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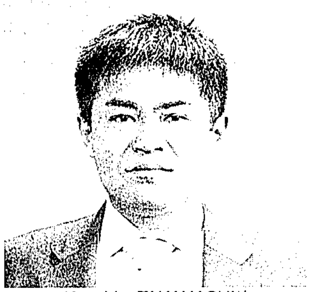
Effect of Heating Atmosphere on Hardening Layer in Hot Rolled Strip of Ti-15V-3Cr-3Sn-3Al



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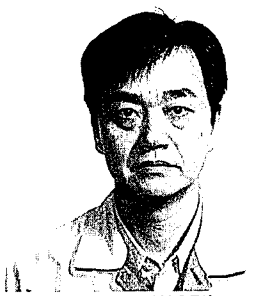

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Abstract

Since beta alloys that possess higher hot deformation resistance than commercially pure titanium are heated at higher temperatures in hot rolling, they harden remarkably by oxidation. The hard layers that remain at surfaces after hot rolling often lower cold workability. The authors have evaluated the effects of heating atmospheres on the depth of harden layers using as heated and commercially hot rolled samples of beta alloy Ti-15V-3Cr-3Sn-3Al. As a result, the depths of hard layers formed at approximately 1,000℃ heating are 500micro meters in air and 150micro meters in nitrogen gas. In addition the hardness decreases in the latter case. In commercially hot rolling the samples heated in a combustion gas and induction heated in nitrogen gas show the hard layer depths of 90micro meters and less than 40micro meters respectively. In this case the effect of heating atmosphere on the hard layer depth is also confirmed.

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1. Introduction

When titanium is exposed to a high-temperature oxidizing atmosphere, it forms easy-to-peel scale on its surface and a thick subsurface hardened layer where oxygen is dissolved[1]. During hot rolling, titanium alloys of high deformation resistance are heated to higher temperatures than commercially pure titanium, so that they are markedly hardened by oxidation. Especially, the beta titanium alloy Ti-15V-3Cr-3Sn-3Al (hereinafter abbreviated to Ti-15-3) contains a large amount of vanadium, which is known to accelerate oxidation[2,3]. When the surface is acid pickled to remove the scale after hot rolling, the hardened layer sometimes remains to diminish the cold workability of the Ti-15-3 alloy. This study comparatively evaluated the effects of heating atmospheres, particularly a nitrogen gas atmosphere, on the hardened layer depth of the Ti-15-3 alloy in the as-heated condition and in the condition of strip hot rolled on a mill at the Hirohata Works of Nippon Steel. The study results are reported here.

2. Experimental Methods

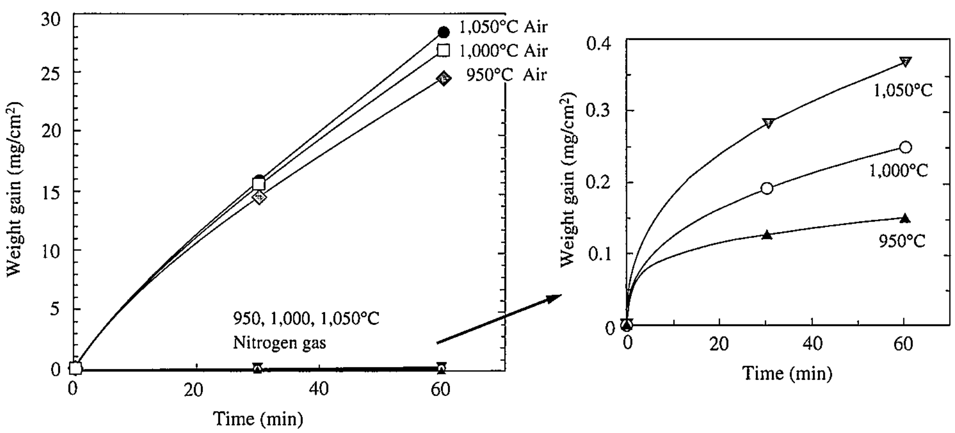
To investigate the effect of heating on the formation of the hardened layer, specimens of acid-pickled Ti-15-3 ally sheet (1.7 mm thick × 50 mm wide × 50 mm long) were held in air or nitrogen gas at 950, 1,000, or 1,050°C for 30 or 60 min. The heating-induced weight gain of the specimens was measured, and the depth of the hardened layer was evaluated according to their subsurface cross-sectional Vickers microhardness distribution. The phases formed in the surface of some specimens during heating were also identified by X-ray diffraction.

To evaluate the effect of nitrogen gas atmosphere heating on hot-rolled strip, a 125-mm thick Ti-15-3 alloy slab was heated in a conventional combustion gas atmosphere or induction heated in a nitrogen gas atmosphere, and was hot rolled to strip with a thickness of 4.6 mm at the mill. The hardened layer depth (Vickers microhardness), and the subsurface oxygen, nitrogen and carbon concentration distributions as determined by glow discharge optical emission spectroscopy (GDS) was compared. The nitrogen concentration was also determined after descaling.

3. Experimental Results and Discussion

3.1 Formation of hardened layer by heating

Fig. 1 shows the heating-induced weight gain of the specimens.



(a) Heating in air and nitrogen gas (b) Enlarged view of curves for heating in nitrogen gas

Fig. 1 Weight gain from heating in air and nitrogen gas

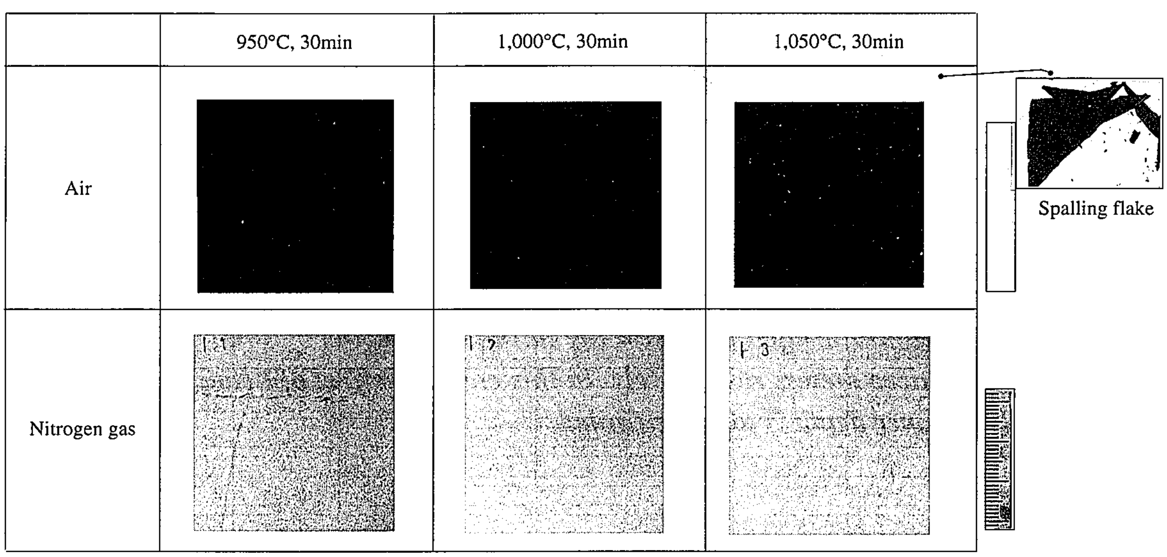


Photo 1 Appearance of Ti-15-3 alloy sheet specimens heated in air and nitrogen gas at 950, 1,000, and 1,050°C

The curves follow the parabolic law (weight gain $\propto\sqrt{t}$ where t is time). The weight gain was approximately 15 and 27 mg/cm^2 when the specimens were heated in air and held for 30 and 60 min, respectively, as shown in Fig. 1(a). When the specimens were heated in nitrogen gas, the weight gain was less than 0.4 mg/cm^2 or approximately one-tenth of that in air as shown in Fig. 1(b). These results indicate that the Ti-15-3 alloy is less likely to react with nitrogen than with oxygen.

As shown in **Photo 1**, the as-heated Ti-15-3 sheet specimens exhibit specific surface appearance characteristics. Dark brown scale is formed on the specimens heated in air (top row in Photo 1). With the specimen heated at the highest temperature of 1,050°C, scale is spalled, and the portions left by the spalled scale appear light brown close to gold. This is known as a color characteristic of tin-containing titanium alloys[4]. The sheet specimens heated in nitrogen gas (bottom row in Photo 1) have no spalled scale and they appear gold. The phases formed by heating were identified by X-ray diffraction in the surfaces of four types of sheet specimens shown in **Photo 2**: (a) specimen heated in air at 1,000°C for 30 min and without spalled scale (dark brown), (b) specimen heated in air at 1,050°C for 30 min and with spalled scale (light brown close to gold), (c) specimen heated in nitrogen gas at 1,000°C for 30 min and without spalled scale (gold), and (d) specimen heated in nitrogen gas at 1,050°C for 30 min and without spalled scale (gold).

The results are given in **Fig. 2**. In the surface of the specimen (a) without spalled scale after heating in air is detected Al_2O_3, although with weak peaks, in addition to TiO_2. In the surface of the specimen (b) with spalled scale after heating in air, TiN is formed in addition to TiO_2. The formation of TiN is a phenomenon peculiar to tin-containing titanium alloys. This titanium nitride (TiN) is reported to be

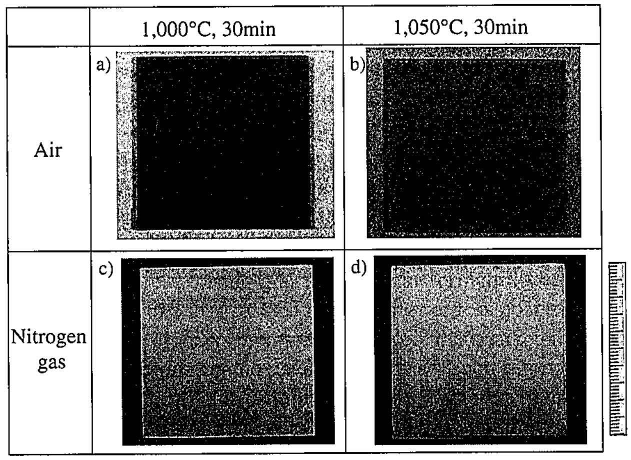


Photo 2 Surface of Ti-15-3 alloy sheet specimens examined by X-ray diffraction after heating
(a) Heated in air at 1,000°C for 30 min: Scale not spalled (dark brown)
(b) Heated in air at 1,050°C for 30 min: Scale spalled (light brown close to gold)
(c) Heated in nitrogen gas at 1,000°C for 30 min: Scale not spalled (gold)
(d) Heated in nitrogen gas at 1,050°C for 30 min: Scale not spalled (gold)

the TiN phase present beneath the oxide scale[4, 5] and to accompany a concentrated tin phase. The results of X-ray diffraction by the present authors indicated the absence of titanium-tin intermetallic compounds like Ti_6Sn_5. Beta titanium and alpha titanium phases were not detected in the surface of the specimens (a) and (b) heated in air. This is probably because the surface is covered with thick TiO_2 and TiN

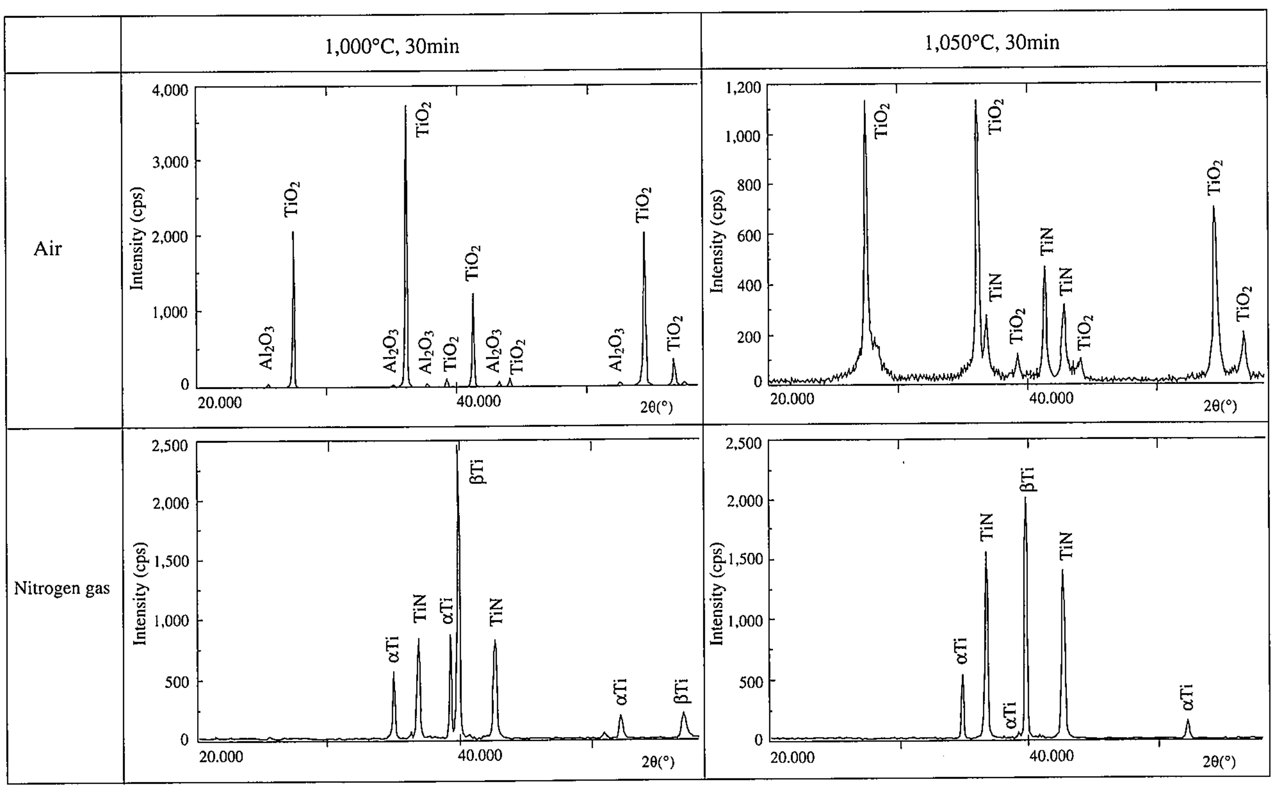


Fig. 2 X-ray diffraction results of Ti-15-3 alloy sheet specimens (four types in Photo 2) after heating

phases. In the surface of the specimens (c) and (d) heated in nitrogen gas, clear alpha and beta titanium peaks are observed in addition to TiN peaks. This suggests that the thickness of the outermost TiN phase in the surface is by far thinner than that of the TiO_2 and TiN phases formed by heating in air.

Fig. 3 shows the subsurface cross-sectional Vickers microhardness distributions of the as-heated sheet specimens. The hardness band of 260 to 290 indicates the hardness levels of nonheated sheet specimens. When the sheet is heated in air, the hardened layer formed is 400 to 600 μm in depth and is 400 to 650 in Vickers microhardness. When the sheet is heated in nitrogen gas, the hardened layer formed is 150 μm in depth and is about 350 or less in Vickers microhardness. The above results indicate that heating in nitrogen gas at 950 to 1,050°C for 30 to 60 min reduces the intrusion of the light elements (nitrogen and oxygen) from air by about nine tenths and the depth of the hardened layer by about two-thirds as compared with heating in air at 950 to 1,050°C for 30 to 60 min.

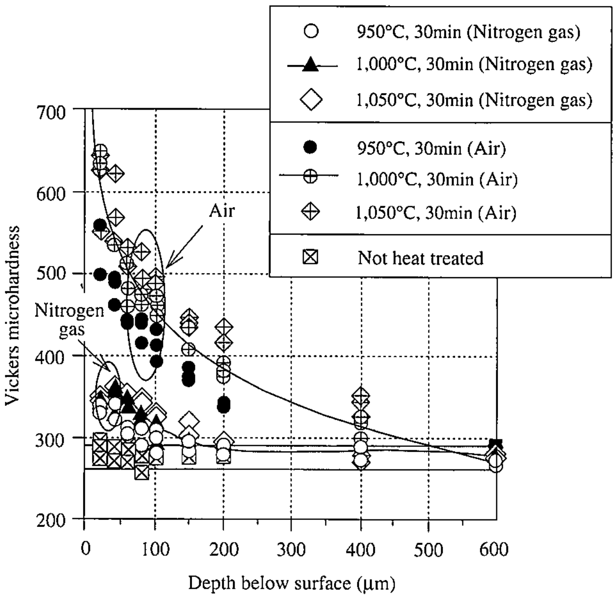
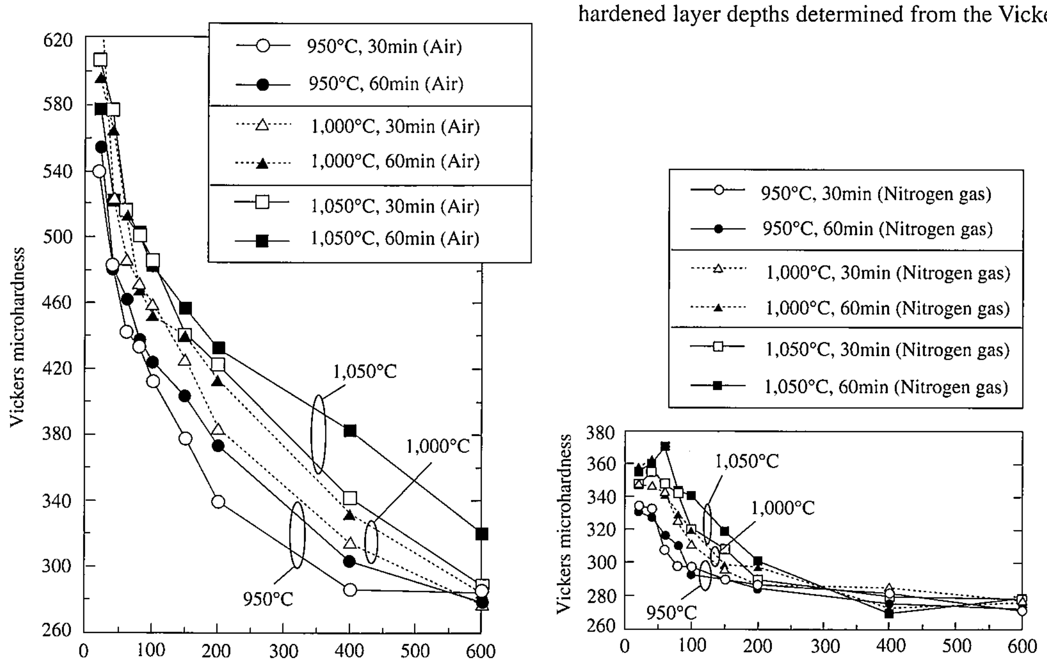


Fig. 3 Subsurface Vickers microhardness distribution of as-heated Ti-15-3 alloy sheet specimens

Fig. 4 shows the effects of the heating time and holding time on the subsurface Vickers microhardness distribution of the specimens when heated in air (a) and nitrogen gas (b). When the specimens are heated in both air and nitrogen gas, the diffusion amount and depth of oxygen and nitrogen into the titanium increase with increasing heating temperature and holding time. When the specimens are heated in nitrogen gas, the effects of the heating temperature and holding time are not more pronounced than when the specimens are heated in air. These tendencies correspond to the facts that the nitrogen-caused weight gain is about one-tenth of the weight gain in air and that the amount of nitrogen entering the titanium is absolutely small.

As shown in **Photo 3**, the effects of the heating temperature and atmosphere are clearly evident on the cross-sectional microstructures. As the heating temperature in air increases (top row in Photo 3), a structure consisting of an oxygen-rich alpha case, inner alpha phase, and acicular subsurface structure, presumed to be an alpha-plus-beta two-phase structure, is formed deep. When the specimens are heated in nitrogen (bottom row in Photo 3), the results of X-ray diffraction indicate the deep formation of a fine-grained structure, probably a nitrogen-rich alpha-plus-beta two-phase structure. The thickness of the characteristic surface structures is 20 to 60 μm and 10 to 20 μm when the specimens are heated in air and nitrogen gas, respectively. Since these thicknesses are one order of magnitude smaller than the hardened layer depths determined from the Vickers hardness distri-



(a) Air (b) Nitrogen gas

Fig. 4 Effects of heating temperature and holding time in air and nitrogen gas on subsurface Vickers microhardness distribution of Ti-15-3 alloy sheet specimens

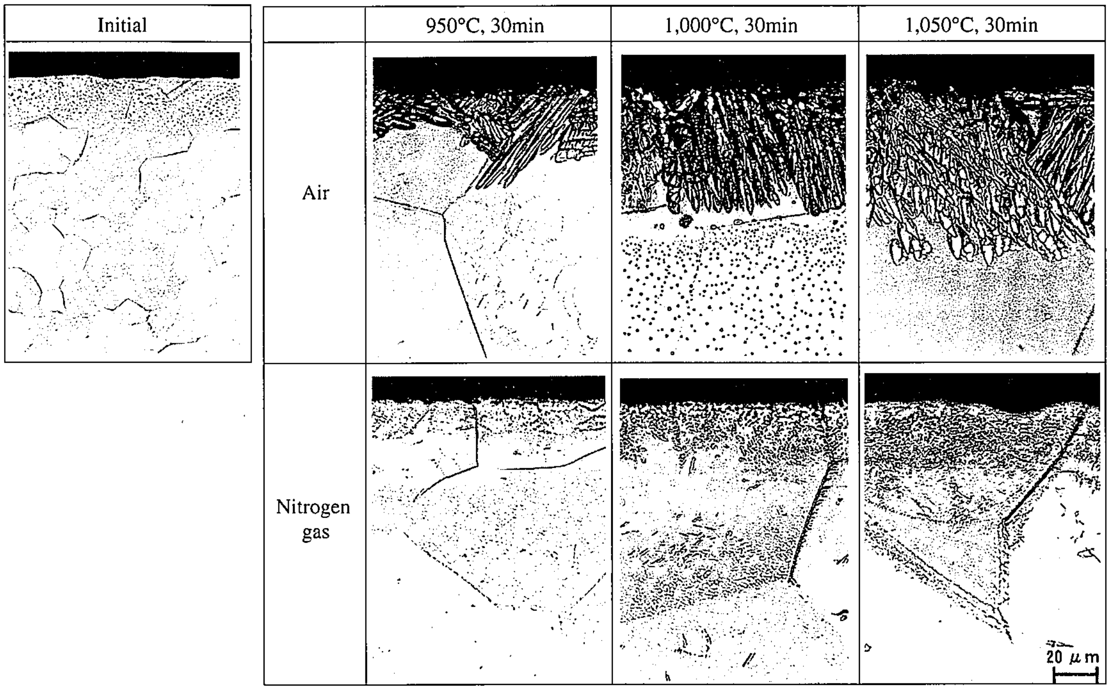


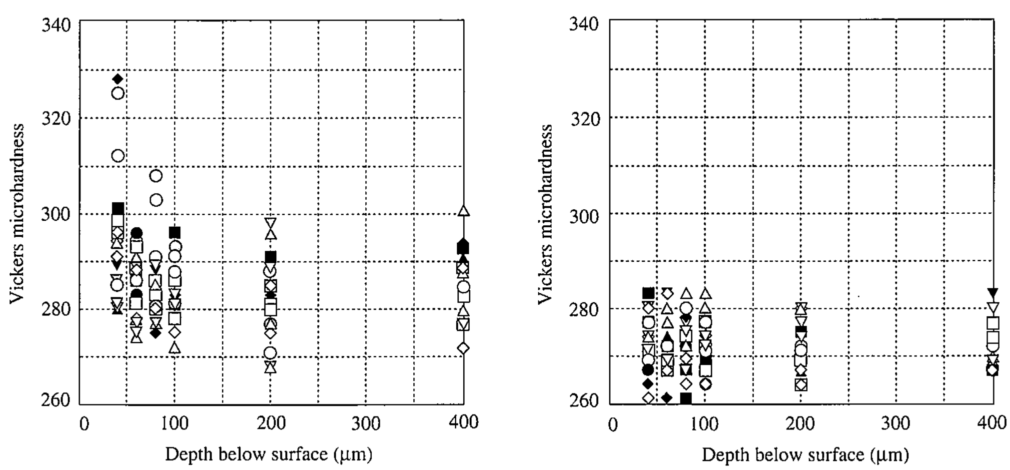
Photo 3 Change in subsurface cross-sectional microstructure of Ti-15-3 alloy sheet specimens heated in air and nitrogen gas at 950, 1,000, and 1,050°C

butions, the hardened layer is found to mainly consist of dissolved oxygen and nitrogen phases.

3.2 Evaluation of strip hot rolled at mill

Fig. 5 shows the subsurface Vickers hardness distributions through the specimens of strip hot rolled from slabs heated in a conventional combustion gas atmosphere (a) and induction heated in a nitrogen gas atmosphere (b) at the mill. The hardened layer depth of the hot-rolled strip is 80 to 100 μm in (a) and less than the measuring range of 40 μm in (b). Induction heating in the nitrogen gas atmosphere reduces the hardened layer after hot rolling. This is probably because the nitrogen gas atmosphere acted effectively in diminishing the formation of the heating-formed hardened layer. The surface GDS results of the specimens (a) and (b) indicate that oxygen penetrates deeper into the specimens (a) than into the specimens (b) as shown in **Fig. 6**. This agrees with the results of Vickers microhardness measurement shown in Fig. 5.

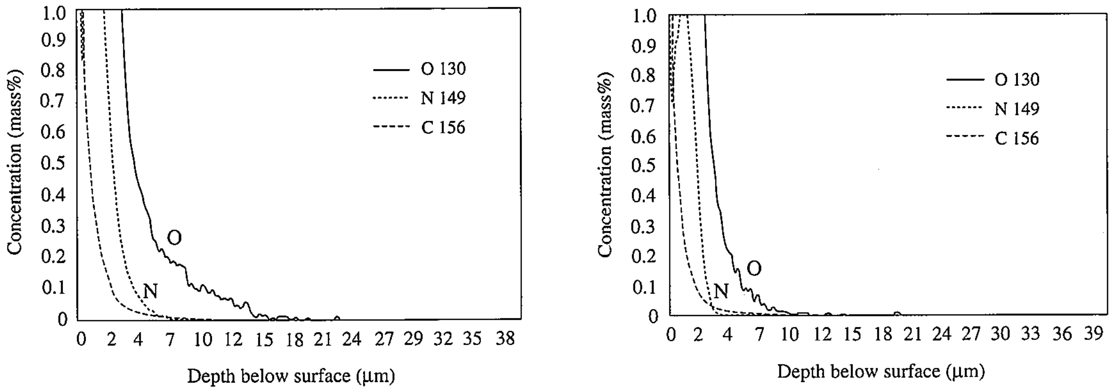
The hot-rolled strip specimens (a) and (b) were descaled and analyzed for nitrogen. The results are shown **in Table 1**. The nitrogen concentrations of the hot-rolled strip specimens are about 0.02 mass% and are practically unchanged from those of the slab specimens. They meet the maximum nitrogen limit of 0.05 mass% specified in Aerospace Material Specification 4914 (AMS 4914). As the hardened layer of the hot-rolled strip is reduced in thickness, the acid pickling amount of hot-rolled strip to remove the hardened layer can be reduced.



(a) Heated in conventional combustion gas atmosphere

(b) Induction heated in nitrogen gas atmosphere

Fig. 5 Subsurface Vickers microhardness distribution of Ti-15-3 alloy strip hot rolled at mill



(a) Heated in conventional combustion gas atmosphere

(b) Induction heated in nitrogen gas atmosphere

Fig. 6 Subsurface nitrogen concentration distribution of Ti-15-3 alloy strip hot rolled at mill (GDS results)

Table 1 Nitrogen concentration in Ti-15-3 alloy strip hot rolled at mill and after descaling

Slab heating condition at mill	Nitrogen concentration in slab (mass%)	Nitrogen concentration in strip after descaling (mass%)
(a) Heating in conventional combustion gas atmospher	0.02	→ 0.021
(b) Induction heating in nitrogen gas atmospher	0.01	→ 0.016

AMS $\leq$ 0.05

When the Vickers microhardness distributions of the specimens shown in Fig. 4(a) are compared with those of the hot-rolled strip specimens shown in Fig. 5(a), it is evident that the hardened layer after hot rolling is shallower than that after heating in air and is less than 370 in hardness. The subsurface hardened layer is accordingly estimated to change as described below.

Of the heating-formed layers where oxygen and nitrogen are enriched, the outermost layer with the higher oxygen and nitrogen concentrations has no hot deformability and is brittle, so that it is broken and removed during hot rolling. The underlying layer has such a degree of hot deformability that it is considered to be elongated and thinned by the hot rolling operation and to remain as surface layer after the hot rolling operation.

When the Ti-15-3 alloy is heated in air at 1,050°C for 4 h to simulate its heating in the combustion gas atmosphere at the mill and the heating-induced hardened layer is divided into layers A and B at the Vickers microhardness boundary of 370 as illustrated in **Fig. 7**, the hardened layer B with a Vickers microhardness of 370 or less is about 2,000 μm in depth (against about 1,000 μm for the hardened layer A with a Vickers microhardness of over 370 and about 3,000 μm for the entire hardened layer). Since a 125-mm thick slab is hot rolled to strip with a thickness of 4.6 mm and assuming that the hardened layer B is elongated and thinned in proportion to the reduction taken on the strip, the depth of the hardened layer B is calculated to be about 74 μm (2,000 μm × 4.6/125). This is of the same order as the hardened layer depth of 80 to 100 μm measured on the hot-rolled

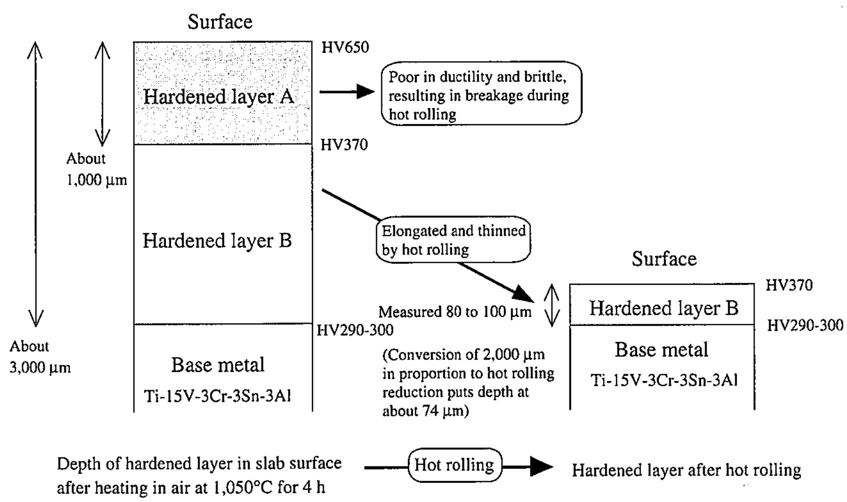


Fig. 7 Schematic illustration of change in heating-formed hardened layer in Ti-15-3 alloy with hot rolling

strip as shown in Fig. 5(a). The high hot rolling temperature makes it necessary to take the effects of oxidation and scale regeneration into account, but these effects are considered to be negligible because the hot rolling operation is completed in a short time.

4. Conclusions

The effect of heating atmospheres, especially a nitrogen gas atmosphere, on the formation of hardened layers in the Ti-15-3 alloy during heating and after hot rolling was studied to arrive at the following conclusions.

(1) The heating atmosphere has a very large effect on the formation of the hardened layer by heating. Heating in nitrogen gas at a temperature of about 1,000°C reduces the weight gain by about nine-tenths and the hardened layer depth by about two-thirds (from 500 μm to 150 μm) as compared with heating in air at the same temperature.

(2) When the Ti-15-3 alloy is heated in air at a high temperature, the scale is spalled off, and Al_2O_3 and TiN as well as TiO_2 are formed in the surface. When the Ti-15-3 alloy is heated in nitrogen gas, the scale does not spall and appears gold, and TiN is formed in the surface.

(3) When the Ti-15-3 alloy strip hot rolled at a mill is heated in a conventional combustion gas atmosphere, it forms a hardened layer to a depth of about 90 μm. When the same strip is heated in a nitrogen gas atmosphere, the depth of the hardened layer can be reduced below the measuring range of 40 μm, and the nitrogen concentration is about 0.02 mass% and is lower than the maximum nitrogen concentration limit of 0.05 mass% specified in AMS 4914. The amount of acid pickling required to remove the hardened layer can be thus reduced.

(4) Of the heating-formed hardened layers, the outermost layer that has oxygen and nitrogen enriched and is brittle is broken and removed during hot rolling. The underlying layer with hot deformability is elongated and thinned during hot rolling, and is considered to remain on the surface of the Ti-15-3 alloy strip after hot rolling. The calculated depth of this layer agrees with the depth of the hardened layer measured on hot-rolled strip of the Ti-15-3 alloy.

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