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論文・Paper

Sintering of Titanium Oxynitride

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Sintering of titanium oxynitride, TiO_xN_y ($x+y \approx 1$, $x=0.07\sim 1.00$, $y=0\sim 0.89$) was studied at $1000^\circ\sim 1400^\circ\text{C}$. The rate of sintering decreased markedly with increasing nitrogen content, y . The results were tentatively analyzed with an initial stage sintering equation. The diffusion coefficient of rate limiting species of sintering changes four orders of magnitude for TiO in which $\sim 90\%$ of oxygen was substituted with nitrogen. The relation between the defect concentration and the diffusion coefficient of rate limiting species of sintering was discussed.

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酸化チタンの焼結

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本研究ではさまざまな組成をもった酸化チタン, TiO_xN_y ($x+y \approx 1$, $x=0.07\sim 1.00$, $y=0\sim 0.89$) の粉末成形体について $1000^\circ\text{C}\sim 1400^\circ\text{C}$ の温度範囲で焼結性の検討を行い, 酸化物中の窒素含有量 y が増すにしたがって焼結速度が減少する結果を得た。実験結果について初期焼結の速度式を適用して解析を行い, 焼結を律速する原子種の拡散係数は TiO に含まれる酸素のうちの約 90% を窒素で置換すると 4 桁減少することを示し, 併せて焼結を律速する原子種の拡散係数と欠陥濃度との関係を考察した。

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Key-words : Sintering, Titanium oxynitride, Oxynitride, Oxide, Nitride, Diffusion

1. Introduction

Difficulty of sintering in nitrogen ceramics is clearly due to the presence of nitrogen in these materials¹⁾. Densification was appreciable in titanium nitride only when ultra-fine powder material was used^{2), 3)}. In clear contrast to this, oxide ceramics cause far less problem on sintering. Marked densification was reported for TiO below 1400°C ⁴⁾. In an attempt to understand this difference, the role of nitrogen in sintering is studied systemati-

cally with referring to the sintering behavior of oxide.

Titanium oxynitride, TiO_xN_y ($x+y \approx 1$), was chosen as a model material. Nitride and mono-oxide of titanium have the same crystal structure (NaCl-type)⁵⁾. They form a continuous solid solution for the entire region of the system, in which titanium atoms form fcc metal sub-lattice and oxygen and nitrogen atoms occupy the octahedral interstices, forming non-metal fcc sub-lattice⁶⁾. Starting from

TiO, gradual substitution of oxygen with nitrogen makes the material vary from oxide to nitride continuously. Specimens with various compositions were prepared, on which initial to intermediate sintering was studied. The results were analyzed and the relation between the defect structure and the transport property of the rate limiting species of sintering was discussed.

2. Experiment

Starting materials were sponge titanium, titanium dioxide (both from Toho Titanium Co., Ltd.), hydrogen and nitrogen. An intermediate material, fine titanium hydride (TiH₂), was prepared from sponge titanium and hydrogen from a commercial gas cylinder. Sponge titanium was placed in a mullite muffle tube and reacted with the hydrogen at 600°C for 10 h (H₂ : 200 ml/min+Ar : 30 ml/min). The hydride was pulverized with an alumina ball mill for 5 h in air. Titanium oxide (TiO_x : $x=0.65\sim1.0$) was prepared from titanium hydride and titanium dioxide. Specified amount of TiO₂ and TiH₂ mixed in a plastic ball mill for 2 h was placed in an alumina Tamman tube and heated at 1200°C for 2 h in an oxygen-free argon stream (100 ml/min). The oxygen in argon was removed by passing it through heated sponge titanium (800°C). After cooled to the room temperature, the product was pulverized for 10 h in an alumina ball mill in air. Specimens containing nitrogen (TiO_xN_y) were prepared from both hydride (containing a small amount of oxygen) and oxide (TiO_x). Specimens with high nitrogen contents ($y \geq 0.78$) were made by nitriding fine titanium hydride powder in a nitrogen stream (100 ml/min), and those with low nitrogen contents ($y \leq 0.34$) by nitriding

titanium oxides. The nitriding condition for each specimen was summarized in **Table 1**. After cooled to the room temperature and pulverized for 10 h in an alumina ball mill in air, they were annealed at 1200°C for 1 h in an argon stream. Finally, they were pulverized for 10 h in an alumina ball mill in argon and stored in air-tight containers. The composition of specimen was determined by the chemical analysis. Kjeldahl and Dumas methods were used to determine the nitrogen content^{7),8)}. The titanium content was determined after oxidizing the specimen to TiO₂ at 1000°C for 15 h in air. The particle size of specimen was determined from its specific surface area (BET method, Kr adsorption at the liquid nitrogen temperature). The specimens was also examined by a transmission electron microscope (Hitachi, HS-7 D) and the powder X-ray diffractometer (Philips APD-10). The densities were measured pycnometrically.

Specimen pellets (10 mm ϕ $\times$ 3~4 mm) were formed at the pressure of 1000 kg/cm² without binder. After weighed, they were placed in a specimen container (alumina Tamman tube), and its entrance was packed with sponge titanium to protect them from oxidation. A furnace with an air-tight mullite muffle tube and a spiral SiC heating element was used for the sintering experiment. The temperature was controlled to within $\pm 2^\circ\text{C}$ with a PID-type regulator. Argon was always passed through the muffle tube (100 ml/min). The container was placed at the cold end of the muffle tube for 20 min to exchange air with argon. The container was then moved to the hot zone of the tube, kept for a specified period for sintering and moved back to the cold end. After cooled to the room temperature, the container was taken out of the tube. The pellets were weighed and their thickness was measured with a micrometer. The temperature in the container was measured at each condition. A Pt-13 Rh-Pt thermocouple covered with a mullite protection tube was placed in the container, and the container was moved quickly to the hot zone of the tube. The temperature arrived at the specified point (within $\pm 10^\circ\text{C}$) in 4 min after the cold container arrived at the hot zone. The shortest sintering period was chosen as

Table 1. Specimen powders.

Composition	Nitriding Conditions		Density (g/cm ³)	Lattice constant(A)	Particle size(μm)
	Temp(°C)	Time(hr)			
TiO _{1.00}	—	—	4.97	4.1792	0.9
TiO _{0.87} N _{0.07}	700	2	4.76	4.1900	1.3
TiO _{0.86} N _{0.26}	870	3	4.86	4.2104	0.8
TiO _{0.65} N _{0.34}	800	16	4.92	4.2229	0.8
TiO _{0.07} N _{0.78}	925	5	5.10	4.2332	0.7
TiO _{0.08} N _{0.89} *	1020	18	5.19	4.2393	0.8

* Al: 0.0007 (at. fraction); Si: less than 0.0007

20 min.

3. Characterization of materials

Table 1 summarized the characteristics of specimens. The compositions of specimens as determined by the chemical analysis showed that the ratio, the total oxygen and nitrogen content to the titanium content ($x+y$), was in the range of 0.85~1.1. X-ray powder diffraction showed that all the specimens had the NaCl-type crystal structure; no other phase was found. Titanium atoms form fcc sublattice and the non-metallic elements, oxygen and nitrogen, occupy the octahedral site. The lattice parameter increased with increasing nitrogen content. The densities of specimens changed with the composition. The average particle size determined from the specific surface area were approximately equal for all specimens (about 1 μm).

Figure 1 shows an example of the transmission electron micrograph of specimen powder. Clearly there is a distribution in the particle size, but the average particle size was approximately equal to that estimated from the specific surface area. Alumina and silica content in the specimen were determined by the chemical analysis. Both were negligibly low.

Fig. 1. TEM of $\text{TiO}_{0.86}\text{N}_{0.26}$ powder

4. Results

Figure 2 shows the relation between the relative shrinkage, $\Delta l/l_0$, and the sintering time, t , for various specimens. At a given temperature, the sintering rate decreased markedly

Fig. 2. Relative shrinkage with sintering time at 1200°C.

▲ : $\text{TiO}_{1.0}$, ○ : $\text{TiO}_{0.87}\text{N}_{0.07}$
● : $\text{TiO}_{0.86}\text{N}_{0.26}$, □ : $\text{TiO}_{0.65}\text{N}_{0.34}$
■ : $\text{TiO}_{0.07}\text{N}_{0.78}$, △ : $\text{TiO}_{0.08}\text{N}_{0.89}$

Fig. 3. Isothermal shrinkage at various temperatures ($\text{TiO}_{0.65}\text{N}_{0.34}$).

Fig. 4. Change of relative density with sintering time at 1200°C.

▲ : $\text{TiO}_{1.00}$, ○ : $\text{TiO}_{0.87}\text{N}_{0.07}$
● : $\text{TiO}_{0.86}\text{N}_{0.26}$, □ : $\text{TiO}_{0.65}\text{N}_{0.34}$
■ : $\text{TiO}_{0.07}\text{N}_{0.78}$, △ : $\text{TiO}_{0.08}\text{N}_{0.89}$

with increasing nitrogen content. The particle size which has a pronounced effect on sintering was approximately equal for these specimens. Similar results were found at other temperatures.

Figure 3 shows the effect of temperature on sintering for $\text{TiO}_{0.65}\text{N}_{0.34}$. The sintering rate increased approximately an order of magnitude for a 100°C increase in temperature. The logarithm of relative shrinkage against the logarithm of sintering time changes linearly for the small shrinkage ($\Delta l/l_0 \leq 0.03$). This corresponds to the initial stage of sintering. The slope of $\log \Delta l/l_0$ vs. $\log t$ was approximately $1/2.5$ for this stage. The results on other specimens were similar. The slope was approximately $1/2.5$ for the region $\Delta l/l_0 \leq 0.03$ for all specimens under all conditions. The slope decreased with increasing $\Delta l/l_0$ for $\Delta l/l_0 > 0.03$.

(a)

(b)

Fig. 5 SEM of sintered specimens.

- (a) $\text{TiO}_{0.65}\text{N}_{0.34}$ sintered for 160 min at 1200°C
 (b) $\text{TiO}_{0.87}\text{N}_{0.07}$ sintered for 160 min at 1100°C

Figure 4 shows the change of relative density, ρ/ρ_0 , with sintering time. In all specimens, the density increased with increasing time at all temperatures. The rate of densification decreased with increasing nitrogen content. Nitrogen clearly has the retardation effect on the densification except in the specimen with low nitrogen content ($\text{TiO}_{0.87}\text{N}_{0.07}$).

Figure 5 shows the SEM of specimens having different compositions. Clearly, sintering proceeded more rapidly in the specimen having lower nitrogen content. The linear shrinkage were 1.3% for $\text{TiO}_{0.65}\text{N}_{0.34}$ and 10% for $\text{TiO}_{0.87}\text{N}_{0.07}$, and the respective grain sizes were approximately $1\ \mu\text{m}$ and $5\ \mu\text{m}$ for the specimens shown in Fig. 5. Grain growth was negligible in the specimen with high nitrogen content, but was significant in the specimens with low nitrogen content.

5. Discussion

In this section, the transport property of TiO_xN_y is discussed using the sintering equation as a guide. In the treatment, numerical accuracy is not attempted, rather, stress is placed on demonstrating the significance of nitrogen on the sintering, semi-quantitatively.

Among various sintering mechanisms, those controlled by volume diffusion and grain boundary diffusion are known to cause considerable shrinkage⁹⁾. The significant shrinkage in the present system suggests that either one or both be operating. In the following treatment, the volume diffusion mechanism is assumed, since the slope of the line in Fig. 2 is approximately equal to $1/2.5$ for the initial stage of sintering.

The analytical relation proposed by Kingery and Berg¹⁰⁾ was chosen for its simplicity. The equation was derived for the case where the matter transport from the grain boundary to the neck region by volume diffusion was the rate controlling process:

$$\frac{\Delta l}{l_0} = \left(\frac{20 \gamma a^3 D^*}{\sqrt{2} k T} \right)^{2/5} r^{-6/5} t^{2/5} \quad (1)$$

where $\Delta l/l_0$: relative shrinkage

γ : surface energy

a^3 : atomic volume

D^* : self-diffusion coefficient

k : Boltzmann constant

T : temperature

r : radius of particle

t : time

For the initial stage of sintering, Eq. (1) $\Delta l/l_0$ vs. logarithm of t suggests that the slope in the logarithm of be 1/2.5, which is in accordance with the result (Fig. 2). From the linear portion of the data, diffusion coefficients were determined readily at low temperatures. In the analysis, τ was assumed to be 1000 dyne/cm and a^3 the 1/4 of the unit cell volume. At high temperatures, however, the shrinkage was large even at the shortest sintering time investigated. The slope differs significantly from 1/2.5 and the data were outside the region where Eq. (1) was applicable.

To estimate the diffusion coefficient of the rate limiting species in sintering at high temperatures, the following method was developed. The method was similar to what was used in studying the viscoelastic property of polymer¹¹⁾. The basic assumption is that the sintering mechanism (volume diffusion) does not change in the temperature region studied. For this case, the effect of temperature is to simply increase the sintering rate. If this assumption is correct, the sintering rate would be increased by a certain factor for a given increase in sintering temperature. Noting Eq. (1), this factor should be equal to the ratio $(D^*/T)_h/(D^*/T)_l$, where the subscripts l and h refer to the low and high temperatures, respectively.

In Figure 6, the sintering data at low temperature (1100°C) are plotted on its own time scale. The sintering data at other temperatures (1000°, 1200° and 1300°C) are plotted on the extension of the data at 1100°C by changing the time scale by the specific factor. All the data were successfully expressed by a sin-

Fig. 6. Shrinkage of $\text{TiO}_{0.65}\text{N}_{0.34}$ at various temperatures plotted on fictive time scale at 1100°C.

○ : 1000°C, □ : 1100°C
× : 1200°C, △ : 1300°C

gle curve. This result suggests that the assumption proposed above was basically correct for the present system, and the diffusion coefficients can be estimated. In the example shown in Fig. 6, the sintering rate increased by a factor of 12 when the temperature was changed from 1100° to 1200°C. The diffusion coefficient of the rate limiting species in sintering at 1200°C is consequently given by;

$$D^*(\text{at } 1200^\circ\text{C}) = \left(\frac{1473}{1373}\right) \times D^*(\text{at } 1100^\circ\text{C}) \times (12).$$

Namely, diffusion coefficient at 1200°C was approximately 13 times larger than that at 1100°C. Similarly, the diffusion coefficient at 1300°C was 14 times of that at 1100°C. The diffusion coefficients at 1000° and 1100°C were calculated from the linear portion of data with Eq. (1). The same procedure was used on the other samples.

Figure 7 shows the diffusion coefficients of the rate limiting species in sintering. They decreased significantly with increasing nitrogen content in the material. Decrease of approximately four orders of magnitude was found for the 90% substitution of oxygen in TiO with nitrogen. The retardation effect of nitrogen in diffusion and sintering is thus clearly shown.

The self-diffusion coefficient of rate limiting

Fig. 7. Diffusion coefficients of species which govern the sintering process. The broken line shows the self-diffusion coefficient of Ti^{2+} in $\text{TiO}_{1.00}$ (11).

species in $\text{TiO}_{1.00}$ was approximately two orders of magnitude smaller than that of Ti^{2+} in $\text{TiO}^{(12)}$. This difference suggests that the sintering of $\text{TiO}_{1.00}$ be probably limited by the diffusion of O^{2-} in $\text{TiO}_{1.00}$. This speculation is however only tentative, since higher diffusion coefficient was suggested for O^{2-} than for Ti^{2+} in TiO in the oxidation study of titanium⁽¹³⁾.

In TiN , reliable transport data is absent. In the nitridation of titanium sheet⁽¹⁴⁾, the diffusion coefficient of nitrogen was suggested to vary with the concentration of nitrogen vacancy, and the vacancy mechanism was tentatively proposed for the nitrogen diffusion in TiN . However, this does not suggest the sintering process controlled by nitrogen diffusion. Nitrogen diffuses faster than titanium in $\text{TiN}^{(14)}$.

In solid solution of TiO-TiN , no transport data has been published.

The vacancy concentration on titanium site and non-metal site were calculated with Eqs. (2) and (3).

$$[V_{\text{Ti}}] = 1 - \frac{\rho_0}{\rho_x} \quad (2)$$

$$[V_{\text{O+N}}] = 1 - (1 - [V_{\text{Ti}}]) \times (x + y) \quad (3)$$

where ρ_0 is the density determined pycnometrically, ρ_x the X-ray density (perfect titanium sub-lattice assumed), and $[V_{\text{Ti}}]$ and $[V_{\text{O+N}}]$ are the vacancy concentrations on titanium site and non-metal site, respectively.

Figure 8 shows the effects of composition on the diffusion coefficient of the rate limiting species in sintering at 1200°C and on the vacancy concentrations. High concentration of vacancies on both metal and non-metal sites in TiO ($\sim 15\%$) agrees with the reported value⁽¹⁵⁾. The presence of significant concentration of vacancy on metal site in nitrogen rich region ($\sim 3\%$) was not a priori expected. TiN is known to have vacancies on nitrogen site but not on titanium site⁽¹⁶⁾. Small amount of oxygen is likely responsible for the creation of these vacancies since it makes the property of the material change slightly to oxide. In the figure, the diffusion coefficient changes significantly with composition but the vacancy concentration did not change considerably. This implies that the mobility of defect changes with composition or some other mechanism such as interstitial mechanism.

The explanation of retardation effect of ni-

Fig. 8. Effect of composition on the diffusion coefficient of species which govern the sintering, and on the vacancy concentrations.

□ : Metal vacancy, △ : Non-metal vacancy

trogen by a simplest vacancy mechanism is thus not probable. Further study is clearly needed to understand the transport mechanism of the rate limiting species in sintering. The diffusion coefficient determined in this study is tentative, but is the first transport data in TiO-TiN system.

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実験・技術・調査報告・Report

シラスと琉球サンゴ石灰岩の 1200°~1280°C の反応生成物*

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シラスと琉球サンゴ石灰岩をポルトランドセメントの調合法に準じて配合し、水硬率 (H.M.) を 1.1 から 0.2 おきに 3.1 まで変化させた粉末試料を電気炉中 1200°C から 1280°C の 20°C おきの各温度に 1 h 焼成したのち冷風で急冷した。これらの焼成物について粉末 X 線回折を行い、生成化合物を同定して焼成過程を検討した。生成化合物は水硬性化合物である β -C₂S, C₃A 及びゲーレンナイト (C₂AS), 遊離の CaO, ガラス物質で、シラスと琉球サンゴ石灰岩の配合割合及び焼成温度によって生成物の種類と量が変化する。例えば β -C₂S 及び C₃A は H.M. の値が大きくなるにつれて、それらの回折強度は増大し、H.M.=2 付近で最大値を示したのち減少した。遊離の CaO は H.M.=2 付近から生成し、H.M. の値が大きくなるにつれて急激に回折強度が強まる。いずれの生成化合物も 1200°C 焼成物の回折強度が大きく、焼成温度の上昇に伴って減少した。

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Reaction Products of Shirasu and Ryūkyū Coral Limestone Mixtures Fired at 1200°~1280°C

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The mixtures of Shirasu and Ryūkyū coral limestone were fired at 1200°~1280°C for 1 h in the electric furnace and quenched by air blowing. The X-ray diffraction analysis was conducted on these fired samples and the hydraulic compounds of β -C₂S and C₃A, gehlenite C₂AS, free CaO and glassy material were recognized. The X-ray diffraction analysis revealed that the species and the amount of each reaction products were related to the mixing ratio of Shirasu to Ryūkyū coral limestone and firing temperature.

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Key-words : Shirasu, Ryūkyū coral limestone, Reaction products

1. 緒 言

シラスと琉球サンゴ石灰岩 (以下サンゴ石灰岩と称す

る) を主原料として、水硬性セメントをつくることを試み、シラスとサンゴ石灰岩の粉末混合物を 1200°C から 1280°C の 20°C おきの各温度に焼成したのち急冷し、焼成物について X 線回折を行い、生成化合物を同定して焼

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