less than about 25 nm [31]. The size of Ti-Cr precipitates is, however, about 2–10 µm as shown in Fig. 9, and then their precipitation hardening effect is very limited. On the other hand,

![Fig. 11. YS increment of theoretical using Labusch model and revised experimental as function of oxygen content of extruded Ti-Cr$_2$O$_3$ materials. Effect of grain refinement on YS increment was removed from original experimental values.](image-url)

![Fig. 12. Relationship between experimental YS increment* and chromium contents of extruded Ti-Cr$_2$O$_3$ materials. Effects of grain refinement and oxygen solid solution on YS increment were removed from original experimental values.](image-url)

Table 1: Oxygen content, mean grain size and YS increment estimated by Hall-Petch equation of extruded Ti-Cr$_2$O$_3$ and Ti-TiO$_2$ materials.

<table>
<thead>
<tr>
<th>Oxygen content (at%)</th>
<th>Mean grain size, $d$/μm</th>
<th>YS increment by grain refinement, Δσ$_{gr}$/MPa</th>
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</thead>
<tbody>
<tr>
<td>Cr$_2$O$_3$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.98</td>
<td>5.8</td>
<td>94.0</td>
</tr>
<tr>
<td>1.16</td>
<td>2.9</td>
<td>136.2</td>
</tr>
<tr>
<td>1.35</td>
<td>2.3</td>
<td>230.2</td>
</tr>
<tr>
<td>1.90</td>
<td>1.5</td>
<td>232.1</td>
</tr>
<tr>
<td>3.53</td>
<td>1.4</td>
<td></td>
</tr>
<tr>
<td>TiO$_2$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.65</td>
<td>11.6</td>
<td></td>
</tr>
<tr>
<td>1.35</td>
<td>9.3</td>
<td>19.5</td>
</tr>
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<td>31.7</td>
</tr>
<tr>
<td>2.34</td>
<td>8.7</td>
<td>25.9</td>
</tr>
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</table>
in consideration of the Cr solubility in α-Ti matrix of 0.35 at% and the saturated Δσ,[d] of about 40 MPa in Cr content of 0.35 at% or more, it is concluded that the difference ofΔσ,[ss] between the theoretical and experimental values shown in Fig. 11 is due to Cr solution strengthening effect, not by Ti4Cr precipitation hardening behavior.

4. Conclusions

Microstructural and mechanical properties of PM Ti-Cr2O3 materials, containing the dissolved O and Cr atoms and Ti4Cr precipitates after a thermal decomposition of Cr2O3 particles in sintering, were investigated. The Cr dissolved atoms and Ti4Cr compounds were effective to obstruct the grain growth by the solute drag and Zener pinning, respectively, and resulted in the mechanical strength improvement by α-Ti grains refinement. Both O and Cr elements had important roles to improve yield stress by each solution hardening behavior. The former, however, was much effective to the strength improvement compared to Cr solution atoms. Ti4Cr precipitates with 10–20 µm diameters were not so fine, and then hardly contributed to their precipitation hardening for the mechanical improvement of PM Ti-O-Cr materials.

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