cesses are responsible for the limiting current behavior of oxygen reduction on Fe-Cr alloys, while the simplest explanation may be the catalytic decomposition mechanism which claims that the peroxide-decomposition activity decreases with increasing Cr content.

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References:

- 1) J.P. Hoare, "The Electrochemistry of Oxygen", p. 117 (1968), Interscience Pub..
- 2) J.P. Hoare, "Advances in Electrochemistry and Electrochemical Engineering" Ed. by P. Delahay, Vol. 6, p. 201 (1967), Interscience Pub..
- 3) M. Nagayama, M. Cohen, *J. Electrochem. Soc.* **109**, 783 (1962).
- 4) S. Haruyama, M. Okuyama, M. Mukai, *This Journal* **36**, 534 (1968).
- 5) M. Okuyama, S. Haruyama, M. Mukai, *ibid.* **37**, 670 (1969).
- 6) M. Okuyama, T. Tsuru, S. Haruyama, K. Nagasaki, *ibid.* **38**, 8 (1971).
- 7) A. Damjanovic, M.A. Genshaw, J.O'M. Bockris, *J. Phys. Chem.* **70**, 3761 (1966).

Technical Paper

Phases Found in Quenched Specimens of TiO_2 -CaO System*

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TiO_2 -CaO system was studied by means of an arc imaging furnace. The primary heat source was a xenon arc lamp with ellipsoidal reflecting optics. The specimen of TiO_2 and CaO mixture was set on a holder at the focus of the concentrator of the furnace and was melted by the radiation of the light beam. The specimen was quenched from the melt to the room temperature. Quenched specimens were examined by chemical analysis, X-ray diffraction method, infrared absorption spectroscopy and dielectric constant measurement. Phases found in the quenched specimens were $\text{CaO} \cdot \text{TiO}_2$, $3\text{CaO} \cdot 2\text{TiO}_2$ and $4\text{CaO} \cdot 3\text{TiO}_2$. From the X-ray diffraction data and the infrared spectroscopic data, the existence of TiO_6 octahedral configuration was confirmed in all phases. The dielectric constant of pure $\text{CaO} \cdot \text{TiO}_2$ was much higher than that of other specimens.

1 Introduction

An arc imaging furnace as well as a solar furnace has been proved to be useful for the heat treatment of the specimen at high temperatures.

The phase study of some binary oxides systems such as ZrO_2 - CaO ¹⁾, ZrO_2 - MgO ²⁾, ZrO_2 - SrO ³⁾, ZrO_2 - TiO_2 ⁴⁾, ZrO_2 - La_2O_3 ⁵⁾, ZrO_2 - Gd_2O_3 ⁶⁾, Al_2O_3 - Y_2O_3 ⁷⁾ and La_2O_3 - Cr_2O_3 ⁸⁾ were reported, in which the specimens were melted by using the solar and arc imaging furnaces and then quenched from the melt.

The phase diagram on TiO_2 -CaO system were studied by other researchers^{9),10)}, however, the data on the property and the structure of the quenched specimen are scarcely reported.

In this paper, a study on the property and the structure of the quenched specimen from the melt of TiO_2 -CaO system, by using a xenon arc imaging fur-

nace to attain the high temperatures, is reported.

2 Experimentals

2.1 Materials

TiO_2 (rutile type powder prepared by Toho Titanium Mfg. Co. and had a purity of 99.9% up) and CaO (guaranteed reagent grade powder prepared by Kanto Chemical Co.) were mixed in desired ratio in an agate mortar. One gram of mixed powder was pressed into a cube of $20 \times 5 \times 5$ mm.

2.2 Apparatus

The apparatus for melting of the specimen was an arc imaging furnace (made by Nippon Plasma Flame Co.) and is shown in Fig. 1.

The primary heat source is a xenon arc lamp (5 kW, made by Ushio Electric Co.) with ellipsoidal reflecting optics ($f_1=900$ mm, $f_2=110$ mm). The light beam is reflected by the reflecting mirror and then turned by a plate mirror toward the reimaging mirror. The specimen was set on a holder at the focus of the reimaging mirror. TiO_2 (m.p. $1,640^\circ\text{C}$) could be melted by using this furnace.

The infrared absorption spectrum was examined by

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- 1: Reflecting ellipsoidal mirror
2: Xenon arc lamp
3: Reflecting plate mirror
4: Melting sample

Fig. 1 Arc imaging furnace

Fig. 2 Apparatus for dielectric constant measurement

the use of the infrared spectrometer (IR-G type made by Japan Spectroscopic Co.). The dielectric constant was measured by the universal bridge (TR-10 type made by Ando Electric Co.). The cell used for the measurement of the dielectric constant is shown in Fig. 2.

2.3 Experimental procedure

(a) Melting and quenching of the specimen: The mixed specimen of TiO_2 and CaO set on the holder was melted by the radiation of the light beam. The temperature of the specimen was kept at a temperature $100\sim 150^\circ\text{C}$ higher than the melting point of the specimen. The duration time of the radiation was about 5 min. Then the light beam was shut out and the specimen was quenched to the room temperature.

(b) Chemical analysis: Chemical analysis of calcium and titanium in the specimen was carried out as follows. About 100 mg of the quenched specimen was taken in a platinum crucible and was fused with the addition of KHSO_4 . The fused mass was dissolved in a dil. HCl solution. Calcium and titanium contents were determined by the CaC_2O_4 - KMnO_4 titration method and the Zn-Hg reduction method, respectively.

(c) Infrared absorption spectroscopy: Infrared absorption spectrum was taken by using the KBr pellet method.

(d) Dielectric constant measurement: The quenched specimen was crushed into the powder under 300 mesh and about 0.1 g of the powder was pressed into a pellet which had a thickness of 0.5 mm. The dielectric constant of the pellet was measured with a frequency of 1.592 Hz by the apparatus, which is shown in Fig. 2. During the measurement of the dielectric constant, the specimen was set in a dry box.

3 Results

3.1 Chemical analysis of the quenched specimens

In order to examine the stoichiometry of the quenched specimens from the melt, chemical analysis of TiO_2 and CaO were made. Results obtained are listed in Table 1. CaO and TiO_2 contents in the quenched specimens deviated 1~4 mole % from those in the mixture. The analytical values of CaO were almost larger than the mixed values in every specimen. On the other hand, the analytical values of TiO_2 were smaller than mixed values in every specimen. This fact suggests that a small amount of TiO_2 might vaporize in the melted state.

Table 1 Chemical analysis data of quenched specimens

Sample No.	Mixed value (mole %)		Analytical value (mole %)	
	CaO	TiO_2	CaO	TiO_2
1	90.0	10.0	90.1	9.05
2	80.0	20.0	80.6	18.9
3	75.0	25.0	75.7	24.1
4	70.0	30.0	72.8	27.8
5	69.0	31.0	71.5	28.0
6	68.2	31.8	70.4	28.7
7	66.6	33.4	68.1	29.9
8	60.0	40.0	60.7	37.8
9	57.2	42.8	58.8	39.7
10	52.0	48.0	51.6	46.6
11	50.0	50.0	50.7	48.3
12	40.0	60.0	40.6	58.5
13	30.0	70.0	29.9	68.5
14	20.0	80.0	21.1	78.2
15	10.0	90.0	12.7	86.1

3.2 X-ray diffraction data of quenched specimens

X-ray diffraction data of the quenched specimens are listed in Table 2. Identified compounds in the specimens were CaO , $\text{CaO}\cdot\text{TiO}_2$, $3\text{CaO}\cdot 2\text{TiO}_2$, $4\text{CaO}\cdot 3\text{TiO}_2$ and TiO_2 . Except for the specimen obtained

Table 2 X-ray diffraction data of quenched specimens

Sample No.	Identified compounds				
1	CaO (s)	3CaO·2TiO ₂ (m)			
2	CaO (s)	3CaO·2TiO ₂ (m)			
3	CaO (m)	3CaO·2TiO ₂ (m)			
4	CaO (m)	3CaO·2TiO ₂ (m)			
5	CaO (m)	3CaO·2TiO ₂ (m)			
6	CaO (m)	3CaO·2TiO ₂ (m)			
7		3CaO·2TiO ₂ (m)		CaO·TiO ₂ (m)	
8		3CaO·2TiO ₂ (m)		CaO·TiO ₂ (m)	
9		3CaO·2TiO ₂ (m)		CaO·TiO ₂ (m)	
10			4CaO·3TiO ₂ (m)	CaO·TiO ₂ (m)	
11				CaO·TiO ₂ (m)	
12				CaO·TiO ₂ (m)	TiO ₂ (m)
13				CaO·TiO ₂ (m)	TiO ₂ (m)
14				CaO·TiO ₂ (m)	TiO ₂ (m)
15				CaO·TiO ₂ (m)	TiO ₂ (m)

at 50 mole % of CaO, two phases were identified in quenched specimens.

From the X-ray diffraction data and the chemical analysis of the quenched specimens, identified phases and their boundaries are shown in Fig. 3 with referring to the liquidus presented by Roth¹⁰⁾. In this figure, the melting temperature of specimens in the present experiment are also shown.

Numbers in this figure represent those of the sample in Table 1
The points indicate their melting temperatures

Fig. 3 Phase diagram of TiO₂-CaO system

3.3 Infrared absorption spectra

The observed infrared absorption spectra of quenched specimens in the range of 800~400 cm⁻¹ are shown in Fig. 4. The absorption band at about 540 cm⁻¹ was observed in every specimen. In the specimen of 40~52 mole % of CaO, the absorption band at about 430 cm⁻¹ was also observed.

Numbers in this figure represent those of the sample in Table 1

Fig. 4 Infrared absorption spectra of TiO₂-CaO system

The infrared absorption spectra of quenched specimens stated above were similar to that of TiO₂. It may be said that the atomic arrangement in these crystals are similar to that of TiO₂. In the rutile type TiO₂, six oxygen atoms are coordinated around a central titanium atom. Also in the perovskite type CaO·TiO₂, six oxygen atoms are coordinated around a central titanium atom octahedrally.

The infrared absorption band at about 540 cm⁻¹ was assigned to the Ti-O stretching vibration and that at about 430 cm⁻¹ was assigned to the Ti-O bending vibration in TiO₆ octahedral configuration¹¹⁾. Therefore, TiO₆ octahedral configuration may exist in every specimen obtained by various CaO compositions.

3.4 Dielectric constant measurement

Dielectric constants of quenched specimen of each

composition were measured. Being assumed that the pellet of the specimen is a mixture of a crystal and the air, the dielectric constant of the crystal was calculated from apparent value (ϵ) by using eq. (1)¹²⁾

$$\epsilon = X_1 \log \epsilon_1 + X_2 \log \epsilon_2 \quad (1)$$

where ϵ_1 , ϵ_2 are the dielectric constants of the crystal and the air, and X_1 and X_2 are their volume fractions.

Apparent dielectric constants (ϵ) and volume fractions of the crystal in the pellet (X_1) are listed in Table 3.

Table 3 Apparent dielectric constant (ϵ) and volume fraction of the crystal in the pellet (X_1)

Sample No.	ϵ	X_1
CaO	5.30	0.61
1	10.5	0.56
2	7.20	0.44
3	8.47	0.51
4	6.80	0.55
5	7.70	0.49
6	8.30	0.51
7	10.0	0.52
8	8.70	0.60
9	10.1	0.58
10	17.2	0.67
11	55.0	0.53
12	13.5	0.66
13	13.8	0.62
14	15.6	0.64
15	16.9	0.66
TiO ₂	7.25	0.53

The relation between the dielectric constant of the crystal and the composition of specimen is shown in Fig. 5. The dielectric constant of the specimen of 50 mole % of TiO₂ was much larger than that of the

Fig. 5 Dielectric constants of TiO₂-CaO system

other specimens.

4 Discussion

The infrared absorption band at about 540 cm⁻¹ was observed in every specimen of 10~90 mole % of CaO. The absorption band may be due to Ti-O stretching vibration in TiO₆ octahedral configuration that was mentioned above. Therefore, every crystal observed in the present experiment may contain TiO₆ octahedral configuration.

From the X-ray diffraction data, the existence of CaO·TiO₂, 3CaO·2TiO₂ and 4CaO·3TiO₂ were observed in TiO₂-CaO system.

In the crystal structure of the perovskite type CaO·TiO₂, six oxygen atoms are coordinated around a cen-

Table 4 X-ray diffraction data of 3CaO·2TiO₂, 4CaO·3TiO₂ and CaO·TiO₂

	X-ray diffraction data				a_0, c_0 (Å) from ASTM cards
	2θ (°) CuK α	d (Å)	hkl	a_0, c_0 (Å)	
3CaO·2TiO ₂	32.73	2.743	105	$a_0=3.83$	$a_0=3.832$
	47.40	1.916	200	$c_0=19.5$	$c_0=19.505$
4CaO·3TiO ₂	32.84	2.725	107	$a_0=3.83$	$a_0=3.827$
	47.43	1.915	200	$c_0=26.9$	$c_0=27.147$
CaO·TiO ₂	33.10	2.706	044	$a_0=15.29$	$a_0=15.25$
	47.63	1.909	008

Fig. 6 Structure of 3CaO·2TiO₂

Fig. 7 Structure of 4CaO·3TiO₂

tral titanium atom¹¹⁾. Crystal systems and lattice parameters of $\text{CaO}\cdot\text{TiO}_2$, $3\text{CaO}\cdot 2\text{TiO}_2$, and $4\text{CaO}\cdot 3\text{TiO}_2$ were determined as listed in Table 4. Lattice parameters of $3\text{CaO}\cdot 2\text{TiO}_2$ and $4\text{CaO}\cdot 3\text{TiO}_2$ almost agreed with these of $3\text{SrO}\cdot 2\text{TiO}_2$ and $4\text{CaO}\cdot 3\text{TiO}_2$ ¹²⁾, respectively. By referring to the crystal structure of $3\text{SrO}\cdot 2\text{TiO}_2$ and $4\text{SrO}\cdot 3\text{TiO}_2$ ¹³⁾, the crystal structure of $3\text{CaO}\cdot 2\text{TiO}_2$ and $4\text{CaO}\cdot 3\text{TiO}_2$ are assumed to be as shown in Figs. 6 and 7. The lattice parameters of the assumed structure agreed with the present experimental data. In these structure, TiO_6 octahedral configuration exist. The infrared absorption spectra of the specimens containing these compounds may be attributed to the configuration.

The dielectric constant of the specimen that contained only $\text{CaO}\cdot\text{TiO}_2$ was much larger than that of the other specimen. It is considered that the dielectric constant relates to the crystal structure. The crystal structure of $\text{CaO}\cdot\text{TiO}_2$ is a pseudo-cubic as shown in Table 4. This structure is similar to that of $\text{BaO}\cdot\text{TiO}_2$ which is known to be ferromagnetic. The dielectric constant of $\text{CaO}\cdot\text{TiO}_2$ formed in the present experiment is considerably large, although the crystal of cubic system is non-polar and has no spontaneous polarization. Therefore, the crystal of $\text{CaO}\cdot\text{TiO}_2$

formed in the present experiment may be distorted similarly in the case of $\text{BaO}\cdot\text{TiO}_2$.

Quenched specimens except for the specimen at 50 mole % of CaO were mixtures of cubic and tetragonal systems or those of pseudo-cubic and tetragonal systems. Therefore, the dielectric constants of quenched specimens except for $\text{CaO}\cdot\text{TiO}_2$ were considerably smaller than that of $\text{CaO}\cdot\text{TiO}_2$.

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Literatures:

- 1) T. Noguchi, M. Mizuno, W.M. Coun, *Solar Energy* **11**, 145 (1967).
- 2) T. Noguchi, M. Mizuno, *Bull. Chem. Soc. Japan* **41**, 1583 (1968).
- 3) T. Noguchi, T. Okubo, O. Yonemochi, *J. Am. Ceram. Soc.* **52**, 178 (1967).
- 4) T. Noguchi, M. Mizuno, *Bull. Chem. Soc. Japan* **41**, 2895 (1968).
- 5) A. Rounaet, *Compt. Rend.* **267**, Ser. C, 395 (1968).
- 6) A. Rounaet, M. Foex, *ibid.* **267**, Ser. C, 873 (1968).
- 7) T. Noguchi, M. Mizuno, *Kogyo Kagaku Zasshi* **70**, 843 (1967).
- 8) T.S. Laszlo, "Image Furnace Techniques", p. 132 (1965), John Wiley & Sons, N.Y..
- 9) R.C. Devries, R. Roy, E.S. Osborn, *J. Phys. Chem.* **58**, 1069 (1954).
- 10) R.S. Roth, *J. Res. Nat. Bur. Std.* **61**, 437 (1958).
- 11) J.T. Last, *Phys. Rev.* **105**, 1740 (1957).
- 12) W.D. Kingery, "Introduction to Ceramics", p. 719 (1960), John Wiley & Sons, N.Y..
- 13) S.N. Rudlesden, P. Popper, *Acta Cryst.* **11**, 54 (1958).

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