Effect of Hydrogenation Treatment on Grain Refinement of Reaction Sintered Ti-6Al-4V Alloy Composites*1

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The current study was conducted to develop a Ti-6Al-4V alloy composite material with a fine structure with improved mechanical properties by precipitating TiC particles via reaction-sintering and, additionally, by incorporating the effects of hydrides formed by hydrogenation treatment, using powder to which Mo2C had been added. The effects of precipitated TiC particles, and the subsequent generation of hydrides by hydrogenation treatment, heavy-strain working, and recrystallization treatment on grain refinement during the forming process were studied by means of structural observations. Warm rolling and multi-axial alternate forging (MAF) were employed as the heavy-strain working methods. The base metal structure of the Ti-6Al-4V composite material prepared by hydrogenation treatment on the sintered body was investigated. The particle size of TiC formed by reaction sintering, however, is not changed by heavy-strain working after hydrogenation. Its room temperature tensile strength increases with the amount of TiC precipitation, and is higher than that of non-hydrogenated material.

1. Introduction

Titanium alloys are useful materials due to their superior mechanical properties such as good corrosion resistance and high strength-to-weight ratio. However, these alloys have the drawbacks of poor wear resistance and limited workability. To overcome these deficiencies, a particle-dispersed composite using a reaction-sintering technique to create fine grained matrix structure is preferable.

The authors have developed TiB dispersed Ti-6Al-4V alloy composites, which were blended with boride powders, TiB2, MoB, and CrB.1,2) It was found that fine TiB particles created by reaction were effective in enhancing mechanical properties such as wear resistance. However, concerning fracture resistance behavior, their needle-shape particle morphology was less useful than equiaxial particles. Investigation into reactive TiC particles showed that the wear resistance was favorable on a large scale compared with that of TiB particles and that the shape of the reacted particles was equi-axial.3) Furthermore, addition of Mo2C powder results in the formation of TiC and Mo through reaction with Ti in the base powder. Dissociated Mo has the effect of transforming base metal grains from the α phase to the β phase. Hence, the Mo2C powder was effective as a secondary blending powder.

Several techniques for the grain refinement of bulk samples have recently been investigated, utilizing a process of continuous recrystallization that is induced by high plastic strain through hard strain working methods such as ECAP, ARB and ARF.4–6) These methods were found to induce a greater strain energy in materials without changing their geometrical shapes. This means that, under external deformation, it is necessary to produce in materials, as much as possible, a non-homogeneous microstructure containing such as micro bands, shear bands and lamellar boundaries. In the early stages of deformation, even a small increment of dislocation pile-up sources has an important role in inducing dense dislocation walls and cells.

Ti alloys have high hydrogen absorbing capacity, and readily form hydrides at the right temperature and pressure. Hydride precipitates and TiH2 obtained in this treatment were useful in developing high-density dislocation structures in the alloy as dislocation pile-up sources. This refinement treatment, which utilizes hydrogen in titanium alloys, produces a homogeneous, fine, and equiaxial grain structure.7) Based on the techniques described above, a severe plastic deformation method combined with a hydrogenation treatment would appear to have the greatest potential to produce a fine grain structure in Ti-6Al-4V alloy composites with dispersed TiC particles.

In this paper, the effect of hydrogenation treatment on Ti-6Al-4V powder blended mechanically with Mo2C powder using various sintering techniques followed by server plastic deformations to produce a fine grain structure was investigated.

2. Experimental Procedures

2.1 Fabrication of composite materials

The powder material used was Ti-6Al-4V powder with an average diameter of 45 μm. This powder was blended mechanically with Mo2C powder with an average diameter of 1.6 μm for 36 ks using a planetary ball mill. The volume fractions of blended Mo2C powder were 3 and 5 vol%. The chemical composition of each powder is shown in Table 1.

Two different processes were used to fabricate the sintered materials. The first was a general sintering method (GS). Blended powder was pressed into dies at room temperature
under 431 MPa and then the green compacts, 10 × 10 × 50 mm³ were consolidated by reaction sintering at 1323 K for 2.4 ks under vacuum. A temperature rising rate of 0.16 K/s was used up to 1173 K, which was then reduced to 0.1 K/s at temperatures above 1173 K. Sintered samples were encapsulated in a cylindrical steel can filled with BN power, and then subjected to HIP treatment. The samples were compressed at 196 MPa at 1373 K for 7.2 ks.

The second sintering technique used was a spark plasma sintering technique (SPS). Samples 20 mm in diameter and 10 mm in height were compressed at 50 MPa at 1373 K for 300 s under vacuum.

The densities of the reaction-sintered samples were measured using Archimedes’ method. Microstructures were observed by using a field emission scanning electron microscope (FE-SEM), a transmission electron microscope (TEM) and X-ray diffractometry. The factors that influenced the volume fractions of the added Mo₂C are described below. EBSP measurements show that the addition of 3 and 5 vol% Mo₂C precipitated 0.5 and 2 vol% TiC, respectively.

2.2 Grain refinement with hydrogenation treatment

The grain refining process of the matrix material included the following: a hydrogenation treatment to obtain finely dispersed Ti hydride precipitates which act as dislocation pile-up points, severe plastic deformation to induce heavy strain energy, heat treatment for recrystallization, and finally a dehydrogenation process to recover ductility. For sintered samples, hydrogenation was carried out in hydrogen gas at 1373 K for 300 s under vacuum. The hydrogen contents of these samples subjected to two kinds of sintering methods are listed in Table 2. The hydrogen contents for each sample subjected to two kinds of sintering methods are listed in Table 2. The hydrogen contents of these samples at various treatment times were examined by gas chromatography using pure argon as carrier gas. A constant heating rate was used. The total hydrogen content increases as the volume fraction of blended Mo₂C powder increases. The hydrogen absorbed by the sintered bodies increased with the absorption period. No difference was observed in the hydrogen content according to sintering method, since their material densities were almost the same. To obtain a finer grain structure, after the hydrogenation process, heavy warm rolling and two-axial alternative forging (MAF) with severe plastic deformation, respectively, were applied to the GS and the SPS samples. For these samples, the working temperatures were determined on the basis of a differential scanning calorimetric measurements, which were used to derive their β transus temperature. The GS samples packed in a steel box and then insulated with BN powder, which were rolled with a reduction ratio of 28% per pass, reaching a total reduction of about 84% after heating at 1073 K for 1.8 ks and were hydrogenated.

As shown in Fig. 1, the SPS samples given the MAF treatment were heated to 1123 K lower than the β transus temperature and kept for 1.8 ks. The MAF process included repeated pressing of samples from two axial directions per pressing while rotating them by 90 degrees. The forging reduction ratio was 20% relative to the original plate thickness. Therefore, a strain of 2.4 was applied over four cycles. The samples were reheated and kept at the same initial conditions during each pressing treatment, then quenched in water. The length, width and thickness of the sample were defined as L, LT and ST, respectively. After the severe plastic deformation process, the samples were heated to 1073 K for 115.2 ks under vacuum at 10⁻⁶ Pa for recrystallization and dehydrogenation, and then cooled in water.

2.3 Mechanical testing

Tensile strength was measured at room temperature using an Instron machine at an initial strain rate of 2.78 × 10⁻⁴ s⁻¹. The specimen cross sectional area was 3 × 1.0 mm², with a 3 mm gauge length.

3. Results and Discussion

3.1 Microstructure of reaction-sintered materials

The precipitation of TiC in the Ti-6Al-4V alloy matrix blended with Mo₂C during sintering is based on the following equation:

\[ \text{Ti} + \text{Mo}_2\text{C} \rightarrow \text{TiC} + 2\text{Mo} - 104.2 \text{kJ/mol} \]

In the case of general sintering, it is possible to increase the relative densities of these samples to over 97% by HIP treatment after sintering. The spherical pores observed in part of the sintered green compacts were almost eliminated by the HIP treatment. Equiaxial dispersed TiC particles were

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**Table 1 Chemical composition of powders [mass%].**

<table>
<thead>
<tr>
<th>Powder</th>
<th>Fe</th>
<th>Si</th>
<th>C</th>
<th>N</th>
<th>O</th>
<th>Al</th>
<th>V</th>
<th>Ti</th>
<th>Mo</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti-6Al-4V</td>
<td>0.03</td>
<td>0.01</td>
<td>0.01</td>
<td>0.27</td>
<td>5.92</td>
<td>3.8</td>
<td>bal.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mo₂C</td>
<td>0.04</td>
<td>5.88</td>
<td>0.34</td>
<td>bal.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Table 2 Hydrogen content in Mo₂C-blended specimens.**

<table>
<thead>
<tr>
<th>Sintering method</th>
<th>Mo₂C volume fraction (vol%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Hydrogenation time)</td>
<td>0</td>
</tr>
<tr>
<td>GS</td>
<td>0.030</td>
</tr>
<tr>
<td>(0.18 ks)</td>
<td>0.040</td>
</tr>
<tr>
<td>SPS</td>
<td>0.055</td>
</tr>
<tr>
<td>(0.3 ks)</td>
<td>0.040</td>
</tr>
</tbody>
</table>

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**Fig. 1 Schematic illustration of the working process for two axial alternative forging.**
confirmed by EPMA. However, since the fabrication process for the SPS samples is rapid and simple, grain growth of the matrix phase and TiC particles was significantly lower than with the GS method.

Reacted TiC particles increased with Mo$_2$C content. Figure 2 shows SEM micrographs of TiC dispersed Ti-6Al-4V alloy composites obtained by the GS and the SPS methods after blending with Mo$_2$C. The matrix shows a typical $\gamma$ phase structure as shown in Figs. 2(a) and (c) for the Ti-6Al-4V alloy. In the case of the Mo$_2$C blended composites, however, the $\beta$ phase structure became more prevalent with increased Mo$_2$C content as shown in Figs. 2(b) and (d). For 5 vol% blended Mo$_2$C, the $\beta$ phase increases, as shown by EPSP measurement, because reactive Mo acts as a $\beta$ phase stabilizing element, as shown in Fig. 3. EBSP micrographs revealed that the matrix shows a typical $\alpha + \beta$ lamellated structure for 3 vol% of Mo$_2$C, as shown in Figs. 3(b) and (e). However, for the sample with 5 vol% blended Mo$_2$C in Figs. 3(c) and (f), the $\alpha$ phase was preferentially remained along the initial $\beta$ phase grain boundaries. This structure shows no improved material strength. However, the structure might be improved if a suitable deformation ratio and working temperature were found.

Figure 4 shows the relationships between matrix grain size and blended Mo$_2$C content, and the precipitated TiC particle size and the blended Mo$_2$C content of the Ti-6Al-4V alloy made using the two sintering methods. It shows the average values measured for five samples. The matrix grain size decreases considerably with increasing Mo$_2$C content. However, it was also seen that the TiC particle size change does not have a strong influence up to a Mo$_2$C content of 5 vol%, and addition of Mo$_2$C over this level results in a tendency, which does not depend on the sintering method, for the formed TiC particles to link with each other. However, it was confirmed that as the heating and cooling process was performed rapidly in the SPS sintering, the growth of the matrix grain size and TiC particle size was quickly suppressed. These experimental results indicate that the SPS sintering method is superior to the GS method.

3.2 Microstructure of hydrogenated samples

Figures 5(a) and (b), and (c) and (d) show, respectively, SEM photographs of the samples prepared by the GS method and warm-rolled with a high reduction rate, and the samples subjected to the SPS method and worked using the MAF process. In comparison with the microstructure after HIP
treatment in Fig. 2, the matrix grain size was up to 3 μm for composites blended with 5 vol% Mo2C. This size also decreases with increased Mo2C content. However, SEM microstructure observations reveal no change in dispersed TiC particle size after the hydrogenation treatment in the sample blended with 3 vol% Mo2C. Figures 5(c) and (d) show SEM micrographs of hydrogenated Ti-6Al-4V alloy samples, which were subjected to MAF, recrystallization and dehydrogenation treatment. The trends of Mo2C dependence on the matrix and TiC particle sizes are almost the same. However, the values are much smaller than those of the GS samples. Figure 6 shows the relationship of matrix grain size versus blended Mo2C content and the precipitated TiC particle size versus the Mo2C blended content for the GS and the SPS samples after dehydrogenation treatment.

Due to decreased grain size resulting from the hydrogenation treatment and growth of TiC particle sizes during the MAF process, the TiC particles grew larger than those in the matrix.

3.3 Influence of the hydrogenation treatment on grain refinement

The grain sizes in the non-hydrogenated SPS sample matrix were 3 μm, as shown in Fig. 6. The grain size of the matrix was about 0.9 μm for composites with a hydrogen content of 0.09 mass% for the 5 vol% Mo2C blended composite samples given the hydrogenation treatment. The grain size decreased markedly with increasing the hydrogen content. This relationship is shown in Fig. 7. The factors affecting grain refinement could be as follows: The micro-
structure of the hydrogenated matrix sample causes a partial dynamic recrystallization process that leaves a dense dislocation network near the grain boundaries or TiC particles during severe plastic deformation at temperatures lower than the recrystallization temperature. Recrystallization during the MAF process can be predicted by the presence of fine crystal grains with comparatively low dislocation density in the vicinity of TiC particles after heavy-strain working, as shown in the TEM photograph in Fig. 10(a), after warm heavy-strain working by MAF. As shown in Fig. 7, the formed structure becomes finer with increased absorbed hydrogen content. Therefore, a large amount of hydrogen introduction is required. The introduced hydrogen amount increases, as shown in Table 2, with increased amount of added Mo$_2$C, i.e., TiC formed by sintering. Diffusion of hydrogen occurs mainly through the grain boundaries. Therefore, despite the increase in the amount of TiC formed at the grain boundaries, grain size becomes smaller, which leads to a further increase in hydrogen introduction.

The samples were examined using autoradiography. Hydrogen or hydrides distributed in the samples with hydrogen absorbed by this hydrogenation technique were not uniform and were present mainly at grain boundaries. However, for the MAF plastically deformed samples, hydrides were also found partially near the grains. Ti hydrides or hydrogen, which were found near TiC particles, acted as dislocation pile-up sources and nucleation sites for recrystallization, as in the TEM microstructure shown in Fig. 8. Small recrystallized grains and some grains with a high dislocation density are seen near TiC particles. It was found that the amount of hydrogen that was fixed at these barriers increases as the Mo$_2$C increases by measuring the amount of hydrogen at a constantly increasing temperature. These results suggest that the reacted TiC particles and Ti hydrides are more important factors in arresting grain growth, as found in Figs. 2 and 4. Clearly, the introduction of hydrogenation treatment is an effective method for grain refinement of the Ti alloy. Furthermore, following the hydrogenation process, it is necessary to carry out a dehydrogenation treatment to recover elongation. Figure 9
shows the results of X-ray diffraction analysis on 5 vol% Mo$_2$C blended GS samples after hydrogenation and dehydrogenation treatments. Figure 9(a) shows the result of an as-sintered sample. The X-ray peaks for the reacted TiC particles are clearly observed. Figures 9(b) and (c) are the diffraction results for hydrogenated and dehydrogenated samples, respectively. X-ray analysis results confirm the existence of precipitated TiC particles (a), appearance (b), and the disappearance (c) of Ti hydride (TiH$_2$), due to the hydrogenation and dehydrogenation treatments.

### 3.4 Effects of sintering method and severe plastic deformation on hydrogenation for grain refinement

In this study, two severe plastic deformation methods were applied to the hydrogenated samples. The sample densities were almost the same for the two sintering methods, GS and SPS. However, there was a large difference in the grain sizes between two samples due to treatment time, as shown in Fig. 4.

Furthermore, even though the same hydrogen content is seen in both sintered samples, as seen in Table 2, Fig. 6 indicates that the matrix average grain size for the 5 vol% Mo$_2$C-blended SPS samples subjected to warm MAF is one-half of that of the GS sample subjected to warm rolling. Also, a comparison of microstructures between rolling and MAF deformation revealed that the distributions of misorientation angles at boundaries were different between the two plastic deformation methods. In addition, the sample given the MAF process had high angle grain boundaries. Figure 10 shows microstructures of dehydrogenated and recrystallized materials that were obtained by SPS following MAF working. These samples were taken from the middle sections of the MAF-worked samples.

These results clearly show that structural refinement occurs in the middle part of the sample. The hydrogen
distribution through the material is clearly different between the surface and the middle. However, the structural uniformity in the material can be improved by following with a warm MAF working.

3.5 Mechanical properties at room temperature

Figure 11 shows the Mo$_2$C-dependence of tensile strength and elongation of the GS and the SPS samples that have undergone hydrogenation treatment with warm rolling and intensive MAF plastic working, respectively. Tensile strength increased with the Mo$_2$C content, as shown in the Figure, and the tensile strength of the SPS sample was higher than that of the GS sample. While elongation decreased drastically with the 5 vol% Mo$_2$C sample, this was due to the oxygen content, which increased by 7% in comparison with the 3 vol% Mo$_2$C sample. The precipitated TiC particle size was twice that of the matrix. Furthermore, the $\alpha$ phase present along the grain boundaries of equiaxial $\beta$ phase grains appears to decrease elongation.

4. Conclusion

Ti-6Al-4Al alloy sintered composite was reinforced with TiC particles precipitated by adding Mo$_2$C powder and using two types of sintering methods: general sintering and spark plasma sintering. Grain-refining treatments for the matrix material included hydrogenation, which causes precipitation of finely dispersed Ti hydride particles; warm-rolling for the GS, MAF for the SPS samples to induce heavy strain energy, heat treatment for recrystallization, and the dehydrogenation process to recover ductility. We obtained the following results.

1) The microstructure of the dehydrogenated and recrystallized specimens that had undergone MAF for the SPS samples had a fine grain size of less than 1 $\mu$m in diameter.
2) In the Ti-6Al-4V alloy composites with 3 vol% Mo$_2$C, tensile strength and elongation at room temperature were more than 50% greater than in the non-hydrogenated samples.
3) To obtain a fine-grained Ti alloy with high strength, it was effective to combine the Ti-6Al-4V alloy composites with particle-dispersed TiC using the SPS, hydrogenation and the dehydrogenation treatments.

REFERENCES