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A New Oxidation Process of Potassium Titanium Dioxide Bronze with the Hollandite Structure

MAMORU WATANABE, YŪ KOMATSU, TAKAYOSHI SASAKI,
AND YOSHINORI FUJIKI

National Institute for Research in Inorganic Materials, Namiki 1-1, Tsukuba, Ibaraki 305, Japan

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Potassium titanium dioxide bronze ($K_xTi_8O_{16}$) was synthesized by heating a mixture of K_2CO_3 and TiO_2 at about 1000°C under a mixed gas flow of H_2 and CO_2. The dioxide bronze was obtained as dark blue powder having the hollandite structure and underwent isomorphous oxidation up to about 680°C by heating in the air to change to a nonstoichiometric titanate. Raw bronze products elute potassium into HCl aqueous solution, which is rapid in the very early stages and slows successively. Oxygen uptakes with the isomorphous oxidation indicate that the content of Ti^{3+} in raw bronze is considerably smaller than that expected from reaction mixtures and almost constant. The elution behavior shows that the nonstoichiometric parameter "x" is near 1.1 and not very dependent on valves expected from the starting mixtures. It is suggested from the new oxidation process that the migration of oxygen atoms and holes from the surface to the inside of the bronze grains is preferred, in air, to that of K^+ ions and electrons in the opposite direction.

Introduction

Potassium titanium dioxide bronze, $K_xTi_8O_{16}$, was first prepared by a reducing reaction of $K_2Ti_2O_5$ in hydrogen gas at a high temperature (*1*). The nature of this compound has remained almost unknown except that it was specified as a bronze-like compound of the hollandite host structure. This structure has large tunnels, as shown in Fig. 1, which have been noted as paths for one-dimensional transport of alkali metal ions (*2, 3*) or cavities for immobilization of radioactive large elements like Cs (*4, 5*). For instance, some of titania-based hollandites such as $K_xAl_xTi_{8-x}O_{16}$ and $K_{2x}Mg_xTi_{8-x}O_{16}$ have a high ac conductivity of K^+ in the microwave frequency range. The purification of those compounds was found to result in a frequency-independent component of complex ionic conductivity (*6*). However, the direct current of K^+ ions has not been observed yet. This has been attributed to the blocking of tunnels by residual impurities and dislocations. Very recently, it was reported that $K_xTi_8O_{16}$ undergoes oxidation in an acidic solution of hydrogen peroxide (*7*). In this process, K^+ ions in the compound are eluted into the solution, while Ti^{3+} ions in the framework structure are converted to Ti^{4+}. The final material was TiO_2 isostructural with the starting bronze. This property, namely the elution of K^+ ions, suggests that one-dimensional ion transport in the KAl- and KMg-hollandite-type compounds described above might not necessarily be blocked by impurities and dislocations and also that the potassium dioxide bronze would be mixed-conductive.

With respect to the oxidation phenome-

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non of alkali titanium dioxide bronze, another process was found for the sodium analogue (*8*) which had the $TiO_2(B)$ host lattice (*9*). The sodium analogue is oxidized isomorphously by heating in the air. In this oxidation process, Na^+ ions remain in the structure and the bronze changes to a sodium titanate (Ti(IV)). The atmosphere for oxidation seems to determine which process occurs. It is interesting, therefore, to determine whether potassium titanium dioxide bronze is subject to an oxidation pathway to potassium titanate on heating in the air. In the present work, the dioxide bronze has been synthesized by a new method. The preparation conditions of the bronze are described and the products are characterized by DTA-TG and X-ray diffraction techniques. Chemical analyses indicated that the nonstoichiometric parameter x in $K_xTi_8O_{16}$ is near 1.1 in spite of it being $1.6 \sim 2$ in the reactant mixture. This result is different from that of the sodium analogue in which there is little discrepancy between starting and final sodium contents. In order to clarify the reason for the large discrepancy in $K_xTi_8O_{16}$, we examine the elution behavior of K^+ ions from the bronze.

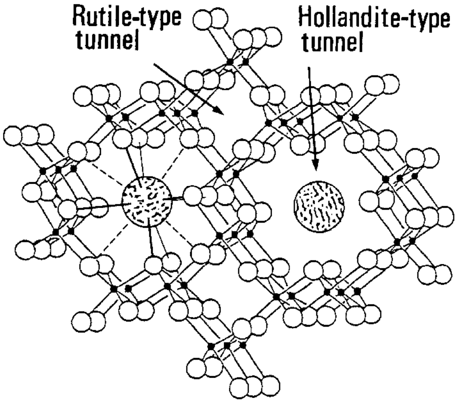

FIG. 1. Hollandite-type tunnel structure. The atomic arrangment is viewed nearly along the tunnels. Titania-based hollandites usually have a tetragonal lattice of which the unique axis is parallel to those tunnels. The unit cell (a = 10.2 Å and c = 2.96 Å) contains a chemcial formula of $K_xTi_8O_{16}$. The framework structure consists of a linkage of TiO_6 octahedra. The hollandite-type tunnel is constructed by an alternate stacking of two kinds of oxygen square-rings with 6.5 and 5.5 Å in diagonal length which are effectively 3.8 and 2.5 Å, respectively. K^+ ions are accommodated in the tunnels. Large, medium, and small circles represent K, O, and Ti atoms, respectively.

Experimental

K_2CO_3 (99.5% purity) and rutile (99.9% purity) powders supplied by Kojundo Kagaku Chemicals Co. Ltd. were used for starting materials. Starting mixtures were prepared at a molar ratio of K_2OTiO_2 of 1/8 to 1/12. Hereafter, a reaction mixture with the ratio of $1/x$ is represented by "reactant ($1/x$)" and a bronze product obtained from a reactant ($1/x$) is designated by "bronze ($1/x$)." A reaction mixture packed in a platinum crucible was put in a gas flow of H_2 (O_2 : 1 ppm, H_2O : 1 ppm, CO_2 : 0.1 ppm) or a mixture of H_2 and CO_2(O_2 : 0.01 ppm, H_2O : 1 ppm) ranging from 0.01 to 1 in mixing ratio. The mixed gas was dried at room temperature by silica gel and then introduced into a reaction chamber at a flow rate of more than $13 \sim 20$ liters/hr. A reactant in the chamber was held for 4 to 15 hr in the temperature range of 950 to 1150°C after the thermal decomposition of the carbonate at 950°C. Products were cooled down to 300°C in the reducing atmosphere before being exposed to air. They were then identified by the X-ray powder diffraction method (XRD). Chemical analyses were made for bronze products (1/8, 1/10) as follows. Raw bronze (or as prepared) was heated in a 2 *M* solution of HCl for an hour at around 97°C, washed with distilled water, and dried at 110°C. The dried powder was dissolved in a mixed solution of HF and H_2SO_4, and titanium was determined by cupferron titration and potassium by atomic absorption spectroscopy (AAS).

The DTA-TG analysis of raw bronze was performed in the air from 25 up to 900°C. A sample powder ($<$100 mg) was heated along with a reference material (α-alumina) at 20°C/min. DTA curves were measured with $\pm 50\ \mu V$ sensitivity and TG curves on a full scale of 5 mg. Ashes which were brought back to 25°C from various stages on a DTA curve were weighted to compare with increments on the TG curve and then identified by XRD. The ash obtained by heating bronze (1/10) up to 620°C in air was chemically analyzed as follows. After being boiled in hot water for 2 hr and washed with water, the ash was dissolved and the potassium and titanium contents were determined as described above.

Raw bronze powders were somewhat hygroscopic, and their sintered pellets were sometimes covered with a white thin layer (probably KOH) when being taken care of in contact with air. In order to examine the behavior of K^+ ion, potassium elution curves were plotted at 25°C for raw bronze (1/8 to 1/10). The reaction of ca. 0.1 g powder and 100 m*l* of 1 *M* HCl aqueous solution was performed in a Teflon beaker at 25°C by a batch method. The reaction was continued for 10 to 80 min, 3 days, and 4 months. After the duration, the residue was identified by XRD and the potassium concentration in the supernatant was measured by AAS. To examine whether K^+ ions in a supernatant are from elution or not (that is, whether the dissolution in HCl aqueous solution is negligible during the elution experiment or not), the residue (1/9) obtained after 4 months of reaction was dissolved and its potassium concentration determined by AAS.

Lattice parameters were obtained by least-squares calculation (*10*) on the reflections between $2\theta = 25$ and 70°. The X-ray diffraction profiles were measured with Cu$K\alpha$ radiation by the $\omega - 2\theta$ step scan method at 0.5°/min in 2θ and a sampling width of 0.01°. The observed diffraction angles were corrected with an internal standard of Si supplied by NBS. The wavelength used was 1.5406 Å.

Results

1. Products

Bronze products (1/8, 1/8.5) and (1/9, 1/10) were produced as black and dark blue powders, respectively. A typical XRD pattern of the raw bronze is shown in Fig. 2a and the lattice constants in Fig. 3. Under a constant temperature and a fixed K_2O/TiO_2 ratio, bronze only was obtained over a certain range of the CO_2/H_2 ratio. The upper limit of this range is listed for bronze (1/8, 1/8.5, 1/9) in Table I. The figures in parentheses represent the oxygen partial pressure, which was estimated from the gas mixing ratio assuming that the gas mixture is in equilibrium at a given temperature. When reactant (1/8 to 1/9) was heated with a gas mixing ratio higher than the upper limit, the product contained hexatitanate ($K_2Ti_6O_{13}$) as well as bronze. For reactant (1/10) the high mixing ratio resulted in a mixture of rutile and bronze. On the other hand the lower limit of the CO_2/H_2 ratio for producing a single phase bronze is uncertain. Pure bronze can be produced by heating reactant (1/8 to 1/10) in the flow of H_2. The exception is reactant (1/8) at 950°C, which changed to a mixture of bronze and $K_2Ti_6O_{13}$. As silica gel is in equilibrium with about 0.03 mg/liter of water vapor at about 30°C, the equilibrium oxygen partial pressure in the H_2 flow would not be lower than 10^{-24} atm at 950°C and 10^{-21} atm at 1150°C. This is because of the contamination with oxygen and so on in the flow-path. Reactants (1/11 and 1/12) changed to a mixture of rutile and bronze under all preparation conditions tried. The chemical analysis of bronze products (1/8, 1/10) gave 0.135 and 0.137 in K/Ti atomic ratio, which corresponded

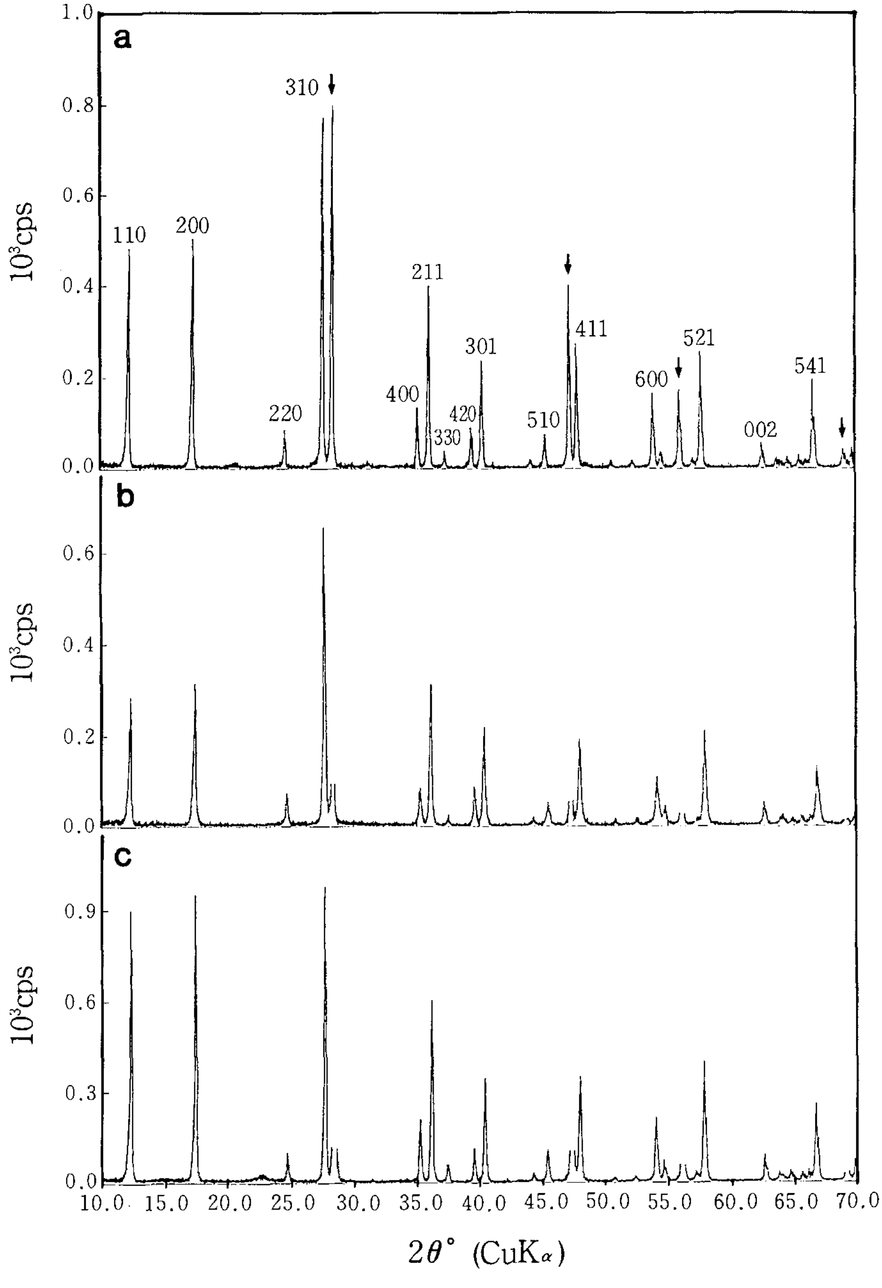

FIG. 2. Powder X-ray diffraction patterns. From raw bronze (1/9) (a), its oxidized form (b), and the bronze reacted with HCl aqueous solution for 4 months at 25°C (c). The reflections with an arrow in the pattern (a) are from Si used as an internal standard.

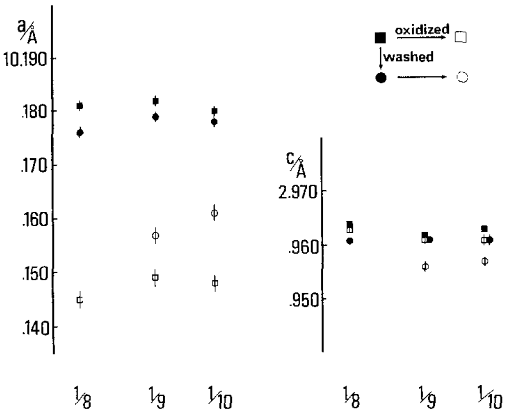

FIG. 3. Lattice constants. The number on the horizontal axis shows the initial K_2O/TiO_2 molar ratio in reactant mixtures. Lattice constants of bronze products as prepared and washed are indicated by black squares and circles and their oxidized forms by open squares and circles, respectively. Error bars are 3σ.

TABLE I

THE UPPER LIMITS OF THE CO_2/H_2 MIXING RATIO FOR OBTAINING BRONZE AS A SINGLE PHASE

K_2O/TiO_2: Temperature (°C)	1/8	1/8.5	1/9
950	—	0.01 (3×10^{-20})	0.02 (2×10^{-19})
1050	0.01 (3×10^{-18})	0.03 (1×10^{-17})	0.07 (9×10^{-17})
1150	0.07 (3×10^{-15})	0.10 (6×10^{-15})	0.20 (2×10^{-14})

to $x \cong 1.1$ for the chemical formula $K_xTi_8O_{16}$.

2. *Oxidation by Heating in Air*

When heated in air, raw bronze showed a heat evolution and a weight increase because of oxidation between 400 and 700°C. Figure 4 illustrates DTA and TG curves of raw bronze (1/9). The oxidized form which was cooled down from 620 to 25°C after the heat evolution (see position I in Fig. 4) was a white material. Its XRD pattern (see Fig. 2b) can still be indexed as a tetragonal hollandite and the oxidized form is isostructural. The ash from position III revealed decomposition of the oxidized form into rutile and hexatitanate. The same goes for the other bronze products (1/8, 1/8.5, 1/10), but the heat evolution occurs in a different temperature range. Raw bronze (1/8) was exothermic between 500 and 680°C and the others between 440 and 620°C. When bronze underwent oxidation after being allowed to stand for a long period in contact with air or washed with water, its ash from around position II was sometimes found to contain a small amount of anatase in addition to the oxidized form. Lattice constants of the oxidized form, which are compared to those of raw bronze in Fig. 3, were almost independent of the initial composition in a reactant mixture. This oxidation brings about a shrinkage of the *a*-axis but little change of the *c*-axis. The oxygen uptake in this process was about 0.45 atoms per unit cell, which amounts to 0.9 Ti^{3+} (or K^+) ions. By chemical analysis the oxidized form (1/10) was revealed to contain 55.9 wt% Ti and

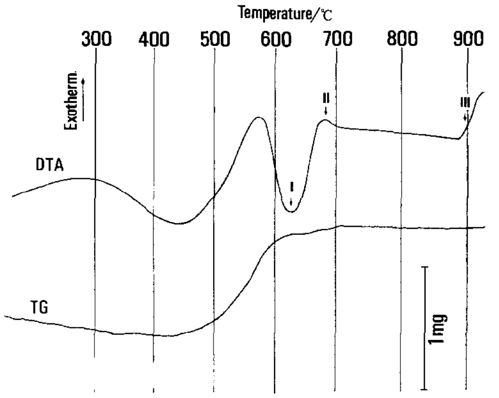

FIG. 4. DTA-TG curves obtained for bronze (1/9). The arrows with I, II, and III represent the positions where ashes were cooled down to 25°C.

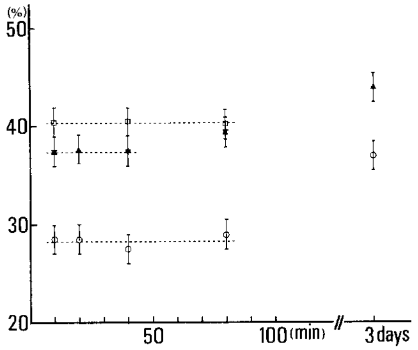

FIG. 5. Time dependence of an integrated amount of eluted K^+ ions. The vertical axis represents the percentage of a time-integrated amount of eluted K^+ ions to the initial potassium content in a reactant mixture, and the horizontal axis a reaction duration for which a bronze product is reacted with HCl aqueous solution. The marks □, ▽, ▲, and ○ represent the results for bronze products 1/8.5, 1/9, 1/8, and 1/10, respectively.

5.1 wt% K, corresponding to $K_{0.9}Ti_8O_{16.45}$ assuming 8 Ti atoms per unit cell. This means the oxidized form has hardly lost K^+ ions during the oxidation process because the starting bronze contains only ca. 1.1 potassium atoms per unit cell, as described below.

3. Elution of Potassium

Elution curves (at 25°C) in Fig. 5 show the time dependence of an integrated amount of K^+ ions eluted during a given reaction time. The vertical axis represents the percentage rate of a time-integrated amount to the total potassium content in a reactant mixture (e.g., $x = 2$ for a reactant (1/8)). As can be seen from the figure, about 30 to 40% of potassium in a sample is rapidly eluted within 10 min of the start. In the following 30 to 40 min, the elution rates are of very weak time dependence and then have a tendency to increase gradually. The bronze which was reacted with HCl aqueous solution for 4 months at 25°C gave a rate of 50% for 1/8 and 63% for 1/9 and 1/10. Figure 2c is an XRD pattern of this long-eluted bronze (1/9). In Fig. 3, lattice constants of the eluted phase and its oxidized form are compared with those of the corresponding raw bronze. The XRD pattern shows the residual bronze isostructural to the starting one, but the *a*-axis is slightly shortened through elution. The changes in lattice constants become more distinct between their oxidized forms. The relative enhancement of 110 and 200 reflection intensities by elution is consistent with the result observed for the conversion of $K_xTi_8O_{16}$ to the hollandite-type TiO_2 (*7*). Chemical analyses showed the potassium content $x = 0.66$ to 0.73 in residue (1/9), namely 58 to 63% in elution rate. Accordingly, the extra elution of K^+ ions by dissolution and/or decomposition of the sample would be within about 5% at room temperature.

Discussion

Potassium titanium dioxide bronze is subject to isomorphous oxidation by releasing K^+ ions and electrons into an acidic solution of hydrogen peroxide (*7*). The reaction is given by the chemical equation $K_xTi_x^{3+}Ti_{8-x}^{4+}O_{16} + x'O + 2x'H^+ \rightarrow 2x'K^+ + x'H_2O + K_{x-2x'}Ti_{x-2x'}^{3+}Ti_{8-(x-2x')}^{4+}O_{16}$, where x) $2x'$. Another process of isomorphous oxidation occurs in air where it combines with oxygen atoms keeping K^+ ions in the hollandite framework. The chemical equation could be formulated as followed; $K_xTi_x^{3+}Ti_{8-x}^{4+}O_{16} + x'O \rightarrow K_xTi_{x-2x'}^{3+}Ti_{8-(x-2x')}^{4+}O_{16+x'}$, that is, the migration of oxygen atoms and holes from the surface to the inside of bronze grains is preferred to that of K^+ ions and electrons in the opposite direction. This could be attributed to the fact that there is no mechanism at a solid–gas interface (like hydration in solid–water interfaces) which takes K^+ ions out of the ends of the tunnels and stabilizes them. The former oxidation process results in the hollandite-type TiO_2

for $x' = x/2$ (*7*), and the latter leads finally to a nonstoichiometric octatitanate of the hollandite structure for $x' = x/2$. Similar nonstoichiometric titanates were also found for the isomorphous oxidation of sodium titanium dioxide bronze, which has a different framework structure (*8*).

The potassium elution process of $K_xTi_8O_{16}$ in HCl aqueous solution consists of two stages. The first is a rapid elution process of K^+ ions in a very early stage and the second a slow elution in the succeeding. This elution behavior indicates the existence of two kinds of potassium components in a raw product of bronze. The steep time dependence in the rapid process suggests that those potassium ions may be supplied by some compound like K_2O remaining in grain boundaries because they are very reactive with water. On this basis, one can estimate the actual potassium content in raw bronze products by extrapolating elution curves to time zero in Fig. 5. The obtained x values are 1.25, 1.12, 1.11, and 1.15 for bronze (1/8, 1/8.5, 1/9, and 1/10), respectively. These are somewhat larger than the values estimated after oxidation in air (x = 0.9). Either of the potassium contents estimated by the two methods is nearly independent of the starting composition and distinctly smaller than the maximum value x = 2. The nonstoichiometric range observed is very narrow and approximates x = 1.05 in bronze obtained by the reduction of potassium dititanate (*1*) but is considerably less than the maximum content (x = 2) in bronze prepared by a reaction of potassium metal with titanium dioxide under vacuum (*7*). In the present preparation method, the CO_2/H_2 ratio was kept constant throughout a heating–cooling cycle, and hence the oxygen partial pressure in the cooling process should become higher than the upper limit with decreasing temperature. The present cooling rate, by which it took about 2 hr from 1150 to 800°C, is not so rapid. Therefore, one can expect a certain shift of composition toward the direction from 1/8 to 1/9 in the table, or the release of a part of the K^+ ions and electrons while undergoing the conversion of Ti^{3+} to Ti^{4+}. This composition shift would require easy migration of K^+ ions and electrons in the bronze, which is consistent with the mixed-conductive property of the bronze. In fact, $Na_xTi_8O_{16}$ ($x \leqq 2$), which is not ion conductive, can be produced even with x = 2 by the same preparation procedure (*8*). The parameter x is crystallographically allowed to increase up to 2 in $K_xTi_8O_{16}$. However, other titania-based hollandites grown by the flux or melt method have been found to contain K^+ ions only in a narrow range of 1.4 to 1.7 (*11, 12*). It has been said that the number of K^+ ions is less than the full occupancy to relax the repulsive interaction between adjacent K^+ ions in the same tunnel; in the case of full occupancy, the distance between the nearest K^+ ions in the tunnel is less than the effective ionic diameter (3.02 Å) of eight-coordinated K^+ ions. The preparation of the fully occupied bronze (*7*), therefore, poses a question on the relaxation of such a repulsive interaction.

The slow elution process in HCl is considered to be made by K^+ ions in bronze itself. This elution would be based on (i) the escape of K^+ ions conjugate to the oxidation of Ti^{3+} into Ti^{4+} in bronze or (ii) the ion exchange of K^+ in bronze with H^+ in solution. The former case was observed for the reaction of bronze with an acidic solution of H_2O_2 as cited above. Usually, HCl aqueous solution is not regarded as an oxidizing acid. However, when it is used in air, the solution may have oxidizing power by the cooperation of oxygen dissolved in it. The oxidizing power in this case could be considered on the basis of the equation $(O_2) + (4H^+) + (4e) = 2H_2O_{(l)}$. Although the solubility of oxygen in water is small, this reaction seems to become effective under the condition of high H^+ concentration like in acidic solution and long reaction duration. The difference between processes (i) and (ii) would be dependent on whether the concentration of Ti^{3+} changes during the slow elution process. Preliminary EPR measurements revealed raw bronze (1/9) to give a remarkably larger signal of Ti^{3+} event at room temperature in comparison with the precipitate which was obtained by treating the bronze for a long duration of elution (*13*). This suggests that the slow elution of K^+ ions would not be caused by ion exchange but by the oxidation process. This detail is under examination.

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