イソテラルメーションのβチタン・マンガニウム合金の
高温熟処理特性に関する研究

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Isothermal Aging Behavior of Beta Titanium–Manganese Alloys

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Although titanium is considered to be a ubiquitous element as it has the 10th-highest Clarke number of all the elements, it is actually classified as a rare metal because its current refinement process is more environmentally damaging than the processes used to refine iron and aluminum. Furthermore, the principal alloying elements of titanium alloys are very expensive, owing to their low crustal abundances; this is especially true of the beta-stabilizing elements. Manganese is also considered to be a ubiquitous element as it has the 12th-highest Clarke number of all the elements. Therefore, manganese is promising as an alloying element for titanium, especially as a beta-stabilizing element. In order to develop beta titanium alloys as ubiquitous metallic materials, it is very important to investigate the properties of Ti-Mn alloys. In this study, the phase constitutions and isothermal aging behaviors of Ti-6.0 to 14.8 mass%Mn alloys were investigated by electrical resistivity and Vickers hardness measurements, X-ray diffraction (XRD), and optical microscopy. In 6.0 mass%Mn alloys quenched from 1173 K, both hexagonal close-packed martensite and the beta phase were identified by XRD, whereas only the beta phase was detected in 8.7 and 14.8 mass%Mn alloys. The resistivity at liquid nitrogen temperature was greater than that at room temperature between 6.0 and 14.8 mass%Mn. The Vickers hardness decreased with an increase in the Mn content up to 11.3 mass%Mn and then increased slightly. On aging at 673 K, the isothermal omega phase was precipitated in 6.0 to 11.3 mass%Mn alloys, while it was precipitated by aging at 773 K in 6.0 and 8.7 mass%Mn alloys. The Vickers hardness increased drastically on isothermal omega precipitation, whereas it increased slightly in the case of direct alpha precipitation with no isothermal omega precipitation. [doi:10.2320/matertrans.MA200902]

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1. Introduction

Titanium and its alloys are very attractive metallic materials because they have high specific strengths, excellent corrosion resistances, and good biocompatibilities.1) Although titanium is considered to be a ubiquitous element since it has the 10th-highest Clarke number of all the elements,2) it is actually classified as a rare metal because its current refinement process is more environmentally damaging than the processes used to refine iron and aluminum. Furthermore, the principal alloying elements of titanium alloys are very expensive owing to their low crustal abundances; this is especially true of the beta-stabilizing elements (e.g., V, Mo, Nb, and Ta). Manganese is also considered to be a ubiquitous element since it has the 12th-highest Clarke number of all the elements.2,3) Therefore, manganese is promising as an alloying element for titanium, especially as a beta-stabilizing element.

In order to develop beta titanium alloys as ubiquitous metallic materials, it is very important to investigate the properties of Ti-Mn alloys. A Ti-8.0 mass%Mn α + β alloy has been developed for aeronautical applications, but this alloy has not been used in such applications because of the development of the Ti-6Al-4V alloy, which has superior mechanical properties to the Ti-8.0Mn alloy.3) In order to use Ti-Mn alloys in other applications besides aeronautical applications, such as in general consumer goods (e.g., glass frames and bicycle parts) and healthcare products (e.g., wheel chairs), it is vitally important to investigate the properties of Ti-Mn alloys. No investigation of beta titanium alloys has been attempted for Ti-Mn alloys.

Therefore, as a basic investigation of beta Ti alloys, the influence of manganese contents between about 6 and 15 mass%Mn on the phase constitution and isothermal aging behavior of the solution-treated and quenched (STQ) alloys was investigated by electrical resistivity and Vickers hardness measurements and X-ray diffraction (XRD).

2. Experimental Procedures

Ti-6.0 to 14.8 mass%Mn alloys (hereafter, abbreviated as 6.0Mn, 8.7Mn, 11.3Mn, and 14.8Mn, respectively) were prepared in a laboratory arc furnace under a high-purity argon atmosphere using sponge Ti (99.8%) and Mn flakes (99.9%) as the raw materials. For the 11.3Mn and 14.8Mn alloys, alloys having a Mn content that was 110% of the nominal Mn content (e.g., 13.2 mass%Mn alloy for a nominal composition of 12 mass%Mn) were melted to avoid reducing the Mn content by vaporization of the Mn during arc-melting. Prior to arc-melting, the surface oxide on the Mn flakes was removed by pickling in 1.555 M HNO3. Button-shaped ingots were hot-forged and hot-rolled to approximately 4-mm-thick plates at about 1120 K. Table 1 shows the notation and the chemical compositions of the alloys produced.

The O content was not measured, but it was estimated to be about 0.1 mass% because specimens with oxygen contents of 0.1 mass% or lower were melted in the furnace. Specimens were prepared by cutting, grinding, and polishing the hot-

<table>
<thead>
<tr>
<th>Alloy mark</th>
<th>Chemical composition/mass%</th>
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<tr>
<td>6.0Mn</td>
<td>6.0</td>
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<tr>
<td>8.7Mn</td>
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<td>11.3Mn</td>
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<td>14.8Mn</td>
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rolled plates. They were encapsulated in quartz tubes under a pressure of about 3 mPa, solution-treated at 1173 K for 3.6 ks and quenched in ice water by breaking the quartz tubes. These specimens were isothermally aged at 673 and 773 K.

The electrical resistivity of the specimens was measured at room and liquid-nitrogen temperatures ($\rho_{RT}$ and $\rho_{LN}$, respectively), whereas the Vickers hardness was measured only at room temperature while applying a load of 4.9 N. The phase constitutions of the STQ and aged specimens were determined by XRD. The microstructures of the STQ specimens were characterized by optical microscopy after mechanical polishing followed by etching with a solution of 5%HF, 5%HNO$_3$, and 90%H$_2$O.

3. Results and Discussion

Only the beta phase was identified by XRD in all the STQ alloys except the 6.0Mn alloy. In the 6.0Mn alloy, the reflection of hexagonal close-packed (hcp) martensite, $\alpha'$, was very weak. The XRD results are shown in Fig. 1. Beta equiaxed structures were observed in all the alloys by optical microscopy (Fig. 2). An acicular structure originating from martensite was observed (Fig. 2(b)) in the 6.0Mn alloy in which the hcp martensite reflection was identified. Figure 3 shows the changes in the resistivity at liquid nitrogen and

![Fig. 1 X-ray diffraction profiles of all alloys in the STQ state.](image1)

![Fig. 2 Optical microstructures of all alloys in the STQ state. (b) An acicular structure was partially observed in the 6.0Mn alloy.](image2)
room temperatures (\(\rho_{LN}\) and \(\rho_{RT}\)), the ratio of \(\rho_{LN}\) to \(\rho_{RT}\) (\(\rho_{LN}/\rho_{RT}\)), and the Vickers hardness as a function of the Mn content. \(\rho_{LN}\) increased and reached a maximum at 11.3 mass%Mn before decreasing, whereas \(\rho_{RT}\) decreased to the 8.7Mn alloy and then increased slightly. These resistivity changes are caused by the sum of the two resistivities decreasing with a decrease in the volume fraction of athermal omega and the resistivity increasing with an increase in Mn dissolution into the beta matrix. The change in the resistivity ratio is similar to the change in resistivity at liquid nitrogen temperature. The resistivity ratio \(\frac{\rho_{LN}}{\rho_{RT}}\) indicates the negative temperature dependence of resistivity, which is a very important characteristic of beta Ti alloys. The Vickers hardness decreased up to the 11.3Mn alloy and then increased. The volume fraction of athermal omega in the beta phase decreased with an increase in the Mn content. It is well-known that the hardness of the beta phase decreases with a decrease in the volume fraction of athermal omega.\(^5\)

Generally, the hardness of the beta phase increases with Mn content due to solution hardening. Using the above explanations, the change in the Vickers hardness shown in Fig. 3 is explained next. The decrease in the Vickers hardness of the 11.3Mn alloy is mainly caused by the reduction of the athermal omega in the beta matrix, although the Vickers hardness of the beta matrix increases because of solution hardening of Mn. The increase in the Vickers hardness of the 14.8Mn alloy is caused for the opposite reason to the reduction in the Vickers hardness given in the previous sentence. Figure 4 shows the relationships between the electron/atom ratio (e/a) and the Vickers hardness in four Ti binary alloys.\(^5\)\(^-7\) The maximum hardness occurs at almost the same e/a for each alloy. These e/a values almost coincide with the lower bound of e/a for which the beta phase is fully retained. The retained beta phase and athermal omega were identified at the lower bound of e/a for which the beta phase is fully retained. The alloying element content at which the beta phase and athermal omega were identified and its e/a are respectively 6.0 mass%Mn and 4.16 for Ti-Mn alloys, 6.89 mass%Cr and 4.13 for Ti-Cr alloys, 4.06 mass%Fe and 4.14 for Ti-Fe alloys, and 15.3 mass%V and 4.15 for Ti-V alloys. Although \(\alpha'\) was also identified in the Ti-6Mn alloy, the 6Mn alloy was taken to be the minimum content at which the beta phase and athermal omega were identified because the \(\alpha'\) reflection was very weak. Since the beta phase at these values of e/a is highly unstable, it is conjectured to contain a high volume fraction of athermal omega. The hardness is generally considered to increase with an increase in the volume fraction of athermal omega.\(^8\)

Figure 5 shows the changes in the electrical resistivities at liquid nitrogen and room temperatures, the resistivity ratio, and the Vickers hardness with isothermal aging at 673 K for the (a) 6.0Mn and 8.7Mn, (b) 11.3Mn, and (c) 14.8Mn alloys. For the 6.0Mn to 11.3Mn alloys, the resistivities at both temperatures and the resistivity ratio decrease abruptly at 0.06 ks and the Vickers hardness increases significantly at the same aging time. Subsequently, the resistivity decreases monotonically up to about 120 ks. A second abrupt decrease in the resistivities at both temperatures was observed at 300 ks and the subsequent reduction in the resistivity is monotonic. The resistivity ratio changes in almost the same way as the resistivity at liquid nitrogen temperature. The Vickers hardnesses of the 6.0Mn and 8.7Mn alloys are almost constant up to about 120 ks and they then decrease significantly at 300 ks. In the 11.3Mn alloy, the change in the Vickers hardness was similar to those in the 6.0Mn and 8.7Mn alloys except for the aging time at which a significant reduction in the hardness was observed, which was 600 ks in the case of the 11.3Mn alloy. Figure 6 shows the changes in the XRD profiles on isothermal aging at 673 K in the 6.0Mn, 8.7Mn, 11.3Mn, and 14.8Mn alloys. In Fig. 6(a), the isothermal omega phase was identified at 0.06 ks and 0.12 ks in the 6.0Mn and 8.7Mn alloys, respectively. The precipitated alpha phase was identified at 120 ks. In Fig. 6(b) for the 11.3Mn alloy, the isothermal omega phase was identified

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**Fig. 3** Changes in electrical resistivity at liquid nitrogen and room temperatures (\(\rho_{LN}\) and \(\rho_{RT}\)), resistivity ratio (\(\rho_{LN}/\rho_{RT}\)), and Vickers hardness with Mn content in the STQ state.

**Fig. 4** Change in Vickers hardness of Ti-V,\(^5\) Fe,\(^6\) Cr,\(^7\) and Mn binary alloys as a function of e/a.
at 0.12 ks, and the precipitated alpha phase was identified at 120 ks. The first abrupt reduction in the resistivity and significant increase in the hardness are caused by precipitation of isothermal omega, which was identified by XRD at 0.06 ks in the 6.0Mn alloy and at 0.12 ks in the 8.7Mn (Fig. 6(a)) and 11.3Mn (Fig. 6(b)) alloys. A second abrupt reduction in the resistivity and significant reduction in the hardness are due to alpha precipitation (Figs. 6(a) and (b)). Figure 5(c) shows the changes in the electrical resistivities at liquid nitrogen and room temperatures, the resistivity ratio,
and the Vickers hardness with isothermal aging at 673 K for the 14.8Mn alloy. The incubation period for the resistivity, the resistivity ratio, and the Vickers hardness continued to 120 ks. After 120 ks, the resistivity and the resistivity ratio decreased and the hardness increased. These changes are closely associated with the precipitation of alpha. In Fig. 6(c), the alpha precipitate can be clearly identified from alpha reflections from the 1200 ks aged specimen.

Figure 7 shows the changes in the electrical resistivities at liquid nitrogen and room temperatures, the resistivity ratio, and the Vickers hardness with isothermal aging at 773 K for the (a) 6.0Mn and 8.7Mn, (b) 11.3Mn, and (c) 14.8Mn alloys. For the 6.0Mn and 8.7Mn alloys, the resistivities at both temperatures and the resistivity ratio decreased drastically at 0.06 ks and the Vickers hardness increased significantly at 0.06 ks. Figure 8(a) shows the changes in the XRD profiles with isothermal aging at 773 K in the 6.0Mn and 8.7Mn alloys. Reflections of isothermal omega were observed at 0.06 ks in the 6.0Mn alloy and at 0.12 ks in the 8.7Mn alloy. Precipitated alpha was identified at 0.6 ks in both alloys. These changes are due to isothermal omega precipitation, which was identified by XRD (Fig. 8(a)). A second drastic reduction in the resistivity and the resistivity ratio in 6.0Mn and 8.7Mn appeared at 1.2 and 3 ks, respectively. At these aging times, the Vickers hardness decreased in both alloys. These decreases are caused by precipitation of the alpha phase (Fig. 8(a)). The incubation period for the resistivity, the resistivity ratio, and the Vickers hardness was observed to be 0.3 ks in the 11.3Mn alloy and 3 ks in the 14.8Mn alloy. Subsequently, the resistivity and the resistivity ratio decreased and the hardness increased slightly. Figure 8(b) shows the changes in the XRD profiles with isothermal aging at 773 K in the 11.3Mn and 14.8Mn alloys. Although no isothermal omega phase was identified in either alloy, alpha phase reflections were observed at 3.0 ks in the 11.3Mn alloy and at 12 ks in the 14.8Mn alloy. These changes are caused by alpha precipitation, which was identified by XRD (Fig. 8(b)).

Comparison of the aging behaviors at 673 and 773 K revealed that the maximum Mn content at which isothermal omega precipitation occurs decreases with an increase in the aging temperature. The same results were observed in other beta Ti alloys, such as Ti-Fe and Ti-Cr.10 It is well known that the temperature range of isothermal omega precipitation decreases with an increase in the content of beta stabilizers (i.e., V, Cr, Fe, and Mn).

Figure 9 shows the changes in the phase constitution of Ti-11.3 mass%Mn and Ti-15 mass%Mn alloys caused by isothermal aging at 773 K. The phase constitution was identified by XRD at room temperature. No isothermal omega was identified in the Ti-11.3Mn and Ti-15Cr alloys aged at 773 K, but precipitated alpha was identified at 3.0 ks in the 11.3Mn alloy and at 6.0 ks in the 15Cr alloy. The aging time at which alpha was identified in the 11.3Mn alloy was shorter than that of in the 15Cr alloy (i.e., alpha precipitation occurred faster in the 11.3Mn alloy than in the 15Cr alloy). The mean number of valence electrons per atom, e/a, is 4.30 for the 11.3Mn alloy and 4.28 for the 15Cr alloy. The equivalent Mo contents can be estimated using the formulas 1.25 \times [mass%Mn] and 1.5 \times [mass%Cr]; these give Mo equivalent contents of 19.2 for the 11.3Mn alloy and 18.8 for the 15Cr alloy. The Mo equivalent content and e/a of the 11.3Mn alloy are slightly higher than those of the 15Cr alloy. Using e/a and the Mo equivalent content as beta stability parameters, the beta stability of the Ti-11.3Mn alloy is predicted to be slightly higher than that of the Ti-15Cr alloy. The changes in the phase constitution of the 11.3Mn and 15Cr alloys on aging at 773 K confirm that alpha precipitation occurs earlier in the 11.3Mn alloy than in the 15Cr alloy. This result is inconsistent with the beta stability predicted from e/a and the Mo equivalent content. Next, the diffusion coefficients for Mn and Cr in beta Ti were calculated, since diffusion plays an important role in precipitation. The diffusion coefficients of Cr and Mn due to impurity diffusion in beta Ti at about 900 K are 1.1 \times 10^{-13} and 2.8 \times 10^{-13} m^2 s^{-1}, respectively.11 Since Ti-Mn and Ti-Cr alloys have almost the same e/a and Mo equivalent content, the aging process in both alloys is considered to be controlled by the diffusion coefficient of the solute in beta Ti.
4. Conclusions

The phase constitution and the isothermal aging behavior of Ti-Mn beta alloys were investigated by electrical resistivity and Vickers hardness measurements and XRD. Only the beta phase was identified by XRD in all the alloys except for the 6.0Mn alloy in which hcp martensite was also identified. The resistivity at liquid nitrogen temperature increased with Mn content and reached a maximum in the 11.3 mass%Mn alloy, and subsequently decreased, while the resistivity at room temperature decreased monotonically. The Vickers hardness decreased up to a Mn content of 11.3 mass%Mn and then increased.

When the 6.0Mn to 11.3Mn alloys were aged at 673 K, the resistivities at both temperatures and the resistivity ratio decreased abruptly at 0.06 ks and the Vickers hardness increased significantly at the same aging time. These changes are due to isothermal omega precipitation, as identified by XRD. A second abrupt reduction in the resistivities and the resistivity ratio in the 6.0Mn and 8.7Mn alloys as STQ 0.06ks 0.12ks 0.3ks 0.6ks 1.2ks 3.0ks 6.0ks 12ks 30ks 60ks 11.3Mn 15Cr β β α or α' α β ω α β ω α β ω α β ω α β ω α β ω α β ω

As STQ

0.06ks 0.12ks 0.3ks 0.6ks 1.2ks 3.0ks 6.0ks 12ks 30ks 60ks

11.3Mn 14.8Mn

as STQ

0.06ks 0.12ks 0.3ks 0.6ks 1.2ks 3.0ks 6.0ks 12ks 30ks 60ks

When the 6.0Mn and 8.7Mn alloys were aged at 773 K, the resistivities at both temperatures and the resistivity ratio decreased drastically at 0.06 ks and the Vickers hardness increased significantly at 0.06 ks due to isothermal omega precipitation. A second drastic reduction in the resistivities and the resistivity ratio in the 6.0Mn and 8.7Mn alloys...
appeared respectively at 1.2 and 3 ks due to alpha precipitation. In the 11.3Mn and 14.8Mn alloys, after the incubation period, the resistivities, and the resistivity ratio decreased and the Vickers hardness increased slightly due to alpha precipitation.

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