

Surface Hardening Treatment for Titanium Materials Using Ar-5% CO Gas in Combination with Post Heat Treatment under Vacuum*¹

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Surface hardening using solute oxygen formed by the dissociation of titanium oxide (TiO₂) layer on commercially pure (C.P.) titanium, $\alpha + \beta$ type Ti-4.5Al-3V-2Fe-2Mo (SP-700) alloy, and β type Ti-15Mo-5Zr-3Al (Ti-15-53) alloy was investigated. This method consists of two steps: surface hardening using Ar-5%CO gas for a short time period and subsequent heat treatment under vacuum. Both treatments were carried out at 1073 K. The maximum surface hardness and hardening layer depth for C.P. titanium obtained by surface hardening in Ar-5%CO gas for 1.8 ks were 420 Hv and 30 μ m, respectively. After post heat treatment for 14.4 ks, these values increased to 820 Hv and 70 μ m, respectively. The increase of surface hardening achieved by post heat treatment was yielded by solid solution hardening of oxygen via the following steps. Solute oxygen was continuously formed at the oxide layer/titanium interface by the dissociation of the oxide layer formed during surface hardening treatment. Oxygen then diffused into titanium matrix, which resulted in solid solution hardening. The highest and lowest values of the maximum surface hardness were obtained in C.P. titanium and Ti-15-53 alloy, respectively. On the other hand, the hardening layer depth was largest for Ti-15-53 alloy and smallest for C.P. titanium. These results can be explained by the differences in solubility and diffusivity of oxygen between the titanium α phase and β phase. This two-step process appears to be a beneficial industrial surface hardening method for titanium materials because it enables the removal of the oxide layer while yielding surface hardness comparable to that obtained by the one-step process under the same total heat-treating time. [doi:10.2320/matertrans.MA200911]

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1. Introduction

Titanium materials have many advantageous properties over other metallic materials, such as low density, high corrosion resistance, high specific strength, and biocompatibility, and a wide variety of mechanical properties can be given to titanium materials by the microstructural control using thermomechanical treatments. Because of these advantages, titanium and its alloys have been employed in the aerospace and military industry and chemical plants, and their applications have been extended, for example, to buildings, sporting goods, and medical implants. However, compared to other metallic materials, titanium materials are known to have poor wear resistance, which is attributed to their inherent physical and chemical properties.¹⁻⁴⁾ In addition, they have a strong tendency to seize because of their thermal properties such as low thermal conductivity and low volumetric specific heat.⁵⁾ Therefore, improvement of wear-resistant property in titanium materials is essentially needed, when they are used for sliding and rotating parts in machinery, automobiles, or medical implants.

Since the microstructure in titanium materials is in general designed to so as to give rise to mechanical properties suitable to specified applications, the improvement in wear resistance via surface hardening treatment is needed to perform without the microstructural change.

Surface hardening treatment of titanium materials has been carried out by various processes based on physical, chemical, thermal or thermochemical techniques.⁶⁾ Surface hardening methods using carbon and nitrogen have been widely employed in the steel industry as represented by surface carburization and nitridation. Titanium is known as an active metallic material that has high chemical affinity with various interstitial elements. On the other hand, both α and β phases in titanium have large solubility for such interstitial elements as carbon, nitrogen, and oxygen as well as high solid solution hardening due to these elements, and thus surface hardening treatment using these elements appears to be reasonable for titanium materials.⁷⁻¹⁵⁾ Many processes are available to penetrate carbon, nitrogen, and oxygen into titanium materials for surface hardening. Surface hardening using gases is very advantageous because of the relatively low cost and high rate of treatment, the possibility to treat parts with the large mass and complex geometry, easy treatment, and the non-necessity to use the specific and expensive equipment.

The authors have studied the surface hardening of α type, $\alpha + \beta$ type, and β type titanium materials using Ar-20%CO₂ gas or Ar-5%CO gas.¹³⁻¹⁵⁾ A hardening layer caused by the interstitial solid solution of oxygen and carbon is formed on the surface of titanium materials by these treatments in the temperature range of 973 K to 1123 K, and the effects of various process conditions on the maximum surface hardness and hardening layer depth have been elucidated in both Ar-20%CO₂ gas and Ar-5%CO gas atmospheres. However, the formation of titanium oxide layer could not be avoided in either atmosphere even under a lower oxygen potential condition using Ar-5%CO gas. Usually, the titanium oxide layer is removed by shot blasting or chemical pickling treatment. Post heat treatment under vacuum is a potential technique for achieving extra solid solution hardening of oxygen supplied by the dissociation and simultaneous

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Table 1 Chemical compositions of C.P. titanium and titanium alloys used in this study (mass%).

Type	Alloy	Ti	H	O	N	C	Fe	Al	V	Mo	Zr
α	C.P. Ti	Bal.	—	0.15	0.01	—	0.07	—	—	—	—
$\alpha + \beta$	Ti-4.5Al-3V-2Fe-2Mo (SP-700)	Bal.	0.03	0.11	0.01	—	2.00	4.42	3.06	2.05	—
β	Ti-15Mo-5Zr-3Al (Ti-15-53)	Bal.	0.01	0.12	0.005	0.01	0.03	3.03	—	14.93	5.02

removal of the titanium oxide layer. Dong and Li⁴⁾ reported the formation of a surface hardening layer with a depth of 300 μm after post heat treatment under vacuum at 1123 K, for which the solute oxygen was supplied from the titanium oxide layer formed by air oxidation. However, they did not discuss the removal of the titanium oxide layer.

In this study, the post heat treatment of α type, $\alpha + \beta$ type, and β type titanium materials under vacuum at 1073 K after surface hardening treatment in Ar-5%CO gas was investigated, and the optimum conditions for the post heat treatment to yield further solid solution hardening and to remove fully the oxide layer were evaluated.

2. Experimental

The chemical compositions of commercially pure titanium (JIS Gr. 2), $\alpha + \beta$ type Ti-4.5Al-3V-2Fe-2Mo alloy, and β type Ti-15Mo-5Zr-3Al alloy used in this study are listed in Table 1. These titanium materials are hereafter referred to as C.P. titanium, SP-700 alloy, and Ti-15-53 alloy, as noted in the alloy column of Table 1. The contents of alloying elements are hereafter expressed as percentage masses. All titanium materials were supplied as commercial sheet products with a thickness of 4 mm. These sheets were cold-rolled to a thickness of 2 mm, and $10^L \times 10^B \times 2^T$ mm specimens were prepared from these sheets. Subsequently, specimens of SP-700 and Ti-15-53 alloys were subjected to recrystallization annealing and solution treatment at 1073 K for 7.2 ks and 0.9 ks, respectively, followed by air cooling. The C.P. titanium specimen was subjected directly to surface hardening treatment without preliminary annealing. The specimen surface was wet-polished using emery papers up to #1500, buff-polished with alumina powder having a diameter of 0.3 μm , and cleaned ultrasonically in acetone. The specimens were then acid-pickled by an aqueous solution containing 1% HF and 14% HNO_3 just before surface hardening treatment and finally cleaned ultrasonically in ethanol.

The surface hardening method proposed in this study consists of two steps: (1) surface hardening treatment resulting in the formation of thin oxide layer in Ar-5%CO gas and (2) post heat treatment under vacuum for additional surface hardening by dissociation of the thin oxide layer formed in the first step and introduction of solute oxygen into the titanium matrix. Hereafter, the first step in Ar-5%CO gas is referred to as surface hardening treatment and the second step under vacuum is referred to as post heat treatment.

The surface hardening treatment in Ar-5%CO gas was carried out at 1073 K for a heating time period of 1.8–21.6 ks. Details of the surface hardening treatment in Ar-5%CO gas have been reported elsewhere.¹⁵⁾ After the surface hardening

treatment, the flow of Ar-5%CO gas was stopped and the post heat treatment was continuously carried out under vacuum (total gas pressure: 10^{-3} Pa) without cooling the specimens. The post heat treatment was carried out at 1073 K for a heating time period of 7.2–43.2 ks, followed by air cooling.

The specimen subjected to surface hardening treatment or post heat treatment was halved and the cross section in the thickness direction was polished for microstructural observation and measurement of the hardness distribution profile. The microstructure was observed using a scanning electron microscope (XL-30FEG, Philips) after etching of the cross section using an aqueous solution containing 1% HF and 14% HNO_3 . The hardness distribution profile in the subsurface region of the specimen was measured using a micro Vickers hardness tester (HM-102, Akashi Corp.) with a load of 10 gf. The hardness distribution profiles were obtained by the measurement of the hardness in 10 μm span in the range from the unaffected part of the base material to the surface of the specimen or the oxide layer/titanium interface. The maximum surface hardness and hardening layer depth, which was the distance from the surface of the specimen or the oxide layer/titanium interface to the location that had the same hardness value as that of the base material, were evaluated using the hardness distribution profiles.¹⁵⁾ The surface products formed by the treatments were identified by X-ray diffraction (XRD, X'Pert, Philips).

3. Results

The hardness distribution profiles after surface hardening treatment in Ar-5%CO gas were first evaluated. Figure 1 shows hardness distribution profiles of C.P. titanium after surface hardening treatment in Ar-5%CO gas at 1073 K. The maximum surface hardness increased from 420 to 830 Hv with an increase in the heating time period from 1.8 to 21.6 ks, and the hardening layer depth also increased from 30 to 100 μm . Figure 2 shows the maximum surface hardness and hardening layer depth of the C.P. titanium, SP-700 alloy, and Ti-15-53 alloy after surface hardening treatment in Ar-5%CO. Both the maximum surface hardness and the hardening layer depth increased with an increase in the heating period for all titanium materials. Thin oxide layer, which was identified as the rutile-type TiO_2 by XRD, was observed on the surface of the titanium materials. The titanium carbide phase was also detected by XRD on the surface after surface hardening treatment in Ar-5%CO at 1073 K for 21.6 ks but not after surface hardening treatment for 1.8 ks, because of the small amount of the titanium carbide phase. Figure 3 shows the cross sectional appearance of the C.P. titanium after surface hardening treatment in Ar-5%CO at 1073 K for 7.2 ks. The formation of surface oxide layer with a thickness

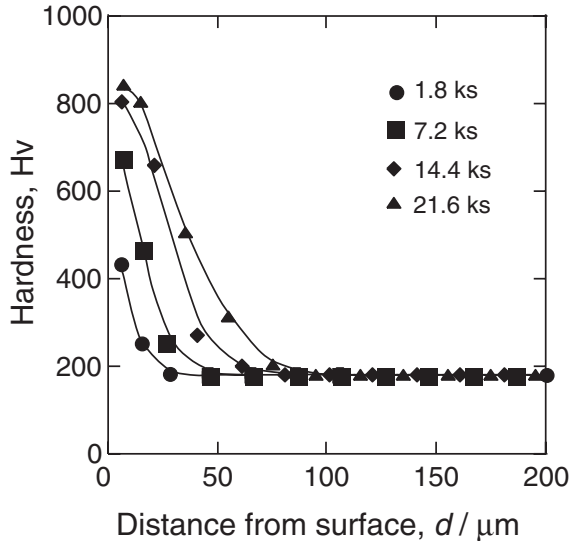


Fig. 1 Hardness distribution profiles of C.P. titanium surface-hardened in Ar-5%CO at 1073 K.

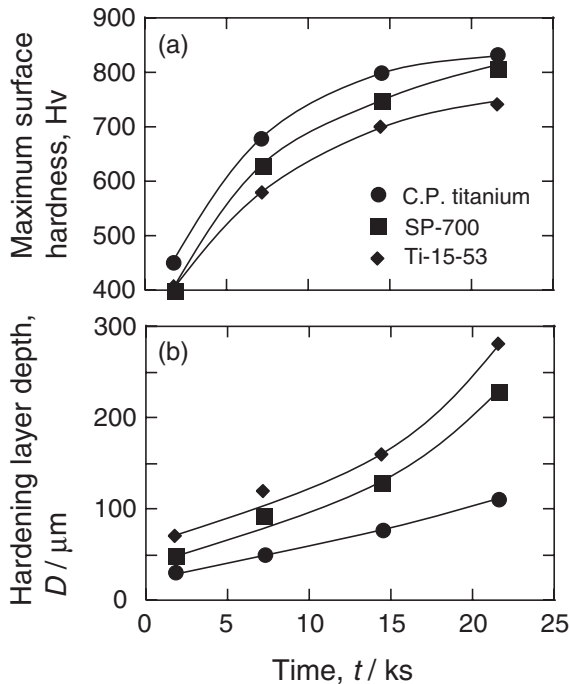


Fig. 2 Variations in (a) maximum surface hardness and (b) hardening layer thickness with heating time period in Ar-5%CO at 1073 K.

of $0.8\ \mu\text{m}$ was observed. Table 2 summarizes the thicknesses of the oxide layers formed on C.P. titanium, SP-700 alloy, and Ti-15-53 alloy by the surface hardening treatment in Ar-5%CO at 1073 K. The thickness of the oxide layer increased with an increase in the heating time period of the surface hardening treatment, and the oxide (TiO_2) layer was the thickest on C.P. titanium and the thinnest on Ti-15-53 alloy under the same surface hardening treatment conditions. Since this study focused on the removal of the oxide layer by post heat treatment under vacuum, the specimens subjected to surface hardening treatment for 1.8 ks, resulting in the formation of thin oxide layer, were mainly used for the post heat treatment. The specimens subjected to surface hardening

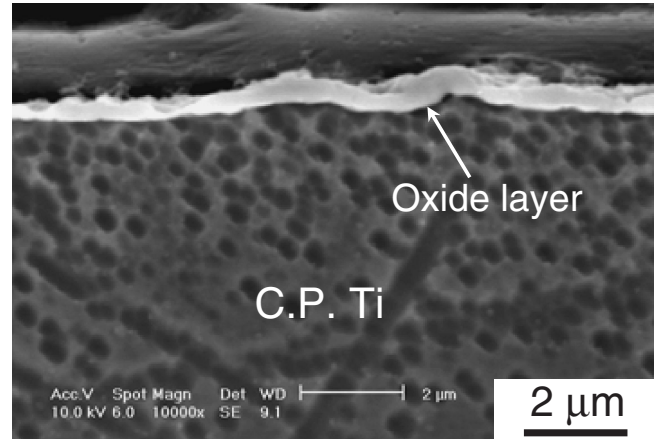


Fig. 3 Scanning electron micrograph of the surface layer of C.P. titanium after surface hardening treatment in Ar-5%CO at 1073 K for 7.2 ks.

Table 2 A variation of oxide layer thickness with heating time period at 1073 K in three kinds of titanium materials.

Time (ks)	Oxide layer thickness (μm)		
	C.P. titanium	SP-700	Ti-15-53
1.8	0.5	0.2	0.2
7.2	0.8	0.4	0.2

treatment for 7.2 ks were used to investigate the effect of the heating time period on the hardening behavior obtained by the post heat treatment.

The hardness distribution profiles of C.P. titanium, SP-700 alloy, and Ti-15-53 alloy after post heat treatment are shown in Figs. 4, 5, and 6, respectively. The maximum surface hardness and the hardness layer depth of the titanium materials can be evaluated using the hardness distribution profiles. Figures 7 and 8 show the variations in the maximum surface hardness and the hardness layer depth of the titanium materials with the heating time period of the post heat treatment at 1073 K after surface hardening treatments in Ar-5%CO at 1073 K for 1.8 ks and 7.2 ks, respectively. As shown in Fig. 7(a), the maximum surface hardness of C.P. titanium increased with an increase in the heating time period of the post heat treatment up to 28.8 ks, whereas the maximum surface hardness of the SP-700 alloy or Ti-15-53 alloy did not clearly increase after post heat treatment for 7.2 ks. On the other hand, the hardness layer depths of all the titanium materials increased as the heating time period in the post heat treatments extended. In the case of the post heat treatment after the 7.2 ks surface hardening treatment, both increases in the maximum surface hardness and the hardening layer depth were observed with an extension in the heating time period of the post heat treatment (Fig. 8).

Figures 9(a), (b), and (c) show the cross sectional appearances of C.P. titanium after surface hardening treatment in Ar-5%CO at 1073 K for 1.8 ks and post heat treatment for 7.2 ks and 14.4 ks, respectively. The thickness of the oxide layer formed during the surface hardening treatment, around $0.5\ \mu\text{m}$, decreased after post heat treatment for 7.2 ks, and no oxide layer was observed after the heating time of 14.4 ks (Fig. 9(c)). Figure 10 shows the cross

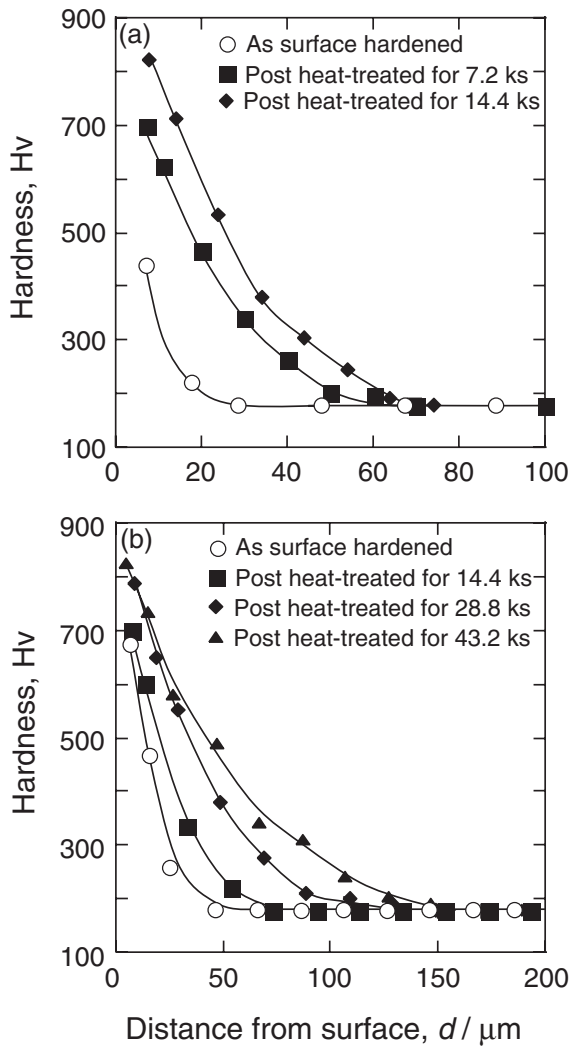


Fig. 4 The effect of post heat treatment at 1073 K on hardness distribution profiles in C.P. titanium after surface hardening treatment in Ar-5%CO at 1073 K for (a) 1.8 ks and (b) 7.2 ks.

sectional appearances of SP-700 alloy before and after post heat treatment for 7.2 ks. The oxide layer observed with a thickness of around $0.2\ \mu\text{m}$ in Fig. 10(a) appears to have been removed by the post heat treatment, as shown in Fig. 10(b). Figures 10(b1) and (b2) show the microstructure with higher magnification in locations indicated in Fig. 10(b). The dark and bright areas in these figures correspond to the α phase and β phase, respectively, and the latter mainly consists of the residual β phase.¹⁶⁾ The α volume fraction increased continuously toward the surface in the subsurface region as shown in Figs. 10(b1) and (b2). This appears to be yielded by the enrichment of oxygen, because oxygen is an α stabilizing element and the increase of its content increases the volume fraction of the α phase in the $\alpha + \beta$ type alloy. In Fig. 5(b), the hardness distribution profiles of SP-700 after post heat treatment show convex shape around at a distance from surface of $60\ \mu\text{m}$. The fine two-phase microstructure, which becomes remarkable in the region with a distance from surface larger than $50\ \mu\text{m}$, might cause the convex shape in the hardness distribution profiles. Figures 11(a) and (b) show the cross sections of the Ti-15-53 alloy after 1.8 ks surface hardening treatment and 7.2 ks post heat treatment, respec-

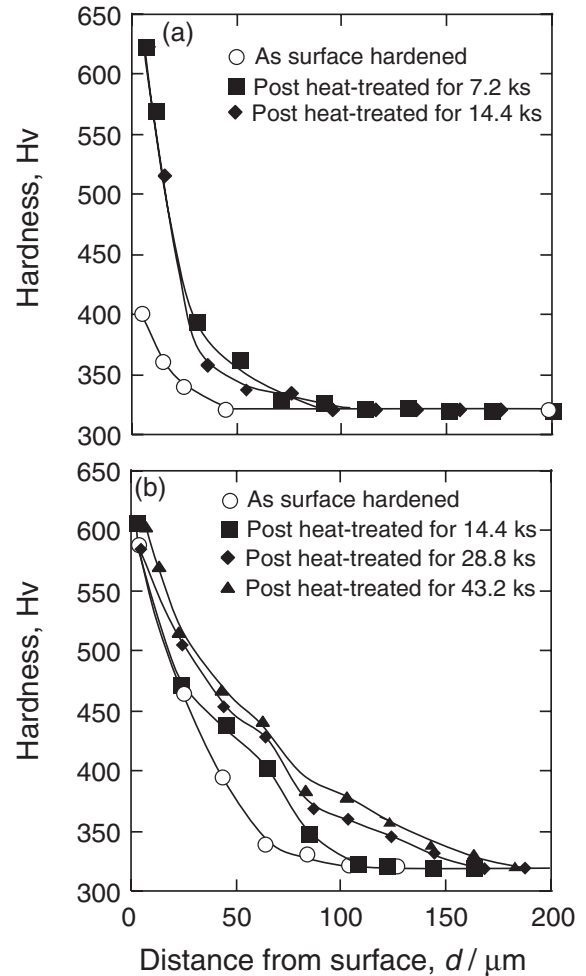


Fig. 5 The effect of post heat treatment at 1073 K on hardness distribution profiles in SP-700 alloy after surface hardening treatment in Ar-5%CO at 1073 K for (a) 1.8 ks and (b) 7.2 ks.

tively. Figures 11(b1) and (b2) show the microstructure of subsurface regions indicated by circles in Fig. 11(b). The increase in the oxygen content in the subsurface region due to surface hardening treatment yielded a continuous variation in the microstructure from the β phase in the base alloy to a finely laminated $\alpha + \beta$ two-phase. The full removal of the oxide layer was confirmed after the 7.2 ks post heat treatment, and the same was observed in the case of the SP-700 alloy.

The oxide layers on C.P. titanium, SP-700 alloy, and Ti-15-53 alloy formed during surface hardening treatment in Ar-5%CO gas at 1073 K for 1.8 ks were fully removed by the post heat treatment under vacuum at 1073 K for 14.4 ks, 7.2 ks, and 7.2 ks, respectively. When surface hardening treatment in Ar-5%CO gas was conducted at 1073 K for 7.2 ks, the time period in the post heat treatment needed for fully removal of the oxide layer were 28.8 ks, 14.4 ks, and 14.4 ks in C.P. titanium, SP-700 alloy, and Ti-15-53 alloy, respectively.

4. Discussion

4.1 Removal of oxide layer by post heat treatment

Post heat treatment under vacuum was found to be effective for enhancement of the surface hardness in titanium

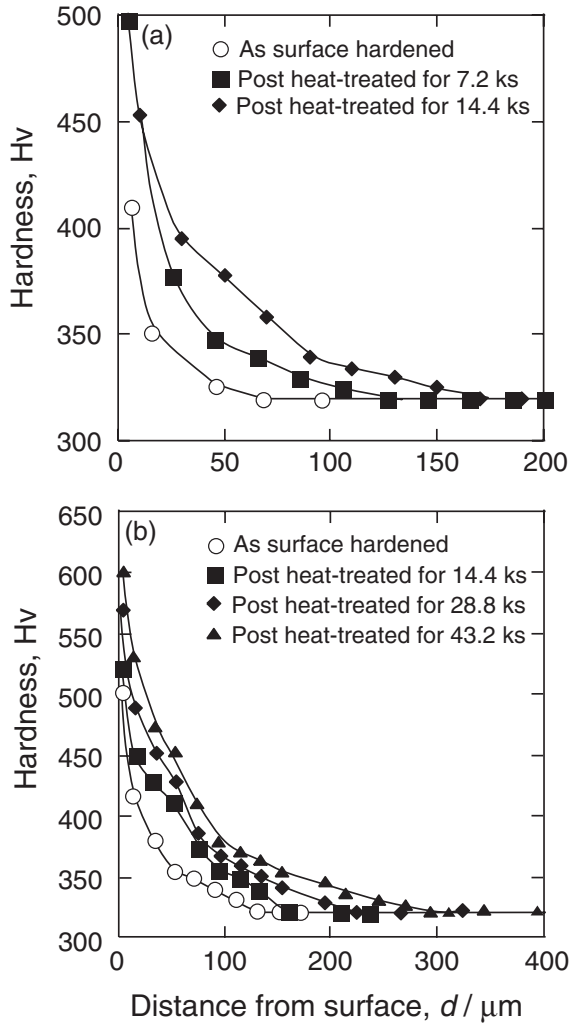
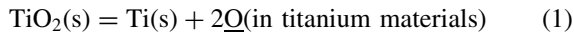


Fig. 6 The effect of post heat treatment at 1073 K on hardness distribution profiles in Ti-15-53 alloy after surface hardening treatment in Ar-5%CO at 1073 K for (a) 1.8 ks and (b) 7.2 ks.

materials subjected to surface hardening treatment in Ar-5%CO gas. During the post heat treatment, the oxide layer formed in the surface hardening treatment is decomposed and removed in the overall reaction represented by eq. (1).⁴⁾



The oxygen atoms formed by eq. (1) diffuse from the oxide layer/titanium interface into the titanium matrix and dissolve in mainly the α phase in titanium materials, resulting in an additional surface hardening and thinner oxide layer. Titanium carbide has been reported to form during hardening treatment in Ar-5%CO gas.¹⁵⁾ However, the effect of titanium carbide on the hardening behavior during post heat treatment is considered to be negligibly small because its formation was such a tiny amount to detect by XRD analysis. Therefore, it is likely that the hardness profile in the subsurface region obtained after post heat treatment is governed by both the solid solution hardening of oxygen and the microstructural change accompanying with the oxygen dissolution.

Figures 12(a) and (b) show the variations in the hardness of C.P. titanium (α type) with the addition of oxygen and carbon contents, respectively. C.P. titanium button ingots with different oxygen or carbon contents were prepared by

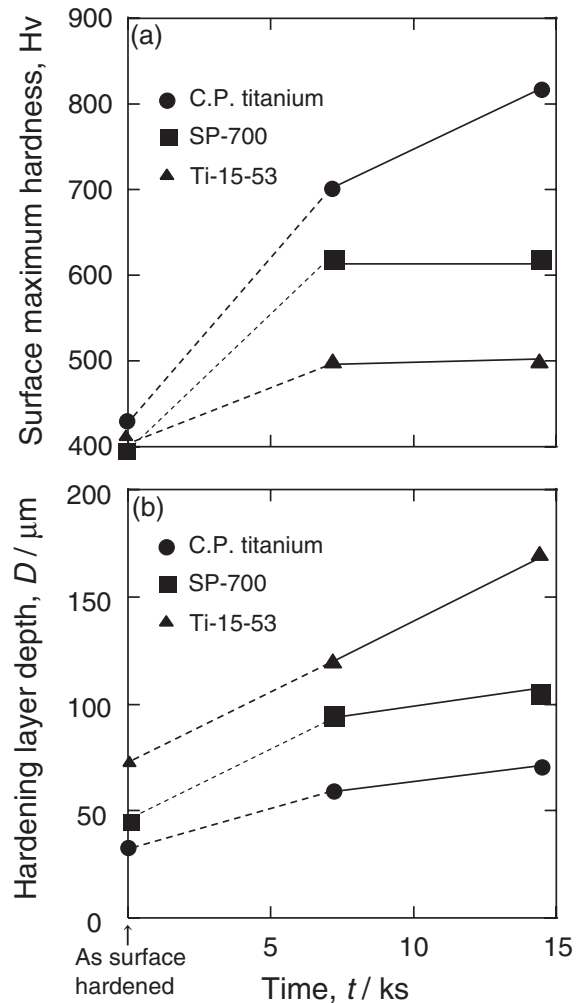


Fig. 7 Variations in (a) maximum surface hardness and (b) hardening layer depth with heating time period at 1073 K. Surface hardening was carried out in Ar-5%CO at 1073 K for 1.8 ks.

Ar-arc melting. Sheets with a thickness of 2 mm were obtained from the button ingots by two-step hot rolling at the heating temperatures of 1373 K and 1123 K, and then hot-rolled sheets were heat-treated at 1023 K to 1123 K for 3.6 ks, followed by air cooling. The hardness of the sheet specimens was measured with a load of 10 gf. A variation of the heating temperature or α grain size was found to exert a tiny effect on hardness in comparison with the effect of interstitial contents. It is confirmed that the oxygen content in the titanium α phase with high oxygen solubility primarily governs the hardness of titanium materials, and so, post heat treatment that can supply the solute oxygen to the titanium matrix via the dissociation of the oxide layer is an effective surface hardening method.

From the results in hardness distribution after post heat treatment, the order of the maximum surface hardness was C.P. titanium > SP-700 > Ti-15-53, and that of the hardening layer depth was Ti-15-53 > SP-700 > C.P. titanium, as summarized in Figs. 7 and 8, respectively. The maximum surface hardness increases with increasing α volume fraction in titanium because the oxygen solubility in α phase is much larger than that in β phase. On the other hand, the diffusivity of oxygen in titanium materials is closely related to the

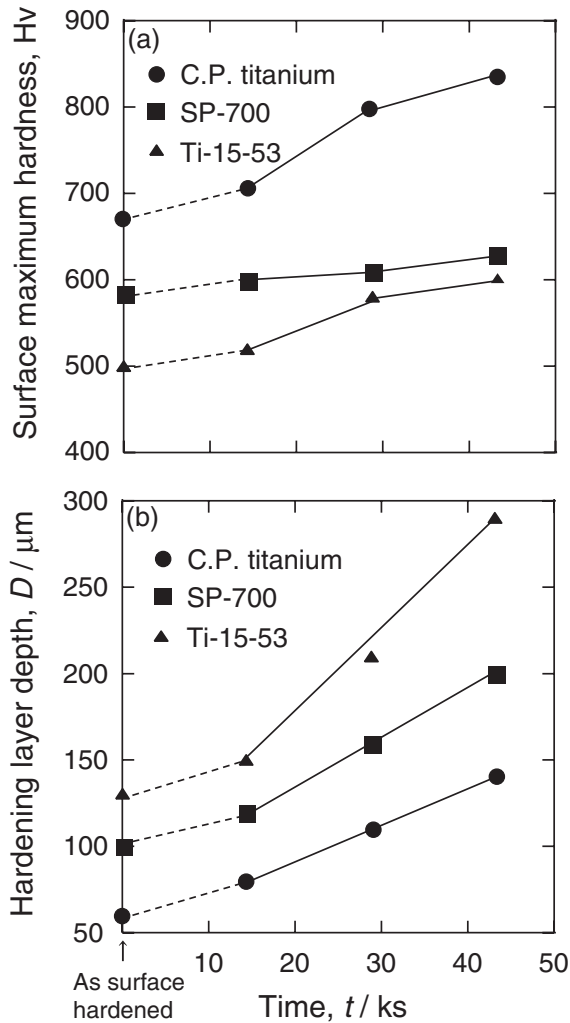


Fig. 8 Variations in (a) maximum surface hardness and (b) hardening layer depth with heating time period at 1073 K. Surface hardening was carried out in Ar-5%CO at 1073 K for 7.2 ks.

hardening layer depth. The diffusion coefficients of oxygen in the titanium α and β phases at the heating temperature of 1073 K have been reported to be $1.1 \times 10^{-14} \text{ m}^2 \cdot \text{s}^{-1}$ and $2.6 \times 10^{-12} \text{ m}^2 \cdot \text{s}^{-1}$, respectively.^{17,18)} Since the diffusion coefficient of oxygen in the titanium β phase is two orders of magnitude larger than that in the α phase, the hardening layer depth increases with increasing β volume fraction in titanium.

4.2 Effect of post heat treatment on surface hardening

In this study, it was confirmed the oxide layer on titanium materials was dissociated, and the most appropriate post heat treatment condition for the complete removal of the oxide layer depended on the thickness of the oxide layer. The maximum surface hardness and the hardening layer depth of C.P. titanium surface-hardened in Ar-5%CO gas at 1073 K for 21.6 ks were 830 Hv and 100 μm , respectively (see Fig. 2). On the other hand, a maximum surface hardness of 820 Hv and a hardening layer depth of 70 μm were obtained by combining the surface hardening in Ar-5%CO gas at 1073 K for 1.8 ks and post heat treatment at 1073 K for 14.4 ks. Under the condition of the same total heat treating time, the two-step process yielded maximum surface hard-

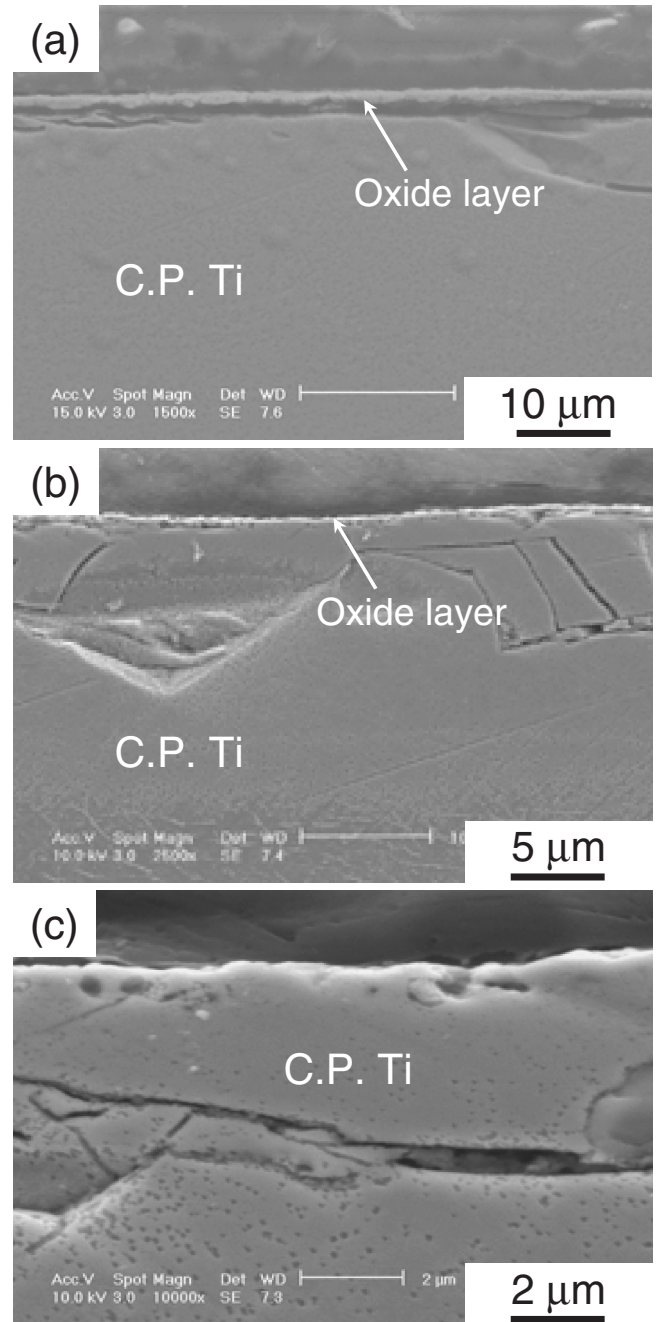


Fig. 9 Scanning electron micrographs in the surface region of C.P. titanium: (a) as surface-hardened in Ar-5%CO at 1073 K for 1.8 ks and after post heat treatment at 1073 K for (b) 7.2 ks and (c) 14.4 ks.

ness and hardening layer depth similar to the corresponding values obtained by the one-step surface hardening treatment. The two-step process that can remove the oxide layer on the titanium surface appears to be an effective industrial hardening method for titanium materials.

It was observed that an extension of a post heat treatment time period did not increase the maximum surface hardening for titanium alloys with high oxidation resistance or after short surface hardening treatment time (e.g. 1.8 ks). In these cases, a very thin oxide layer was formed (Fig. 7), and so the removal of the oxide layer completed during a relatively short post heat treating time period. That is, exhaust of an oxygen supplying source terminates the extra

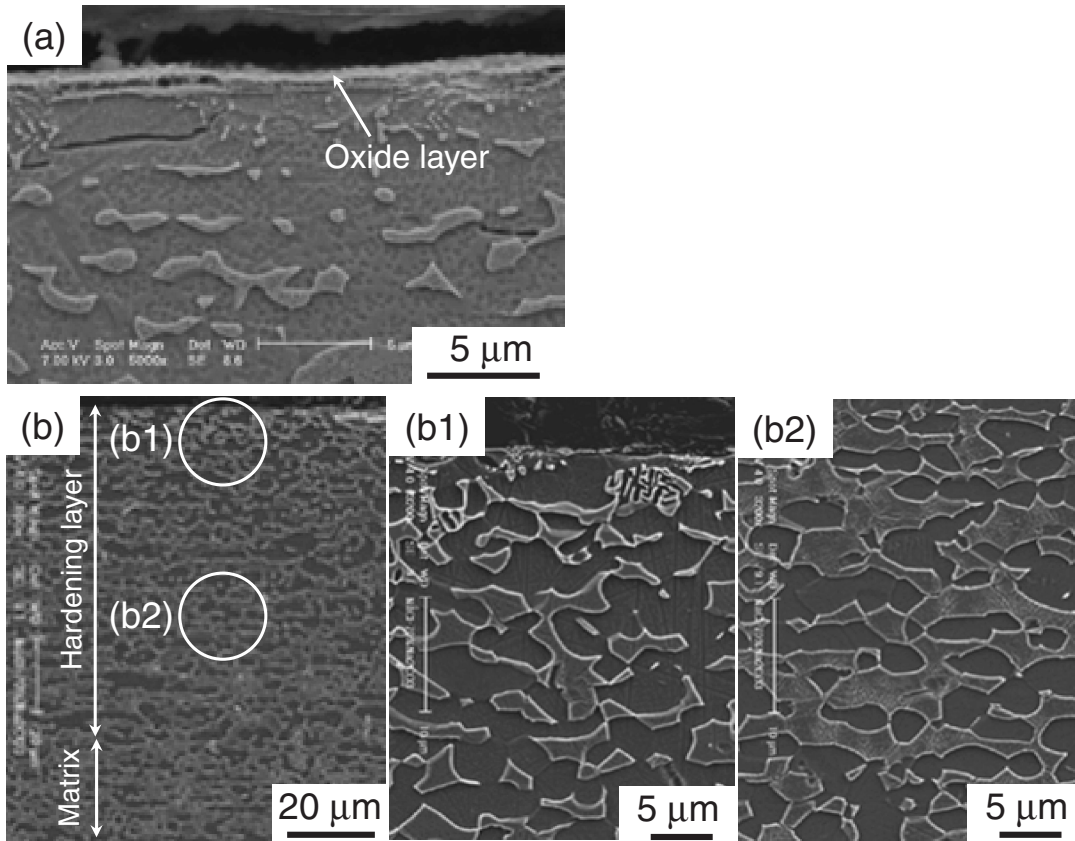


Fig. 10 Scanning electron micrographs in the surface region of SP-700: (a) as surface-hardened in Ar-5%CO at 1073 K for 1.8 ks and (b) after post heat treatment at 1073 K for 7.2 ks. (b1) and (b2) show the higher magnification images of the areas circled in (b).

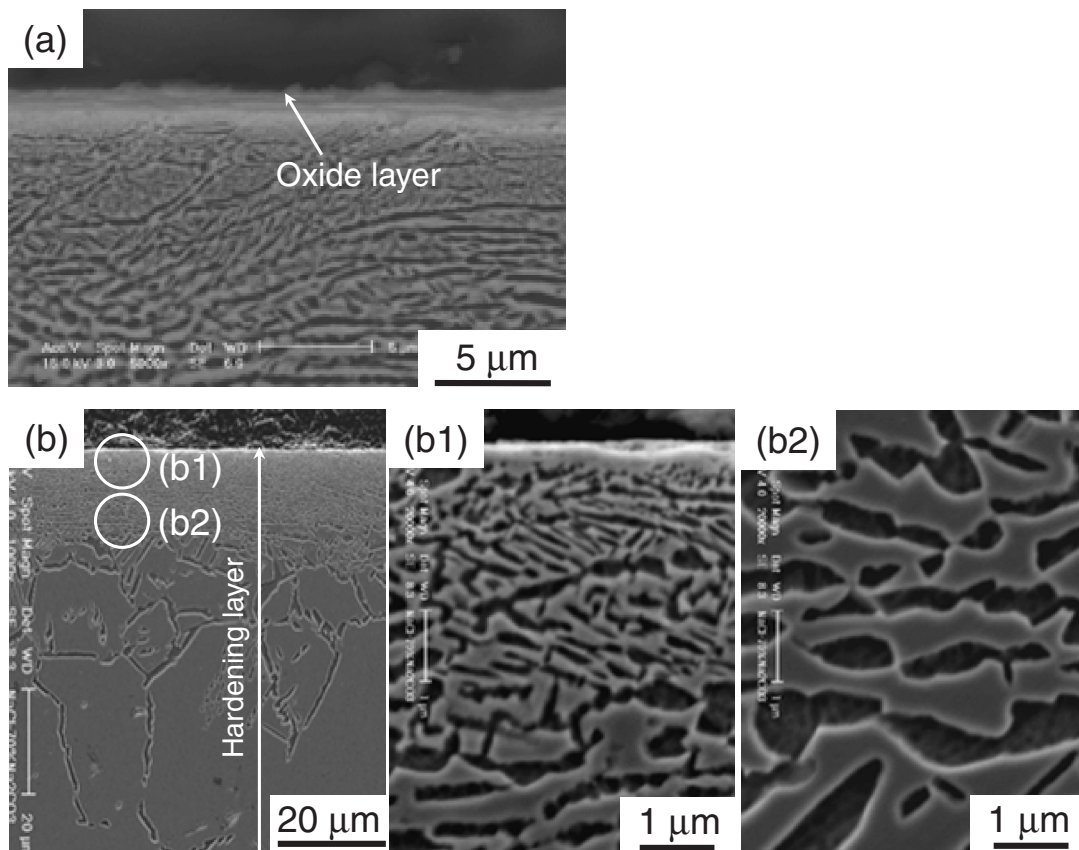


Fig. 11 Scanning electron micrographs in the surface region of Ti-15-53: (a) as surface-hardened in Ar-5%CO at 1073 K for 1.8 ks and (b) after post heat treatment at 1073 K for 7.2 ks. (b1) and (b2) show the higher magnification images of the areas circled in (b).

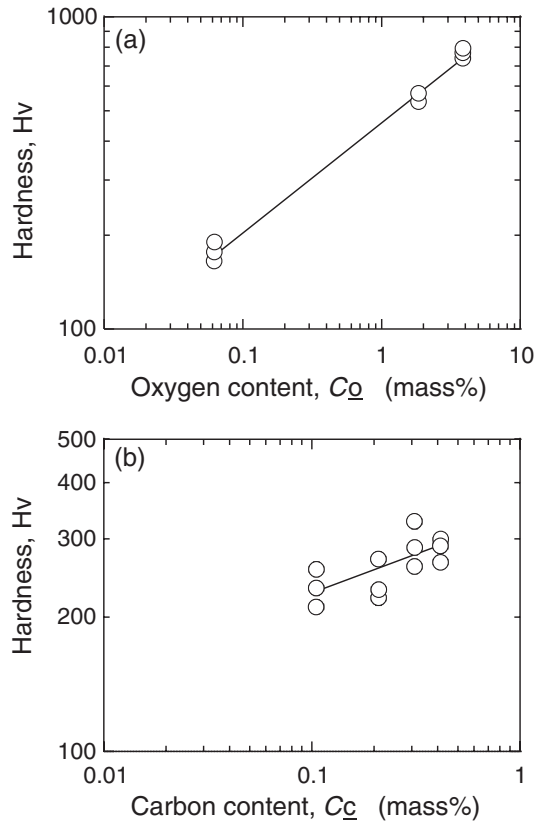


Fig. 12 Variations in Vickers hardness with contents of (a) oxygen and (b) carbon in C.P. titanium.

surface hardening occurring during an extended post heat treating time period. When the post heat treatment continued after the removal of the oxide layer, the maximum surface hardness decreased while the hardening layer depth increased.

A large hardening layer depth in addition to high maximum surface hardness is often required for the application of titanium materials.^{4,19)} For such applications, the desired surface hardening can be achieved by optimizing both conditions for surface hardening treatment and subsequent post heat treatment.

4.3 Heating time period required for complete removal of oxide layer in post heat treatment

The heating time period in post heat treatment required for complete removal of oxide (TiO_2) layer formed on C.P. titanium was estimated using a one-dimensional semi-infinite diffusion model based on Fick's second law.¹⁵⁾ It was assumed that the dissociation of TiO_2 at the interface between the oxide layer and titanium to form oxygen atoms is sufficiently fast and that the diffusion of oxygen in titanium is the rate-controlling step. The change in the position of the oxide layer/titanium interface with the progress of dissociation of the oxide layer was ignored because the oxide layer thickness was much smaller than the hardening layer depth. Figure 13 shows a variation of the calculated thickness values of oxide layer removed with the heating time in post heat treatment. The calculation was conducted for a specimen after surface hardening treatment in Ar-5%CO gas at 1073 K for 1.8 ks. The thickness of the removed oxide layer was

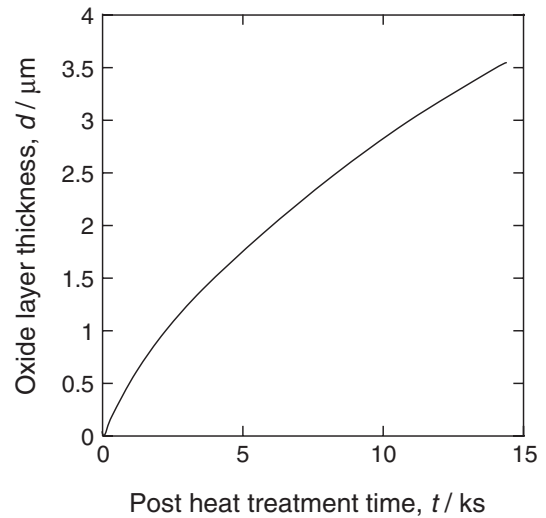


Fig. 13 A variation in calculated values of oxide layer thickness reduced by dissociation at the oxide/titanium interface with the heating time period at 1073 K in post heat treatment of C.P. titanium.

calculated from the difference in oxygen concentration profiles of the subsurface region before and after post heat treatment at 1073 K. The oxygen concentration at the oxide layer/titanium interface and the diffusion coefficient of oxygen in α titanium were set as 13.5 mass% and $1.1 \times 10^{-14} \text{ m}^2 \cdot \text{s}^{-1}$, respectively, in this calculation. It is predicted from this figure that the oxide layer with a thickness of $1 \mu\text{m}$ can be removed within post heat treating time for 3.6 ks. However, experimental results showed that post heat treatment for 14.4 ks and 28.8 ks were needed for full removal of the oxide layers with thicknesses of $0.5 \mu\text{m}$ and $0.8 \mu\text{m}$, respectively. The reason for this discrepancy between calculated and experimental results might be the oxidation of titanium by oxygen impurities in the vacuum atmosphere of the post heat treatment with a total gas pressure of 10^{-3} Pa .

5. Conclusions

Additional surface hardening and removal of oxide (TiO_2) layer of titanium materials taking place during post heat treatments under vacuum were investigated. Post heat treatment was carried out at 1073 K for various heating time periods for C.P. titanium, Ti-4.5Al-3V-2Fe-Mo (SP-700) alloy, and Ti-15Mo-5Zr-3Al (Ti-15-53) alloy subjected to surface hardening treatment in Ar-5%CO gas at 1073 K for 1.8 ks or 7.2 ks. The following results were obtained.

(1) Post heat treatment resulted in both increases in the maximum surface hardness and the hardening layer depth for all three titanium materials. The maximum surface hardness was higher in the order of C.P. titanium > SP-700 alloy > Ti-15-53 alloy, while the hardening layer depth was larger in the order of Ti-15-53 alloy > SP-700 alloy > C.P. titanium.

(2) The increases in the maximum surface hardness and the hardening layer depth were caused by the solid solution hardening of oxygen supplied from the dissociation of oxide layer and the microstructural change in the surface layer accompanying with the increase of solute oxygen content.

(3) The oxide layers on titanium materials formed during the surface hardening treatment at 1073 K for 1.8 ks and 7.2 ks were fully removed by the post heat treatment under vacuum at 1073 K. After the complete removal of the oxide layer, there was no clear increase in the maximum surface hardness.

(4) The experimental heating time period required for removal of the oxide layer was longer than that of calculated one, which was performed by assuming that the diffusion of oxygen into titanium was the rate-controlling step. It was suggested that this discrepancy was caused by the oxidation of titanium by oxygen impurities in the vacuum atmosphere of the post heat treatment.

(5) The two-step process appears to be a beneficial industrial surface hardening method for titanium materials because it enables the removal of the oxide layer while yielding almost the same value of surface hardening as that obtained by one-step surface hardening under the same total heat treating time.

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