

Formation of Anatase on Commercially Pure Ti by Two-Step Thermal Oxidation Using N₂-CO Gas

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The phase of a TiO₂ layer formed on commercially pure Ti by two-step thermal oxidation using N₂-CO gas was investigated. The oxidation process comprised two steps: treatment in an N₂-(0.1, 1 and 5)%CO atmosphere and treatment in air. A Ti(C,N,O) phase was formed after the first-step treatment conducted at 873–1123 K. In the second step, the oxidation of this phase at 573–773 K resulted in the formation of an anatase phase, while its oxidation at 873 K resulted in the formation of a single rutile phase. An increase in the CO partial pressure in the first step lowered the temperature for anatase phase formation. Further, in the second step, a single-phase anatase layer was formed at temperatures of 623 and 673 K. [doi:10.2320/matertrans.ME201315]

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1. Introduction

Titanium (Ti) and its alloys have excellent properties such as high corrosion resistance and an excellent balance of strength and ductility. They have therefore been used in aerospace, military, electrical and chemical industries. Recently, their use has been extended to biomedical applications such as implants because of their low allergenicity and high bone compatibility.^{1,2} A layer of titania (TiO₂) on Ti and its alloys improves their corrosion resistance and biocompatibility³⁻⁵ and affords them photocatalytic activity.⁶ TiO₂ has various polymorphic phases—rutile, anatase and brookite. On the macroscopic scale, rutile is more thermodynamically stable than anatase and brookite. Moreover, it has been reported that an anatase layer on Ti implants improves their bone compatibility.^{3,4,7} Further, anatase and composites of anatase + rutile and anatase + brookite are known to exhibit high levels of photocatalytic activity.^{8,9}

Thermal oxidation in a gas atmosphere is a simple and low-cost method to synthesize a TiO₂ layer on Ti. The merits of thermal oxidation are (1) the synthesized TiO₂ layer adheres well to Ti substrates, and (2) this method can be used even for Ti substrates with complex geometries. Many reports on the formation of the rutile phase by the thermal oxidation of Ti are present.¹⁰ However, only a few studies on the formation of anatase-phase-containing TiO₂ layers by the thermal oxidation of Ti have been reported.¹¹⁻¹³ In contrast, the formation of an anatase layer during the thermal oxidation of TiC is well known.¹⁴ Previously, we proposed a two-step thermal oxidation process for the formation of an anatase layer on commercially pure (CP) Ti.¹¹ The first step involves the treatment of CP Ti in Ar-CO atmosphere, resulting in the formation of a TiC_{1-x}O_x phase. Upon treatment in air in the second step, this phase is oxidized to anatase.

The formation of a carbide-related phase appears to be crucial to the above-mentioned two-step thermal oxidation.

However, the effect of the atmosphere in the first step on the phases of the reaction layers has not been investigated. As in the case of TiC, the oxidation of TiN and Ti(C,N) has been reported to result in the formation of the anatase phase.^{15,16} This suggests that N₂-CO gas is a good candidate for the gas atmosphere in the first step of our two-step thermal oxidation.

In this study, the TiO₂ phase formed on CP Ti during two-step thermal oxidation using N₂-CO gas in the first step were investigated.

2. Experimental

CP Ti plates (JIS Gr.2) with dimensions of 10^L × 10^B × 2^T mm were used as specimens. The plates were mirror-polished and pickled in an aqueous solution containing 1 vol%HF and 14 vol%HNO₃ after being ultrasonically cleaned in ethanol and ultrapure water for 0.3 ks each.

The first-step treatment was conducted in an N₂-(0.1, 1 and 5)%CO atmosphere in a silica tube (inner diameter: 4.6 × 10⁻² m) placed in an electric resistance furnace. The flow rate of N₂-CO gas was 6.7 × 10⁻⁶ m³·s⁻¹ at 0.1 MPa and 273 K. The total gas pressure was 0.1 MPa, and the temperature was maintained between 873 and 1123 K. The holding time was 0 ks; this implies that the specimens were cooled in the furnace immediately after the specimen temperature reached a specified value. The heating rate of the specimens was 0.14 K·s⁻¹. The gas atmosphere during both heating and cooling was the same as that during holding. A Ti sponge was placed at the gas inlet side of the specimen in the tube furnace to remove any oxidant impurities in the reaction gas.

The second-step treatment was conducted in air for 86.4 ks with the temperature maintained between 573 and 873 K. An electric resistance muffle furnace (KBF828N, Koyo Thermo Systems Co., Ltd.) was used for the treatment. Similar to the first step, the heating rate of the specimens was 0.14 K·s⁻¹. After treatment, the specimens were cooled in the furnace. The heating pattern in the two-step treatment is schematically demonstrated in Fig. 1.

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The phase of the resultant layer on the CP Ti plates was analyzed using α - 2θ X-ray diffraction (XRD; RU-200B Cu K α , Rigaku) with an incident angle of 0.3° . The layer cross sections were observed using scanning electron microscopy (SEM; JSM 6500-F, JEOL) and transmission electron microscopy (TEM; JEM-2100, JEOL). Further, the chemical composition of the layer was evaluated using X-ray photoelectron spectroscopy (XPS; Sigma Probe, Thermo Scientific).

3. Results

Figure 2 shows the XPS depth profile for the layer formed after the first-step treatment conducted in an N_2 -1%CO atmosphere at 1073 K. Signals corresponding to carbon, nitrogen and oxygen were detected in addition to that for Ti. Figure 3 shows the XRD patterns for the layer formed after the first-step treatment conducted in N_2 -0.1%CO, N_2 -1%CO and N_2 -5%CO atmospheres between 873 and 1123 K. The reflections were detected near those of TiC. From the XPS analysis results, the phase of the layer was determined to be Ti(C,N,O). TiN, TiC and TiO have a rock-salt-type structure,^{17,18} and it is known that the light elements can interchange.^{19,20} Figure 4 shows a cross-sectional SEM

image of the Ti(C,N,O) layer. From the image, it was confirmed that the film was dense and uniform.

Figure 5 shows the XRD patterns for the reaction layer formed after the second-step treatment conducted between 573 and 873 K preceded by the first-step treatment conducted at 1123 K in N_2 -0.1%CO, N_2 -1%CO and N_2 -5%CO atmospheres. At lower temperatures in the second step, the Ti(C,N,O) phase formed during the first step remained unreacted. At intermediate temperatures, the anatase phase was mainly formed. However, with an increase in the temperature, the formation of the rutile phase increased remarkably till 873 K when only the rutile phase was formed. Figure 6 summarizes the phases formed at different temperatures in the two steps of the thermal oxidation process. Each experimental point in the figure corresponds to the phases,

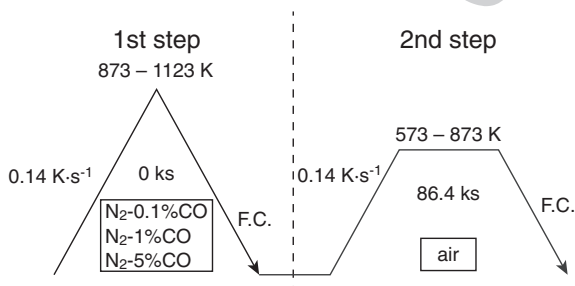


Fig. 1 Schematic diagram of the heating pattern in two-step thermal oxidation.

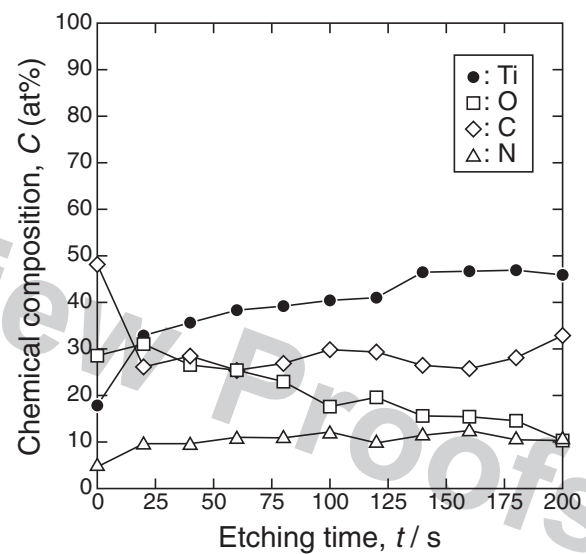


Fig. 2 XPS depth profile for the layer formed after the first-step treatment conducted in the N_2 -1%CO atmosphere at 1073 K.

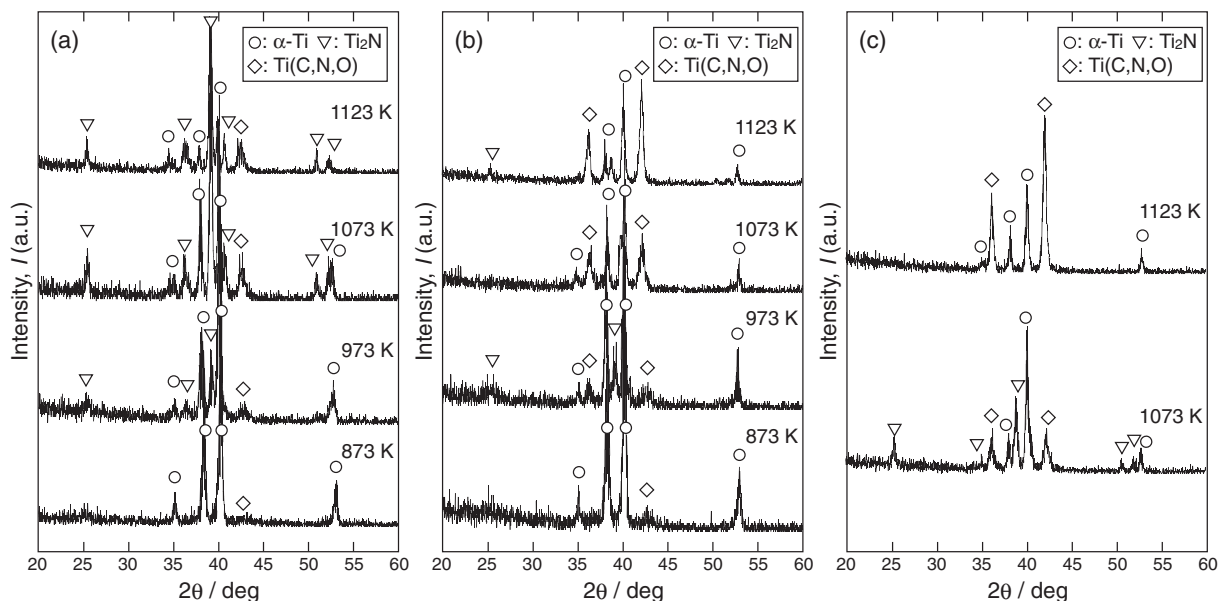


Fig. 3 XRD patterns for the layer formed after the first-step treatment conducted at 873–1123 K in (a) N_2 -0.1%CO, (b) N_2 -1%CO and (c) N_2 -5%CO atmospheres.

which are listed from left to right in the order of decreasing content. A single anatase phase was obtained after the second-step treatment conducted at 623 and 673 K. The compositional analysis of the TiO₂ layer by XPS confirmed the presence of Ti and oxygen; however, no evidence for the presence of nitrogen and carbon was obtained in this analysis.

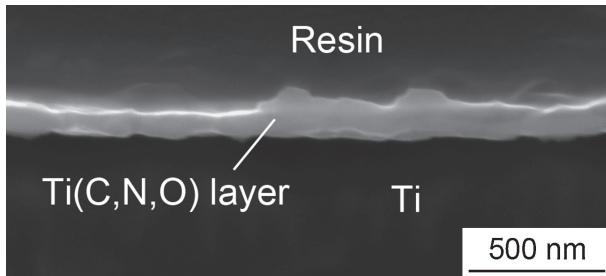


Fig. 4 Cross-section of the layer formed after the first-step treatment conducted in the N₂-1%CO atmosphere at 1073 K.

The chemical state of Ti in the TiO₂ layer was considered to be mainly Ti⁴⁺.

Figures 7(a) and 7(b) show a cross-sectional TEM image and an electron diffraction pattern of the layer, respectively, formed after the second-step treatment conducted at 673 K that was preceded by the first-step treatment conducted at 1073 K in an N₂-1%CO atmosphere. The electron diffraction pattern revealed that the layer comprised both anatase and rutile phases. Figure 8 shows the thicknesses of the layers formed after the second-step treatment conducted at 573–873 K that was preceded by the first-step treatment conducted under various conditions. Irrespective of the first-step conditions, the layer thickness increased sharply at the second-step-treatment temperature of 873 K; at this temperature, the phase formed was primarily rutile. This result suggests that the anatase phase was mainly formed by the oxidation of Ti(C,N,O) formed after the first step, while the rutile phase was mainly formed by the oxidation of the CP Ti substrate.

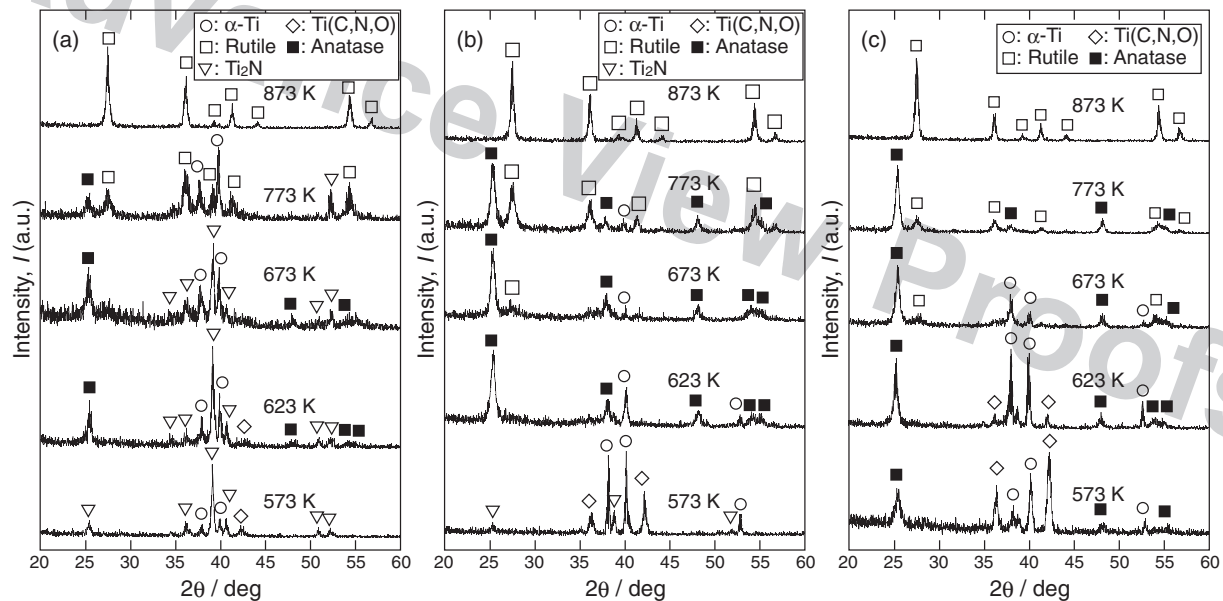


Fig. 5 XRD patterns for the layer formed after the second-step treatment conducted at 573–873 K preceded by the first-step treatment conducted at 1123 K in (a) N₂-0.1%CO, (b) N₂-1%CO and (c) N₂-5%CO atmospheres.

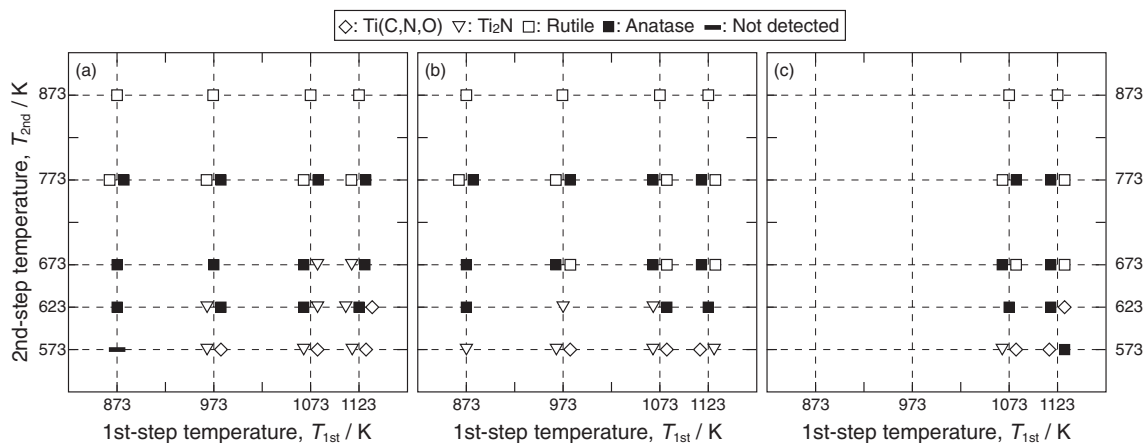


Fig. 6 Phase of the layer formed on CP Ti at different temperatures in the two steps. The atmospheres in the first step were (a) N₂-0.1%CO, (b) N₂-1%CO and (c) N₂-5%CO.

4. Discussion

The Ti(C,N,O) layer was formed during the first-step treatment conducted between 873 and 1123 K in an N₂-(0.1, 1 and 5)%CO atmosphere (Fig. 3). Figure 9 shows the potential diagrams of the Ti-C-N-O system. To our knowledge, the standard Gibbs free energy change of formation of Ti(C,N,O) has not yet been reported. Therefore, the Ti(C,N,O) phase was not included in this potential diagram as a solid substance; instead, Ti(C_{0.5}O_{0.5}) was used in place of Ti(C,N,O) because its standard Gibbs free energy of formation is known²¹⁾ and the content of carbon and oxygen in the Ti(C,N,O) layer is higher than that of nitrogen (Fig. 2). For constructing the potential diagram, the N₂ pressure was set to 0.1 MPa, and graphite, titanium nitrides, titanium oxides and Ti(C_{0.5}O_{0.5}) solids were considered. The phase of

TiO₂ was considered to be anatase. The standard Gibbs free energies of formation of these substances, except Ti(C_{0.5}O_{0.5}), were taken from the NIST-JANAF thermochemical tables.²²⁾ The relationships between the carbon activity and oxygen partial pressure at CO pressures of 0.1, 1 and 5 kPa, which correspond to N₂-0.1%CO, N₂-1%CO and N₂-5%CO, respectively, are represented in Fig. 9. The results indicate that the formation of Ti(C_{0.5}O_{0.5}) is favored at higher temperatures, which is in good agreement with the experimental results. Under a CO partial pressure of 1 kPa, the Ti(C_{0.5}O_{0.5}) phase is considered to be stable at 1073 and 1123 K but is predicted to be absent at 873 and 973 K. However, as shown in Fig. 3, the Ti(C,N,O) layer was formed in the experiments even at 873 and 973 K. Since the holding time in the first step was short (i.e., 0 ks), it is likely that the Ti(C,N,O) phase was present as a metastable product during the formation of TiO₂ from Ti.

Figure 10 shows the effect of the first-step treatment on the TiO₂ phase of the layer formed after the two-step treatment. For the first-step temperature of 1073 K, the anatase phase was formed at second-step temperatures of 623–773 K irrespective of the atmosphere in the first step. For the first-step temperature of 1123 K and N₂-5%CO atmosphere, the anatase phase was formed at second-step temperatures of 573–773 K. For the first-step temperature of 1123 K and N₂-0.1%CO and N₂-1%CO atmospheres, the anatase phase was formed at second-step temperatures of 623–773 K. Lu *et al.*²³⁾ studied the oxidation behavior of sputtered Ti_xN_y films and reported that an increase in the carbon content of the films enhanced their oxidation in air. Figure 11 shows the lattice constants of the Ti(C,N,O) layer formed at 1123 K in N₂-0.1%CO, N₂-1%CO and N₂-5%CO atmospheres. The large lattice constant of the Ti(C,N,O) layer formed in the N₂-5%CO atmosphere suggests that the carbon content in this layer is higher than those in the Ti(C,N,O) layers formed in the N₂-0.1%CO and N₂-1%CO atmospheres. The higher carbon content in the Ti(C,N,O) layer formed in the N₂-5%CO atmosphere in turn leads to the formation of the anatase phase, i.e., the oxidation of Ti(C,N,O), at low second-step temperatures such as 573 K.

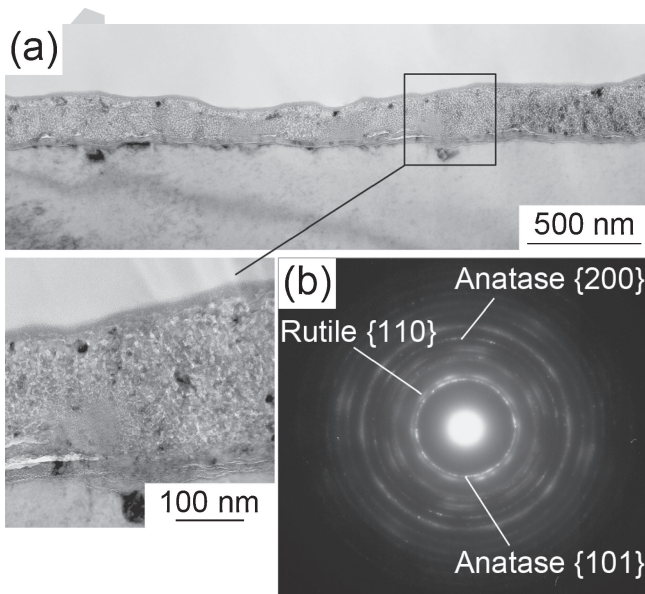


Fig. 7 (a) Cross-sectional TEM image and (b) electron diffraction pattern of the layer formed after the second-step treatment conducted at 673 K preceded by the first-step treatment conducted in the N₂-1%CO atmosphere at 1073 K.

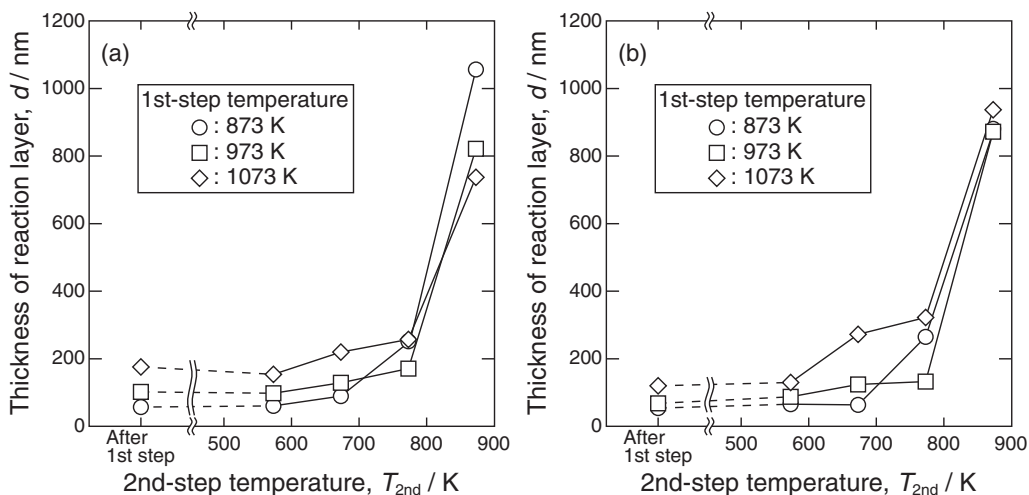


Fig. 8 Thicknesses of the layers formed after the second-step treatment conducted at 573–873 K preceded by the first-step treatment conducted at 1073 K in (a) N₂-0.1%CO and (b) N₂-1%CO atmospheres.

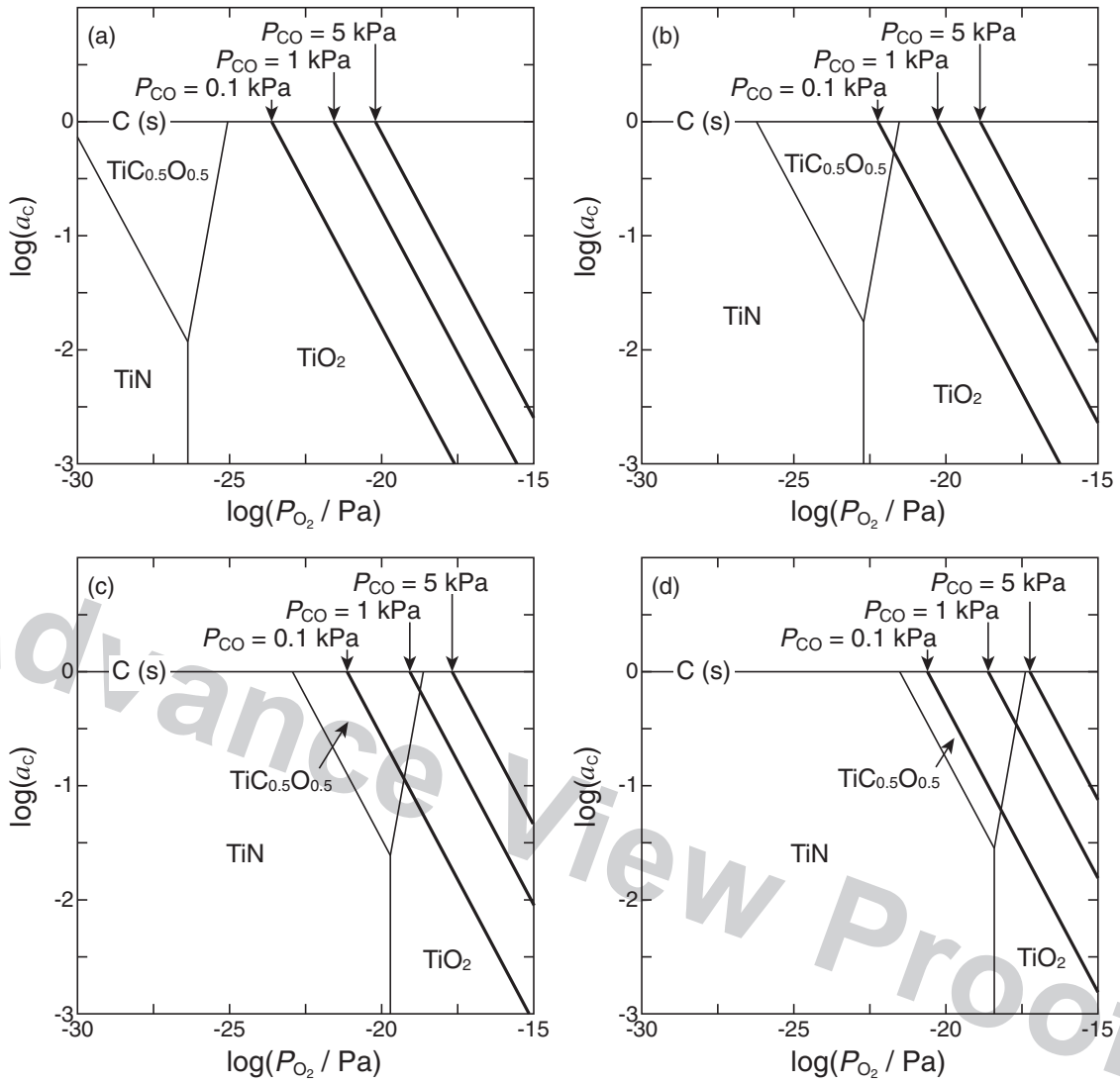


Fig. 9 Potential diagram for the Ti-C-N-O system (N_2 pressure: 0.1 MPa) at (a) 873 K, (b) 973 K, (c) 1073 K and (d) 1123 K.

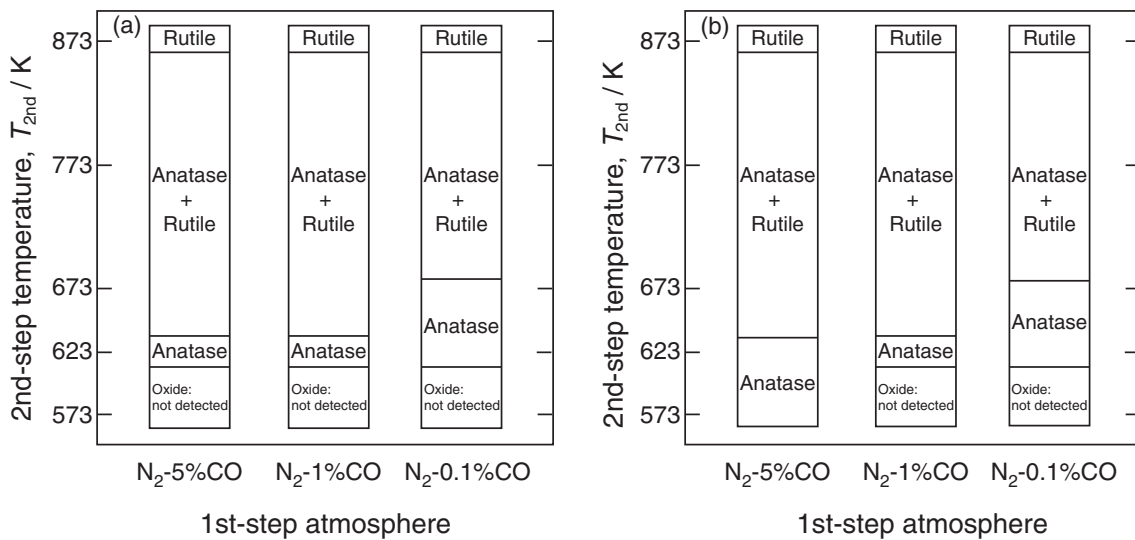


Fig. 10 Phases of the layers formed on CP Ti after the second-step treatment preceded by the first-step treatment conducted at (a) 1073 K and (b) 1123 K.

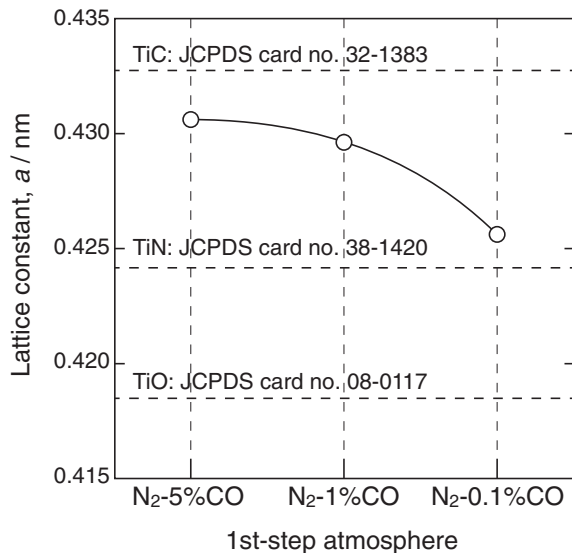


Fig. 11 Lattice constants of the Ti(C,N,O) phases formed at 1123 K in N₂-0.1%CO, N₂-1%CO and N₂-5%CO atmospheres.

In future, we aim to evaluate the properties of TiO₂ layers formed by two-step thermal oxidation; their biomedical and photocatalytic properties are currently being studied.

5. Conclusion

The formation of an anatase phase on CP Ti by two-step thermal oxidation—treatment in an N₂-CO atmosphere followed by treatment in air—was investigated, and the following results were obtained:

- (1) A Ti(C,N,O) layer was formed after the first-step treatment at 873–1123 K in an N₂-(0.1, 1 and 5)%CO atmosphere. The formation of this layer was remarkable at higher temperatures. Moreover, the carbon content in this layer was thought to increase with increasing CO partial pressure in the N₂-CO gas.
- (2) The anatase phase was formed after the second-step treatment of the Ti(C,N,O) layer in air at 573–773 K. However, after the second-step treatment at 873 K, only the rutile phase was formed.
- (3) The first-step treatment in the N₂-5%CO atmosphere lowered the temperature of anatase phase formation in the second-step treatment, which was in contrast with the results for N₂-0.1%CO and N₂-1%CO atmospheres. A single anatase-phase layer was obtained at second-step temperatures of 623 and 673 K.

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