Surface Hardening Treatment for C.P. Titanium and Titanium Alloys in Use of Ar–5%CO Gas

Y. Z. KIM, T. MURAKAMI, T. NARUSHIMA, Y. IGUCHI and C. OUCHI

1) Graduate Student, Department of Materials Processing, Tohoku University, Sendai 980-8579, Japan. 2) Department of Materials Processing, Tohoku University, Sendai 980-8579, Japan. 3) Tohoku University Biomedical Engineering Research Organization, Sendai 980-8579, Japan.

(Received on March 15, 2006; accepted on June 16, 2006)

Surface hardening of C.P. (commercially pure) titanium and titanium alloys in use of Ar–5%CO gas was investigated in the temperature range between 973 K and 1 123 K. Titanium materials used were α+β type alloy of Ti–4.5%Al–3%V–2%Mo–2%Fe (SP-700) and β type alloy of Ti–15%V–3%Cr–3%Sn–3%Al (Ti-15-333). Oxidation accompanied with surface hardening in use of Ar–5%CO gas is much reduced compared with that of Ar–20%CO2 gas. Surface hardening was evaluated by both of the maximum surface hardness and hardening layer depth obtained from hardness distribution profiles in the subsurface region. The former is the highest in C.P. titanium and the lowest in Ti-15-333 alloy, and the latter is the deepest in Ti-15-333 alloy and the shallowest in C.P. titanium. Surface hardening in C.P. titanium is caused by solid solution hardening of oxygen and carbon enriched in the subsurface region. Enrichment of these interstitials in the subsurface region of SP-700 or Ti-15-333 alloys causes the increase of α volume fraction in α+β two phases or phase transformation from β to α+β two phases, respectively, and surface hardening is primarily controlled by volume fraction of α phase hardened by interstitials enrichment. The other β type titanium alloy of Ti–15%Mo–5%Zr–3%Al yields much marked surface hardening over Ti-15-333 alloy. All of these results were analyzed and discussed based on oxygen and carbon concentration profiles, which were obtained by EPMA, and were also calculated by uni-dimensional diffusion model.

KEY WORDS: C.P. titanium; SP-700 alloy; Ti–15V–3Cr–3Sn–3Al alloy; surface hardening; CO gas; CO2 gas; oxidation; maximum surface hardness; hardening layer depth.

1. Introduction

Currently commercial use of C.P. (commercially pure) titanium and titanium alloys has been expanding from the traditional application fields of aerospace, military or chemical plant to general industry use and consumable goods such as automobile, machinery, sport goods, medical implants and so on. Excellent properties of titanium materials such as high specific strength, superior corrosion resistance or biocompatibility are fully utilized in these applications. However, titanium materials have one weak property that is poor abrasion resistance. In application of titanium alloys to sliding or rotating parts of automobile or machinery, severe adhesive wear or fretting wear occurs.1–3) As an example, engine valves made by titanium alloys cause severe fretting or abrasion wear against a valve seat, and thus any surface hardening treatment on titanium alloys is needed for prevention of abrasion.4,5) In a medical hip-joint application, a semi-spherical head of the artificial bone head made of titanium alloys tends to yield debris due to sliding wear with a cap made of high density plastics.6–8) Very fine titanium wear debris resulting from abrasion has been reported to be possibly detrimental to human body, nevertheless titanium itself has excellent biocompatibility.

Poor abrasion resistant property of titanium materials appears to be inherent characteristics caused by both their thermal properties and surface nature.9,10) Such thermal properties of titanium materials as relatively low thermal conductivity and low volumetric specific heat tend to cause a large and rapid rise of the surface temperature due to adiabatic heat in contacted area and result in sticking between titanium materials and contacting metals or alloys under the condition of high speed rotating or sliding. Dong and Li reported that poor tribological behavior of titanium materials is due to their inherent nature, especially surface nature.10)

Several surface hardening processes or methods for improvement of abrasion resistance of titanium materials have been studied.11–13) These are surface plating such as CrN, plasma spraying, chemical or physical vapor deposition or ion implantation, but most of these processes or methods need to prepare special and expensive equipments and have disadvantages such as relatively high treatment cost and low productivity or a limited total weight or numbers of parts per one batch of treatment. On the other hand, surface hardening treatment in steels has been conducted using various gases, where carbon and nitrogen are primarily used for carburizing or nitriding. Gas process of surface hardening treatment is very advantageous due to relatively low cost and high rate of treatment, treatment-ability of parts with a large mass and complex geometry, easiness of
process, and non-use of special expensive equipments. Similarly to steels, surface hardening treatment in use of various gases is also applicable to titanium materials.\textsuperscript{14–17} The authors studied surface hardening treatment of C.P. titanium and titanium alloys in use of Ar–20%CO$_2$ gas, finding marked surface hardening being obtained. However, relatively high rate of oxidation was accompanied with surface hardening.\textsuperscript{18} It was also made clear that surface hardening due to CO$_2$ gas in C.P. titanium was primarily brought about by solid solution hardening of oxygen and carbon in the subsurface region.

The objective of the present study is to investigate surface hardening and oxidation of C.P. titanium and titanium alloys in use of CO gas, comparing with the results obtained in use of CO$_2$ gas. Materials used were C.P. titanium and $\alpha+\beta$ type titanium alloy of Ti–4.5%V–3%V–2%Mo–2%Fe and two $\beta$ type titanium alloys of Ti–15%V–3%Cr–3%Sn–3%Al and Ti–15%Mo–5%Zr–3%Al. The contents of alloying elements are noted by mass% in all hereafter. First, as a preliminary experiment, the effect of CO gas content in Ar–CO mixed gas on surface hardening and oxidation rate was investigated, and such an optimum CO gas content as to minimize oxidation and to achieve the high surface hardening was determined. Then, surface hardening was conducted by heating various titanium materials in the temperature range between 973 K and 1,123 K using the optimum mixed gas, Ar–5%CO. Surface hardening was evaluated by the maximum surface hardness and hardening layer depth obtained from hardness distribution profile. Surface hardness distribution profiles were analyzed and discussed based on oxygen and carbon concentration profiles obtained by EPMA as well as variations of the microstructure in the subsurface region. Concentration profiles of these interstitials in $\alpha$ and $\beta$ phases were also calculated based on uni-dimensional diffusion model, and these were compared with observed surface hardening profiles.

2. Experimental

The chemical composition of C.P. titanium and titanium alloys used in this study is listed in Table 1. Titanium materials used mainly were $\alpha+\beta$ type alloy of Ti–4.5%Al–3%V–2%Mo–2%Fe and $\beta$ type alloy of Ti–15%V–3%Al–3%Cr–3%Sn. These alloys are noted by mass% in all hereafter as SP-700 and Ti-15-333, respectively. Ti–15%Mo–5%Zr–3%Al alloy was used to find any difference of surface hardening or oxidation behavior in the $\beta$ type titanium alloys. All of these titanium materials were supplied with commercial sheet products with a thickness of 4 mm. These sheets were cold rolled to 2 mm thick, and numerous coupon specimens with a size of $10^3\times10^3\times2^T$ mm, where $L$, $B$ and $T$ are the length, the width and the thickness, respectively, were prepared from these sheets. Subsequently, specimens of SP-700 and Ti-15-333 alloys were subjected to recrystallization annealing and solution treatment at 1,073 K for 7.2 ks and 0.9 ks, respectively, and C.P. titanium specimen was subjected directly to surface hardening treatment without preliminary annealing. Specimens were surface-polished and were acid-pickled by a solution containing 2% HF and 13% HNO$_3$ just before surface hardening treatment. The size of a respective specimen was measured for evaluation of surface area.

Surface hardening treatment as well as measurement of mass gain in the specimen during heating was conducted using a vertical electric resistance furnace with a quartz glass tube. An electric balance was set up at the top of the quartz glass tube which was surrounded by movable heating furnace. The specimen was hanged from the bottom of the electric balance and was set in the quartz glass tube. At first, Ar gas was flowed into the tube, and the furnace heated up to the specified temperature was moved up to the upper side. When the specimen was heated to this temperature, flowing gas was changed to mixed gas of Ar and CO. The amount of CO flowing gas in Ar–CO mixed gas was varied from 5 to 20% in flow rate. The amount of a respective flowing gas was set up by a gas flow controller. After heating for a given heating time period, the furnace was moved down to the bottom side, and the specimen was cooled. The heating temperature was varied in the range from 973 to 1,123 K, and the heating time period was 21.6 ks. Variation of mass gain in the specimen during heating was continuously and digitally recorded in a personal computer.

The specimen subjected by surface hardening was halved and the cross section in the thickness direction was polished, and then the microstructure was observed by optical microscopy and scanning electron microscopy (SEM). The etching solution used for microstructural observation contained 2% HF and 13% HNO$_3$. Measurement of microhardness distribution profile in the subsurface region of the specimen was conducted using a micro Vickers hardness tester (Akashi Corp., HM-102) with a load of 10 g. Surface hardening was evaluated by the maximum surface hardness and hardening layer depth that was the distance from the surface to the location with hardness value showing the same one with the base material. Oxygen and carbon concentration profiles in surface hardening layer were analyzed by EPMA (JEOL, JXA-8100).

<table>
<thead>
<tr>
<th>type</th>
<th>Alloys</th>
<th>Ti</th>
<th>H</th>
<th>O</th>
<th>N</th>
<th>C</th>
<th>Fe</th>
<th>Sn</th>
<th>Al</th>
<th>V</th>
<th>Cr</th>
<th>Mo</th>
<th>Zr</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha$</td>
<td>C.P. titanium</td>
<td>Bal.</td>
<td>0.15</td>
<td>0.01</td>
<td>—</td>
<td>0.07</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>$\alpha+\beta$</td>
<td>Ti–4.5Al–3V–2Mo–2Fe (SP–700)</td>
<td>Bal.</td>
<td>0.03</td>
<td>0.11</td>
<td>0.01</td>
<td>2.00</td>
<td>4.42</td>
<td>3.06</td>
<td>—</td>
<td>2.05</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>$\beta$</td>
<td>Ti–15V–3Cr–3Sn–3Al</td>
<td>Bal.</td>
<td>0.01</td>
<td>0.11</td>
<td>0.098</td>
<td>0.01</td>
<td>0.203</td>
<td>3.18</td>
<td>3.23</td>
<td>15.57</td>
<td>3.08</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Ti–15Mo–5Zr–3Al</td>
<td>Bal.</td>
<td>0.01</td>
<td>0.12</td>
<td>0.005</td>
<td>0.01</td>
<td>0.03</td>
<td>3.03</td>
<td>—</td>
<td>—</td>
<td>14.93</td>
<td>5.02</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

© 2006 ISIJ
3. Results

3.1. Effect of CO Content in Ar–CO Mixed Gas on Surface Hardening and Oxidation

As CO gas is an oxidizing gas to titanium materials, surface hardening in use of Ar–CO mixed gas is accompanied with oxidation. High oxidation rate not only reduces the surface hardening layer depth, but also increases material loss. Thus, the effect of mixed gas ratio of CO/Ar on oxidation and surface hardening in C.P. titanium was first examined, and CO gas contents in Ar–CO mixed gas were varied from 5 to 20% under the constant gas flow rate of 300 cc/min. Figure 1 shows variation of mass gain with the heating time up to 21.6 ks at 1073 K under Ar–5, 10 and 20%CO gases. The higher CO gas content yields higher mass gain. Mass gain measured by an electric balance possibly contains not only mass of oxide or carbide layer formed on the surface, but also mass gain brought about by increase of the amounts of oxygen or carbon in the subsurface layer. A liner relationship was observed between mass gain and oxide film thickness obtained by surface hardening experiment at various heating temperatures, being found that the mass gain by the enrichment of oxygen and carbon in the subsurface region was much less than that by the formation of oxide. The oxide layer thickness continuously increases with the increase of CO gas content, and its thickness values after heating at 1073 K for 21.6 ks under Ar–5, 10 and 20%CO gases were 1.8, 5.6 and 9.2 µm, respectively. Figure 2 shows hardness distribution profiles in the subsurface region of C.P. titanium obtained by heating at 1073 K for 21.6 ks. Although difference in hardness distribution profiles among three levels of CO content is a little, Ar–5%CO gas yields the highest surface hardness value. The thinner oxide layer in addition of deeper hardening layer and the higher maximum surface hardness are favorable to surface hardening treatment, and thus, Ar–5%CO gas was determined as the best mixed gas used for surface hardening treatment of titanium materials. Similar experiment was conducted on the amount of total gas flow rate, which was varied in the range from 100 to 1000 cc/min. Total gas flow rate of 300 cc/min was found to be the best condition from both results of the surface hardness distribution profile and the oxide layer thickness. Consequently, all surface hardening experiments described in the following were performed by Ar–5%CO gas with a total gas flow rate of 300 cc/min.

Ar–20%CO2 gas used in the previous study by the authors18) was determined as the best CO2 gas content in Ar–CO2 mixed gas based on similar experiments to the present case. Thus, mass gain and the oxide layer thickness in C.P. titanium were compared between Ar–20%CO2 and Ar–5%CO gases. Variations of mass gain or the oxide layer thickness with the heating temperature under a fixed heating time of 21.6 ks are compared between both gases in Figure 3. It is found that surface hardening in use of Ar–5%CO gas results in markedly reduced mass gain or the oxide layer thickness compared with the use of Ar–20%CO2 gas. Variations of the oxide layer thickness with the heating temperature in C.P. titanium, SP-700 and Ti-15-333 alloys are shown for both cases of Ar–5%CO and Ar–20%CO2 gases in Figures 4(a) and 4(b), respectively. Fairly excellent correlation between the absolute temperature and the logarithmic scale of the oxide layer thickness is found. In Ar–5%CO gas, the oxide layer thickness of SP-700 alloy is slightly thicker over C.P. titanium, and Ti-15-333 alloy
yields the thickest oxide layer. On the other hand, Ar–20%CO₂ gas yields much thicker oxide layer in all titanium materials compared with Ar–5%CO gas, and in particular, oxidation in C.P. titanium is the most marked among three titanium materials. Consequently, Ar–5%CO gas is much suitable for surface hardening of titanium materials compared with Ar–20%CO₂ gas.

3.2. Surface Hardening of C.P. Titanium and Titanium Alloys in Use of Ar–5%CO Gas

Figure 5 shows the effect of the heating temperature on hardness distribution profiles in C.P. titanium. The heating time period at a respective temperature was 21.6 ks. The maximum surface hardness continuously increases from 410 to 920 with the increase of temperature from 973 to 1123 K, and hardening layer depth also increases from 30 to 130 μm in this temperature range. Hardness distribution profiles obtained by heating at various temperatures for 21.6 ks in SP-700 and Ti-15-333 alloys are shown in Figs. 6 and 7, respectively. The maximum surface hardness obtained by heating at the temperature from 973 to 1123 K increases from 520 to 700 in SP-700 alloy and 440 to 550 in Ti-15-333 alloy. On the other hand, hardening layer depth with an elevation of the heating temperature in SP-700 and Ti-15-333 alloys increases from 30 to 250 μm and from 100 to 350 μm, respectively.

Variations of the maximum surface hardness and hardening layer depth with the heating temperature under the heating time of 21.6 ks in three titanium materials are summarized in Figs. 8(a) and 8(b), respectively. It is found that the maximum surface hardness is the highest in C.P. titanium, then SP-700 alloy and the lowest in Ti-15-333 alloy, while hardening layer depth is the shallowest in C.P. titanium and
the deepest in Ti-15-333 alloy, SP-700 alloy being the mid-
dle of them.

Ti-15-333 alloy showed the highest rate of oxidation and
the lowest ranked maximum surface hardness among three
titanium materials in Ar–5%CO gas atmosphere, and en-
hanced oxidation is possibly caused by high vanadium con-
tent of this alloy. Thus, surface hardening and oxidation of
the other β type alloy of Ti–15%Mo–5%Zr–3%Al was in-
vestigated. Hardness distribution profile of this alloy sub-
jected to surfaced hardening at 1 073 K for 21.6 ks in
Ar–5%CO gas is also shown in Fig. 7. It is found that very
high hardness in surface and subsurface region can be
obtained in Ti–15%Mo–5%Zr–3%Al alloy compared with Ti-
15-333 alloy, although hardening layer depth is almost
same in both alloys. The oxide layer thickness was
markedly reduced down to 0.5 μm in this alloy, while that
of Ti-15-333 alloy was 10.3 μm under the same treating
condition. This result indicates importance of retardation of
oxidation rate to obtain the higher maximum surface hard-
ness.

3.3. Microstructures in Subsurface Regions of Sur-
faced-hardened C.P. Titanium and Titanium Alloys

The microstructures of the subsurface regions in surface-
hardened C.P. titanium and titanium alloys were observed
by optical microscopy and SEM. Figures 9(a) and 9(b)
show the optical and scanning electron micrographs in the
subsurface region surface of C.P. titanium heated at
1 123 K for 21.6 ks in Ar–5%CO.

Fig. 9. (a) optical and (b) scanning electron micrographs in the subsurface region surface of C.P. titanium heated at
1 123 K for 21.6 ks in Ar–5%CO.
due to surface hardening treatment yields a continuous variation of the microstructure from β phase in base alloy to α+β two phases or acicular α phase in the subsurface region as shown in Figs. 11(a), 11(b) and 11(c). SEM observation of the microstructure in the subsurface region of Ti–15Mo–5Zr–3Al alloy is shown in Fig. 12. The microstructure in the subsurface region is consisted of finely laminated α+β two-phases, and β grain observed in the inward region and the matrix is much finer than that of Ti-15-333 alloy. Because of higher oxidation resistance of this alloy over Ti-15-333 alloy, the surface region with the highest hardness appears to be reserved without suffering oxidation during surface hardening treatment, which evolves different microstructure just below the surface from that of Ti-15-333 alloy.

4. Discussion

4.1. Mechanism of Surface Hardening of C.P. Titanium and Titanium Alloys in Use of Ar–5%CO Gas

Surface hardening in use of Ar–5%CO gas yielded very low rate of oxidation in C.P. titanium and titanium alloys compared with Ar–20%CO₂ gas, resulting in marked surface hardening, in particular in C.P. titanium. Surface hardening in C.P. titanium is caused by solid solution hardening of oxygen and carbon, which are enriched in the subsurface region through the following steps. Dissociation of CO gas
into atomic oxygen and carbon first occurs on the surface of the oxide layer, and then these interstitials diffuse into the subsurface region through the oxide layer. As diffusion of these elements in the oxide layer is much faster than that in the matrix, concentration profiles of these elements in the subsurface region are controlled by diffusion in the latter. The concentration profiles of Ti, O and C examined by EPMA in the specimen subjected to surface hardening at 1123 K for 21.6 ks are shown in Fig. 13. It is found that oxygen concentration continuously decreases from the location just below thin oxide layer to the depth over 150 μm. The oxygen concentration near the surface almost coincides with solubility of oxygen in α phase of 13.5%, although it includes somewhat oxygen content of the oxide layer with thickness of about 5 μm. The carbon concentration profile shows a sharp peak just below oxide layer. This carbon peak is yielded by a thin layer of TiC phase formed in the subsurface region just below oxide layer, which was confirmed by XRD analysis shown in Fig. 14. The surface of the same specimen as that in Fig. 13 was polished through several steps with measuring specimen thickness precisely, and XRD analysis was conducted after each step of polishing. The oxide layer is confirmed to be rutile from the XRD pattern of the specimen with the oxide layer, and it disappears after polishing by 7 μm thick. The carbide phase of TiC is detected after polishing off by 7 and 11 μm thick, and the peak of this phase disappears after polishing by 25 μm thick. Consequently, both results shown in Figs. 9 and 14 indicate formation of very thin layer of TiC in the subsurface just below oxide layer. As the solubility of carbon in α phase is 0.4%, the carbon concentration profile below TiC phase shows the continuous decrease of carbon content from this value toward carbon content of C.P. titanium, extending to the depth over 150 μm as seen in Fig. 13.

Surface hardening mechanism of titanium alloys is not so simple as that of C.P. titanium, because of occurrence of the microstructural variations accompanied with the increase of contents of interstitials in the subsurface region. Formation of TiC in addition of the oxide layer was also confirmed in both SP-700 and Ti-15-3-333 alloys by XRD analysis. Both oxygen and carbon diffuse into α + β or β phase matrix in a respective alloy, and these α stabilizing elements cause the phase transformation or the increase of α volume fraction during heating in Ar–5%CO gas. The oxygen and carbon contents in α phase are much higher compared with those in β phase, and hardening of α phase due to interstitials is much larger than that of β phase. Therefore, surface hardening profiles in α + β or β type titanium alloys are mostly controlled by α volume fraction in a respective location of subsurface region. An important observation in these changes of microstructure was difference of morphology of α phase formed with the increase of α volume fraction between SP-700 and Ti-15-333 alloys. The former
keeps equi-axis $\alpha$ in two phases microstructure, and the latter exhibited acicular $\alpha$ and grain boundary $\alpha$.

Importance of retardation of oxidation rate to obtain high maximum surface hardness was confirmed by comparison of hardness distribution profiles obtained by two kinds of $\beta$ type titanium alloys shown in Fig. 7. The present study made clear that this could be achieved by selection of an appropriate surface hardening gas species, optimization of its content in mixed gas and also selection of titanium alloy with oxidation resistance against to gas species used for surface hardening.

### 4.2. Analysis of Surface Hardening Profiles Based on Oxygen and Carbon Diffusion into Titanium Materials

Detail analysis of surface hardening with the increase of oxygen or carbon concentration in $\alpha$ or $\beta$ titanium is to report in the other paper by the authors, and here surface hardness distribution profiles and hardening layer depth are analyzed and discussed by uni-dimensional diffusion model based on Fick’s second law shown in the following.

\[
C(x,t) = C_s \text{erfc} \left( \frac{x}{2\sqrt{Dt}} \right)
\]

where $x$ is the distance from the surface just below the oxide layer, $t$ is the time, $C(x,t)$ is the concentration at the time of $t$ and at the distance of $x$ from the surface, $C_s$ is the concentration in the surface, which is assumed to be solubility of oxygen or carbon in $\alpha$ or $\beta$ phase, and $D$ is the diffusion coefficient. Boundary conditions at $t=0$, $C(0, t) = C_s$ and $C(x, 0) = 0$ are.

$C_s$ values in $\alpha$ and $\beta$ phases have tiny temperature dependence in the temperature range investigated, and so $C_s$ values of oxygen and carbon used are 13.5% and 0.4% in $\alpha$ phase, and 3.0% and 0.2% in $\beta$ phase, respectively. Temperature dependence of diffusion coefficients of both interstitials is shown in Fig. 15. It is found that interstitials in $\beta$ phase diffuse much faster than those in $\alpha$ phase, and the diffusion coefficient of carbon is almost 2 orders of magnitude larger than that of oxygen in a respective phase.

The calculated oxygen and carbon concentration profiles in $\alpha$ and $\beta$ phases at the temperatures from 973 to 1 123 K for 21.6 ks are shown in Figs. 16(a) to 16(d). The increase of the temperature continuously extends profiles to the inward direction in all cases, and diffusion depth of a respective element in a respective phase widely changes depending on their diffusion coefficient values. Figure 17 shows comparison of the oxygen concentration profile obtained by EPMA in C.P. titanium subjected to surface hardening at 1073 K for 21.6 ks and the oxygen profile calculated under the same condition shown in Fig. 16(a), and both are well fitted except the most near region to the surface. Surface hardness distribution profile obtained under this condition is also shown in this figure. The shape of both profiles is evidently almost same and hardening layer depth is at a glance similar to that obtained from oxygen concentration profile.
Hardening layer depth, however, is different between measured and calculated values, when hardening layer depth in the calculated oxygen profile is determined as the position of oxygen content of C.P. titanium with 0.15%, which is an initial oxygen content in the C.P. titanium as shown in Table 1. Figure 18 shows comparison of temperature dependence of measured and calculated values of hardening layer depth in C.P. titanium. The former values are higher than the latter, and difference of both values expands with the increase of temperature. This difference between both values appears to be caused by contribution of carbon to surface hardening. Much deeper diffusion of carbon over oxygen is evident from comparison of Figs. 16(a) and 16(b). The solubility of carbon in α phase is very limited, but solid solution hardening of carbon is relatively high compared with that of oxygen.  

While the maximum surface hardness obtained in titanium alloys investigated in this study was lower compared with C.P. titanium, values of the hardening layer depth in alloys were much higher than those of C.P. titanium, in particular in β type Ti-15-333 alloy as shown in Fig. 8(b). Although this result is easily understood from very high diffusivity of interstitials in β phase, hardening layer depth obtained from the calculated oxygen or carbon concentration profile shown in Figs. 16(c) and 16(d) became to be much deeper over by ten times compared with observed one in β type titanium alloy shown in Fig. 8(b). Phase transformation in the subsurface region never occurs during surface hardening in α phase of C.P. titanium, but in β type alloy, the transformation from β to α+β or α phase takes place depending on concentration of interstitials in a respective location of the subsurface region. These variations of volume fractions or phase transformation occurs due to diffusion of not only interstitials but also substitutional elements such as V, Cr or Al contained in alloys, and the latter diffusion rate is 2 or 3 orders of magnitude slower than the former. As a result, surface hardening layer depth obtained in β type or α+β type titanium alloys is controlled by phase transformation kinetics or variation of α volume fraction rather than diffusion of interstitials, and so observed hardening layer depth becomes much shallower compared with calculated one based on simple consideration of diffusion of interstitials in β phase.

5. Conclusion

Surface hardening in C.P. titanium, α+β type Ti-4.5%V–3%Al–2%Fe–2%Mo (SP-700) alloy and β type Ti-15%V–3%Al–3%Cr–3%Sn (Ti-15-333) alloy in use of Ar–5%CO gas was studied in the temperature range between 973 and 1123 K. The following results were obtained.

(1) Oxidation accompanied with surface hardening in Ar–5%CO gas is markedly reduced in all titanium materials compared with Ar–20%CO2 gas, and very thin TiC phase is detected to be formed just below the oxide layer.

(2) The maximum surface hardness is the highest in C.P. titanium and is the lowest is in Ti-15-333 alloys. On the other hand, the hardening layer depth is the deepest in Ti-15-333 alloy and is the shallowest in C.P. titanium.

(3) Surface hardening in C.P. titanium is yielded by solid solution hardening of both interstitials of oxygen and carbon, and the latter with higher diffusivity also contributes to extend hardening layer depth.

(4) Enrichment of these interstitials in the subsurface region in SP-700 alloy or Ti-15-333 alloy causes the increase of α volume fraction or phase transformation from β phase to α+β two phases, respectively, and surface hardening in these alloys is primarily controlled by the volume fraction of α phase hardened by enriched interstitials.

(5) Analysis based on oxygen or carbon concentration profiles calculated by uni-dimensional diffusion model shows that hardness distribution profile of C.P. titanium can be estimated mostly by diffusion of oxygen under a minor consideration of carbon diffusion, and that hardness distribution profiles of titanium alloys are controlled by phase transformation kinetics rather than interstitial diffusion itself.

(6) The other β type titanium alloy of Ti–15%Mo–5%Zr–3%Al yields marked surface hardening over Ti-15-333 alloy, confirming importance of retardation of oxida-
tion rate to achieve higher surface hardness.

REFERENCES