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Phase Relations of the Cr_2O_3–TiO_2 System

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The phase relations of the system Cr_2O_3–TiO_2 were determined at temperatures between 1400 and 1765°C in air. Discrete homologous series of $Cr_2Ti_{n-2}O_{2n-1}$, with $n = 6, 7, 8$, were found to be stable as single phases in the range of certain temperatures, while a continuous solid solution existed in the composition of $n > 8$ below 1425°C. This presence and its stable region of a new compound of Cr_2TiO_5 corresponding to $n = 3$ are revealed in the present paper. $Cr_2Ti_2O_7$, the so-called *E* phase, existed in wide homogeneity range, corresponding to the composition of approximately $3 < n < 5$. High-temperature phases (called *n* and *n'* phases in the present work) existed above 1425°C and seemed to be closely related to each other from the viewpoint of the structure except that some X-ray diffraction lines of *n* phase were strongly diffused. Both rutile and chromia had limited solid solubilities. In the present paper, phase relations between Cr_2O_3 and TiO_2 are summarized in a phase diagram.

Introduction

The phase analysis on the Cr_2O_3–TiO_2 system has been intensively studied by several investigators. Hamelin (*1*) first found the presence of the compound *E* at a composition of 48.75 wt% Cr_2O_3 and the solid solution *B* between about 21 and 34 wt% Cr_2O_3. Andersson *et al.* (*2*), however, reported the existence of discrete homologous series of oxides corresponding to Hamelin's solid solution *B*. These homologous series of the oxides with a general formula of $Cr_2Ti_{n-2}O_{2n-1}$ ($n = 6, 7, 8, 9$) were characterized by an X-ray diffraction technique and the structures have been derived by the application of the concept of the crystallographic shear (CS) to the basic structure of rutile (*3*). The presence of the *E* phase was also confirmed by Andersson *et al.* (*2*), who reported that this phase was not a member of the series. Lee (*4*) studied the Cr_2O_3–TiO_2 system at a temperature range between 1200 and 1500°C and obtained results similar to Andersson *et al.* (*2*) and Flörke and Lee (*5*), however, found afterwards the presence of an apparent homogeneity range for the *E* phase and also reported the reversible transformation of the phases corresponding to $8 \leqq n \leqq 12$ at 1400°C. Anzai *et al.* reinvestigated a phase analysis on the Cr_2O_3–TiO_2 system between 1200 and 1450°C and summarized a phase diagram below 1450°C (*6*). They determined phase boundaries precisely for the *E* phase by measurements of the changes of *d*-spacing at several temperatures (*7*). Recently, Werner (*8*) proposed the phase diagram of this system at temperatures from 1300 to 1600°C under the consideration of the influence of loss of chromia due to the vaporization during the heat treatment. He reported that both rutile and chromia existed as solid solutions. The homologous series found by Andersson *et al.* were also reported to be stable at certain temperatures, and a continuous phase in compositions between rutile and $Cr_2Ti_7O_{17}$ existed below 1400°C. A high-temperature phase existed stably above 1400°C and coexisted with the *E* phase above 1440°C which had a wide homo-

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geneity range. The question still remains to be solved whether the $Cr_2Ti_7O_{17}$ compound had stably existed as the member in the homologous series of $Cr_2Ti_{n-2}O_{2n-1}$ since Philp and Bursill (*9*, *10*) reported that the region rutile plus 8 ~ 24 wt% Cr_2O_3 at 1573°K exhibited a continuous series of highly ordered structures with no diphasic region instead of a $(121)_r$ CS phase.

In Cr_2O_3–Fe_2O_3–TiO_2 system, Kwestroo and Roos (*11*) revealed that Fe in Fe_2TiO_5 (pseudobrookite structure) up to 15% could be replaced by Cr without any change of the structure at 1300°C and another solid solution region appeared as chromia content increased from 55 to 90 mole%. This phase has a structure analogous to the V_3O_5 structure type (*12*) but not analogous to the pseudobrookite one. The phase is assumed to be analogous to the compound Cr_2TiO_5. The possibility of the existence of Cr_2TiO_5 compound was first suggested by Åsbrink *et al.* (*13*) who prepared a very small amount of the specimen by arc melting of the $Cr_2O_3 \cdot TiO_2$ composition. Hence, Kwestroo *et al.* followed them by assuming that the compound Cr_2TiO_5 may be stabilized in the V_3O_5 structural type by addition of Fe. No one has ever prepared the pure end member of the compound Cr_2TiO_5.

More recent work by Grey and Reid (*14*) showed that shear structural compounds of $(Cr,Fe)_2Ti_{n-2}O_{2n-1}$ had the structure based on the high-pressure form of rutile (*15*), isomorphous with the α-PbO_2 type (*16*). This series was characterized by X-ray diffraction analysis based on single crystal data for the compound $CrFeTi_2O_7$ (*17*).

These results on a ternary system strongly suggest that in the Cr_2O_3–TiO_2 system, there may exist a phase which has the V_3O_5 structural type and the phase of the homologous series similar to that of $(Cr,Fe)_2Ti_{n-2}O_{2n-1}$, different from the Andersson series.

The present study was carried out with a great interest in the phase analysis of the Cr_2O_3–TiO_2 system especially at a higher temperature range, above 1400°C, in order to clear up the complicated phase relations, which may provide the basis on the structural studies for the phases present in Cr_2O_3–TiO_2 system and the examination of the presence of the compound Cr_2TiO_5.

Experimental

The chemicals used in this work were guaranteed reagent grade chemical of Cr_2O_3

TABLE I

LOSS IN THE WEIGHT OF Cr_2O_3/TiO_2 SAMPLES AFTER HEAT-TREATMENT IN AIR AT 1650°C

Starting composition (Cr_2O_3 wt%)	Heating time (hr)	Weight before heating (g)	Weight after heating (g)	Loss in the weight (g)	Calculated composition after heating (Cr_2O_3 wt%)	Calculated change of composition (Cr_2O_3 wt%)
20.00	1	0.9330	0.9245	0.0085	19.63	0.37
	2	0.9249	0.9111	0.0138	19.03	0.97
	4	0.9464	0.9245	0.0219	18.43	1.57
	8	0.8948	0.8680	0.0268	17.84	2.16
	24	0.9441	0.8700	0.0741	13.55	6.45
44.00	1	0.8867	0.8787	0.0080	43.71	0.29
	2	0.8749	0.8607	0.0142	43.24	0.76
	4	0.8998	0.8728	0.0270	42.50	1.50
	8	1.4006	1.3406	0.0600	41.71	2.29
	24	0.9360	0.8253	0.1107	36.70	7.30

and TiO_2 (Kanto Chemical Co. Inc., Tokyo, Japan). These oxides were weighed to the desired compositions after drying at 600°C in air. Weighed oxide powders were ground and mixed in an agate motor in the reagent grade of methanol and then were formed into a pellet. The heat-treatment was performed in a vertical type of furnace with an alumina insulating tube using a heating element of SiC or $LaCrO_3$. The temperatures were controlled within ±5°C during the heat treatment. The composition change due to the evaporation of chromia during the heat treatment was examined by weighing the pellet sample before and after heat-treatment at 1650°C in air without embedding the pellet sample in mixed powder of the same composition. Table I shows the results on the weight loss during the heat treatment of the pellet sample for a certain period. The pellet specimen heated for 24 hr showed the different appearance from the surface to the inside. The part near the surface of the quenched pellet specimen was relatively richer in rutile composition than the initial composition of the pellet specimen. The results indicate that the loss of chromia from the sample due to the vaporization was serious at the surface part of the pellet specimen at higher temperature. In order to prevent the change of the composition of the sample itself, the following two methods were used. First, the pellet sample was embedded in mixed powder of the same composition in a platinum–rhodium 20% crucible and then the crucible containing the pellet sample was quenched into cold water after completion of the period of heat treatment. The surface part of the quenched pellet was removed with emery paper, and only the specimen at the central part of the pellet was employed for the phase analysis. Second, several samples were heated in a sealed platinum–rhodium 20% capsule for comparison with data obtained by the above method. X-ray diffraction patterns of the specimen taken from the central part of the pellet were in good agreement with those heat-treated in a sealed capsule. Thus, the former method embedding the pellet sample in the mixed powder of the same composition was employed in the present work. The deter-

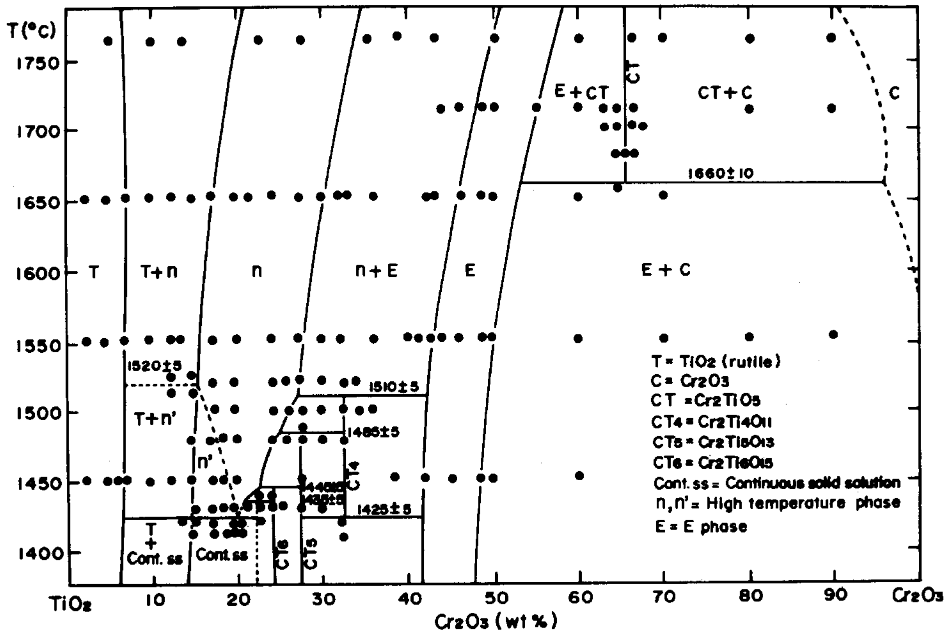

FIG. 1. Phase diagram of the system Cr_2O_3–TiO_2.

TABLE II

Experimental Results in the Cr_2O_3–TiO_2 System

Sample no.	Composition (Cr_2O_3 wt%)	Temperature (°C)	Time (hr)	Phases
137	2.50	1650	24	T
1	2.50	1550	2	T
235	2.50	1450	23	T
246[a]	5.00	1765	1	T
89	5.00	1650	1	T
2	5.00	1550	2	T
236	5.00	1450	23	T
242	6.46	1450	45	T
126	7.50	1650	1	$T + n$
3	7.50	1550	2	$T + n$
237	7.50	1450	23	$T + n'$
247[a]	10.00	1765	1	$T + n$
125	10.00	1650	1	$T + n$
4	10.00	1550	2	$T + n$
238	10.00	1450	23	$T + n'$
109	12.50	1650	1	$T + n$
27	12.50	1550	24	$T + n$
213	12.50	1525	23	$T + n$
178	12.50	1515	24	$T + n'$
190	12.50	1450	41	$T + n'$
248[a]	13.69	1765	1	$T + n$
195	13.69	1540	41	$T + n$
243	13.69	1420	88	T + Cont.SS
110	15.00	1650	1	$T + n$
169	15.00	1525	24	$T + n$
167	15.00	1480	24	$T + n'$
187	15.00	1450	38	$T + n'$
219	15.00	1420	42	Cont.SS
221	15.00	1410	26	Cont.SS
168	15.50	1500	24	$T + n'$
216	15.50	1430	52	n'
111	17.50	1650	1	$T + n$
150	17.50	1550	26	n
151	17.50	1520	26	n
145	17.50	1500	25	n
152	17.50	1480	25	n'
186	17.50	1450	38	n'
224	17.50	1430	73	n'
217	17.50	1420	72	Cont.SS
218	17.50	1410	43	Cont.SS
193	18.50	1480	41	n
189	18.50	1450	41	n'
225	18.50	1430	24	n'
215	19.21	1420	40	Cont.SS
112	20.00	1650	1	n
147	20.00	1550	25	n
149	20.00	1520	25	n
156	20.00	1500	22	n
148	20.00	1480	25	n

TABLE II—*Continued*

Sample no.	Composition (Cr_2O_3 wt%)	Temperature (°C)	Time (hr)	Phases
184	20.00	1450	36	n
198	20.00	1430	45	n
222	20.00	1420	22	Cont.SS
223	20.00	1410	22	Cont.SS
211	21.00	1420	26	Cont.SS
212	21.00	1410	26	Cont.SS
249[a]	21.37	1765	1	n
113	21.37	1650	1	n
119	21.37	1430	45	Cont.SS
206	23.00	1440	25	$CT_6 + n$
207	23.00	1430	23	CT_6 + Cont.SS
244	23.00	1420	100	CT_6 + Cont.SS
114	24.08	1650	1	n
30	24.08	1550	24	n
159	24.08	1520	24	n
138	24.08	1500	20	n
157	24.08	1480	22	n
208	24.08	1440	23	CT_6
201	24.08	1430	47	CT_6
209	25.00	1430	25	$CT_5 + CT_6$
154	26.00	1520	25	n
155	26.00	1500	25	n
153	26.00	1480	25	$CT_5 + n$
250[a]	27.56	1765	1	n
115	27.56	1650	1	n
146	27.56	1550	24	n
158	27.56	1520	22	n
131	27.56	1500	50	$CT_4 + n$
230	27.56	1490	73	$CT_4 + n$
141	27.56	1480	24	CT_5
191	27.56	1450	41	CT_5
202	27.56	1430	47	CT_5
116	30.00	1650	1	n
130	30.00	1550	25	$n + E$
144	30.00	1520	24	$n + E$
135	30.00	1500	25	$CT_4 + n$
139	30.00	1480	27	$CT_4 + CT_5$
245	30.00	1430	70	$CT_4 + CT_5$
127	32.23	1650	1	$n + E$
143	32.23	1550	24	$n + E$
142	32.23	1520	24	$n + E$
132	32.23	1500	50	CT_4
160	32.23	1480	67	CT_4
227	32.23	1420	65	$CT_5 + E$
228	32.23	1410	73	$CT_5 + E$
117	33.00	1650	1	$n + E$
251[a]	35.00	1765	1	$n + E$
118	36.00	1650	1	$n + E$
136	36.00	1500	25	$CT_4 + E$
255[a]	38.80	1765	1	$n + E$
231	38.80	1450	47	$CT_4 + E$

TABLE II—*Continued*

Sample no.	Composition (Cr_2O_3 wt%)	Temperature (°C)	Time (hr)	Phases
17	40.00	1550	2	$n + E$
49	41.00	1550	2	$n + E$
119	42.00	1650	1	$n + E$
241	42.00	1450	45	E
256[a]	43.00	1765	1	$n + E$
120	43.00	1650	1	$n + E$
51	43.00	1550	2	$n + E$
307	44.00	1715	1	$n + E$
52	44.00	1550	2	E
233	45.00	1450	47	E
306	46.00	1715	1	$n + E$
121	46.00	1650	1	E
54	46.00	1550	2	E
305	48.75	1715	1	E
122	48.75	1650	1	E
20	48.75	1550	2	E
234	48.75	1450	47	E
257[a]	50.00	1765	1	E
295	50.00	1715	1	E
123	50.00	1650	1	E
21	50.00	1550	2	E
240	50.00	1450	45	$E + C$
300	55.00	1715	1	E
254[a]	60.00	1765	1	$E + CT$
296	60.00	1715	1	$E + CT$
124	60.00	1650	1	$E + C$
22	60.00	1550	2	$E + C$
239	60.00	1450	45	$E + C$
287[a]	63.00	1715	1	$E + CT$
264[a]	63.00	1700	44	$E + CT$
302	64.54	1715	1	$E + CT$
265[a]	64.54	1700	44	$E + CT$
328[a]	64.54	1680	48	$E + CT$
327[a]	65.00	1650	43	$E + C$
329[a]	65.54	1680	48	CT
260[a]	66.54	1765	24	$CT + C$
291	66.54	1715	1	$CT + C$
267[a]	66.54	1700	44	$CT + C$
330[a]	66.54	1680	48	$CT + C$
268[a]	67.54	1700	44	$CT + C$
261[a]	70.00	1765	24	$CT + C$
102	70.00	1650	1	$E + C$
23	70.00	1550	2	$E + C$
258[a]	80.00	1765	1	$CT + C$
298	80.00	1715	1	$CT + C$
24	80.00	1550	2	$E + C$
259[a]	90.00	1765	1	$CT + C$
299	90.00	1715	1	$CT + C$
25	90.00	1550	2	$E + C$

[a] Heated in a sealed platinum–rhodium 20% capsule: $T = TiO_2$ (rutile), $C = Cr_2O_3$, $CT = Cr_2TiO_5$, $CT_4 = Cr_2Ti_4O_{11}$, $CT_5 = Cr_2Ti_5O_{13}$, $CT_6 = Cr_2Ti_6O_{15}$, Cont.SS = Continuous solid solution, n, n' = High-temperature phase, E = E phase

mination of the phases present in the quenched specimen was carried out using Cu$K\alpha$ radiation through an X-ray diffractometer (JDX-7F, JEOL Co. Ltd., Japan) with a graphite monochrometer. The guaranteed chemicals of Si, SiO_2 (low quartz), or NaCl were added as an internal standard, and slow scan rates (¼°/min) were used to measure the lattice parameter or *d*-spacing. The electron diffraction patterns with H-700 TEM were also observed in order to confirm the structures of the compounds with crystallographic shear structures.

Results

The results obtained in the present study were summarized in Fig. 1 and Table II. In the Cr_2O_3–TiO_2 system, the following compounds existed above 1400°C: *E* phase, Cr_2TiO_5, $Cr_2Ti_{n-2}O_{2n-1}$ ($n = 6, 7, 8$), a continuous solid solution ($n > 8$), rutile, chromia, and high-temperature phases *n* and *n′*.

E phase

The *E* phase, which was first identified by Hamelin (*1*), existed in the wide homogeneity range and extended to the composition of the higher chromia content as the temperature increased. Figure 2 shows the changes of *d*-spacing of the *E* phase as a function of chromia content at several temperatures.

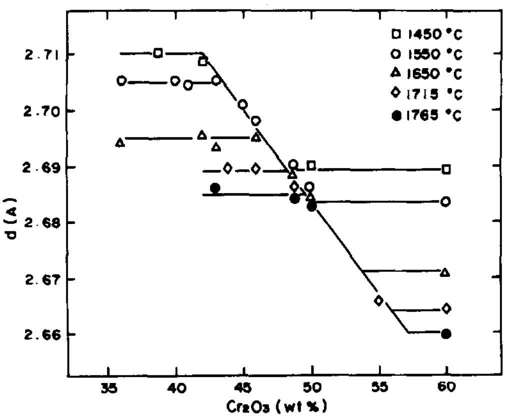

FIG. 2. Changes in the *d*-spacing of the *E* phase as a function of Cr_2O_3 content.

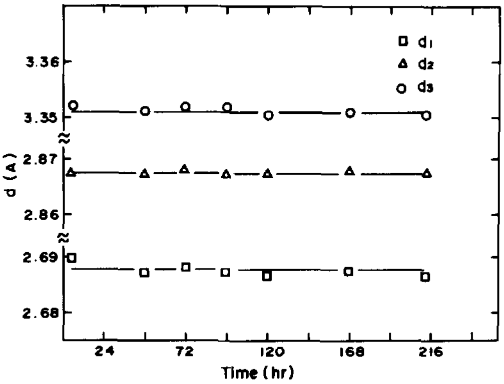

FIG. 3. Changes in the *d*-spacing of the *E* phase (48.75 wt% Cr_2O_3) as a function of heating time at 1500°C.

Continuous changes in *d*-spacing were observed in a region of the single *E* phase and *d*-spacing remained constant at values of 2.710 ± 0.002 and 2.689 ± 0.002 Å at 1450°C in the range of the coexistence with $Cr_2Ti_4O_{11}$ and Cr_2O_3, respectively. The homogeneity range was from 42 to 49 wt% Cr_2O_3 at 1450°C and 50 to 57 wt% Cr_2O_3 at 1765°C. The changes of *d*-spacings obtained from the X-ray diffraction lines at angles around 33 (d_1), 31 (d_2), and 27° (d_3) in 2θ were also illustrated in Fig. 3 as a function of time at 1500°C. There were no detectable changes with heating time longer than at least 2 hr, which may suggest that the reaction to form the *E* phase was completed within a few hours at the temperature range employed in the present work.

Cr_2TiO_5

The existence and the stable region of a new compound with the composition corresponding to $Cr_2O_3 \cdot TiO_2$ ($n = 3$) were found and confirmed in the present work. This compound was stable above 1660 ± 10°C and gave the diffraction pattern closely related to, but in part clearly distinguishable from, that of the *E* phase shown in Fig. 4. Figure 5 illustrated the patterns of quenched specimens after heating above 1660°C with compositions of (a) 64.54, (b) 65.54 (equivalent to $Cr_2O_3 \cdot TiO_2$), and (c) 66.54 wt% Cr_2O_3. Only Cr_2TiO_5 was formed at the stoichiometric composition of 65.54

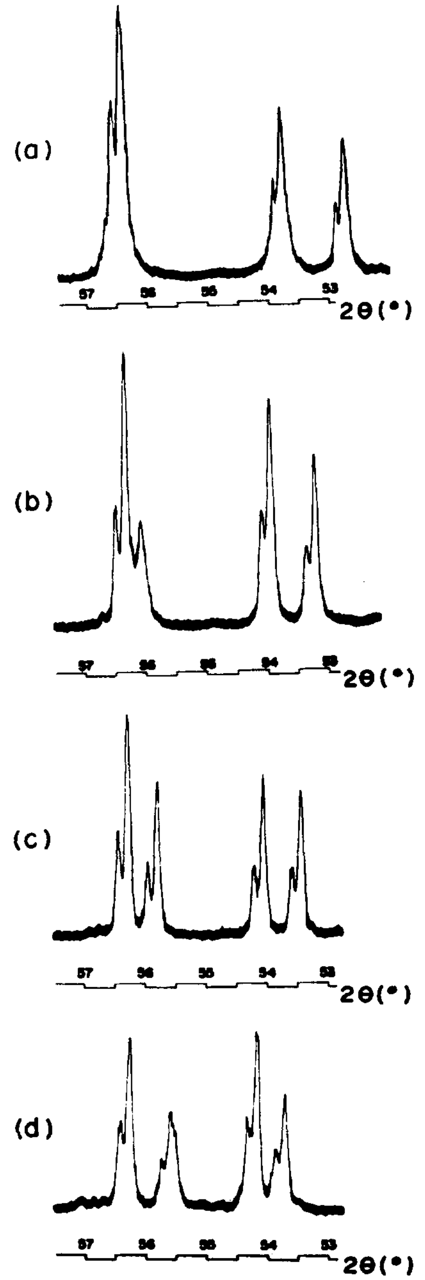

FIG. 4. X-ray powder diffraction patterns of the Cr_2TiO_5 and the *E* phase, (a) 65.54 wt% (Cr_2TiO_5), (b) 55.00 wt%, (c) 48.75 wt%, (d) 42.00 wt% Cr_2O_3.

wt% Cr_2O_3 as shown in Fig. 5b, while the coexistence of a very small amount of the *E* phase or Cr_2O_3 was detected on the diffraction patterns of Fig. 5a or (c). The result was

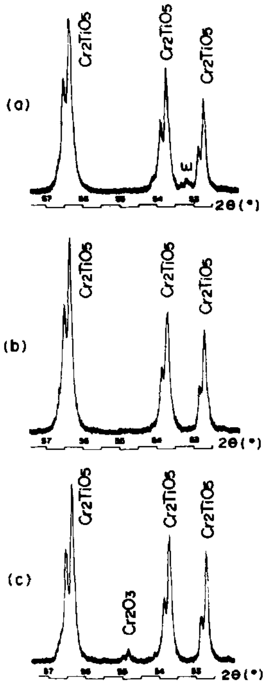

FIG. 5. X-ray powder diffraction patterns of the specimens heated at 1680°C containing, (a) 64.54 wt%, (b) 65.54 wt%, (c) 66.54 wt% Cr_2O_3.

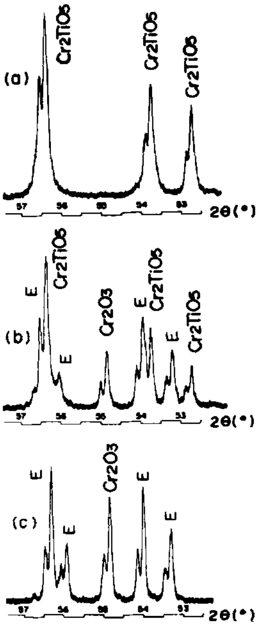

FIG. 6. Changes in the X-ray powder diffraction patterns for the Cr_2TiO_5 compound during reheat treatment in a sealed capsule. (a) Cr_2TiO_5, (b) after 2 hr at 1640°C, (c) after 24 hr at 1600°C.

considered to show that the compound Cr_2TiO_5 had no solid solubility of Cr_2O_3 or TiO_2 within an experimental error but just existed as a single phase. Cr_2TiO_5 was then decomposed gradually to the E phase and chromia by reheating below 1660°C. The changes in the X-ray diffraction pattern during the decomposing process of Cr_2TiO_5 were shown in Fig. 6. The system was composed of three phases of the E phase, chromia, and Cr_2TiO_5 when the compound Cr_2TiO_5 was reheated in a sealed capsule for 2 hr at 1640°C, and furthermore, the Cr_2TiO_5 compound disappeared completely by reheat treatment at 1600°C for 24 hr.

$Cr_2Ti_{n-2}O_{2n-1}$ *(n = 6, 7, and 8) and a Continuous Solid Solution*

A series of discrete oxides with a general formula $Cr_2Ti_{n-2}O_{2n-1}$, with $n = 6, 7, 8$, existed as single phases at temperatures employed in the present study. Stable temperature regions for these homologs were as follows: $Cr_2Ti_4O_{11}$, 1425 to 1510°C; $Cr_2Ti_5O_{13}$, below 1485°C; $Cr_2Ti_6O_{15}$, below 1445°C. $Cr_2Ti_5O_{13}$ and $Cr_2Ti_6O_{15}$ decomposed to a high-temperature phase n and the corresponding adjacent higher member of the series above 1485 and 1445°C, respectively. $Cr_2Ti_4O_{11}$ also decomposed to two phases of $Cr_2Ti_5O_{13}$ and the E phase below 1425°C and of the n phase and the E phase above 1510°C.

The X-ray diffraction studies in the present work could not reveal the existence of another member of the series, $Cr_2Ti_7O_{17}$ ($n = 9$), because the phase with composition of $n = 9$ gave the X-ray diffraction pattern quite similar to that of $Cr_2Ti_6O_{15}$ ($n = 8$), and the resolving power of the X-ray diffraction was not high enough to identify the diphasic region of $n = 8$ and $n = 9$. On the contrary, electron diffraction studies revealed that the heat-treated specimen with the composition of $Cr_2O_3 \cdot 7TiO_2$ ($n = 9$) gave super lattice spots to the high index of rutile close to $(121)_r$, while $n = 9$ $(121)_r$ CS phase was not found. A high-index CS phase also coexisted, associated with the $n = 8$ $(121)_r$ CS member at a composition of between $n = 8$ and $n = 9$ (23 wt% Cr_2O_3). The typical $[1\bar{1}1]_r$ zone axis diffraction patterns which were obtained from the quenched specimen containing 23 wt% Cr_2O_3 were shown in Fig. 7. The specimens in the composition range of less than 22 wt% Cr_2O_3 no longer gave electron diffraction patterns corresponding to $n = 8$ or $n = 9$ $(121)_r$ CS phases, and the direction of the characteristic super lattice

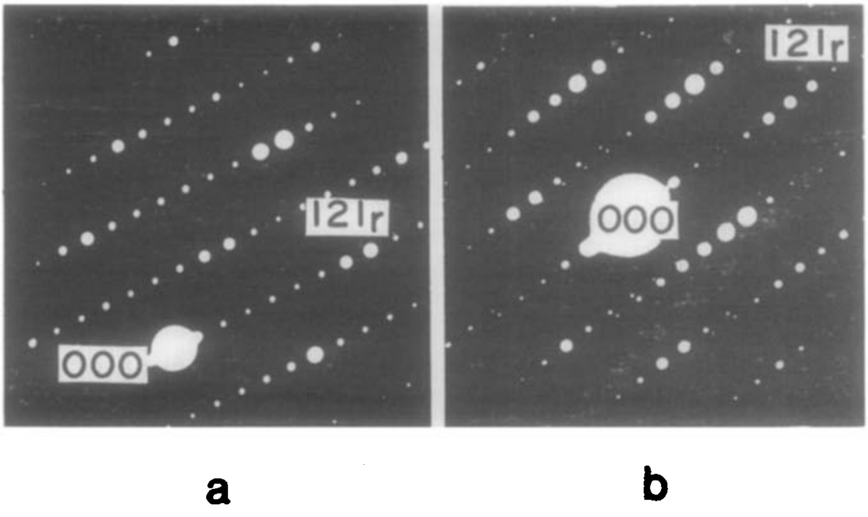

FIG. 7. $[1\bar{1}1]_r$ zone axis diffraction pattrns (a) $n = 8$ $(121)_r$ CS, (b) high index CS close to $(121)_r$.

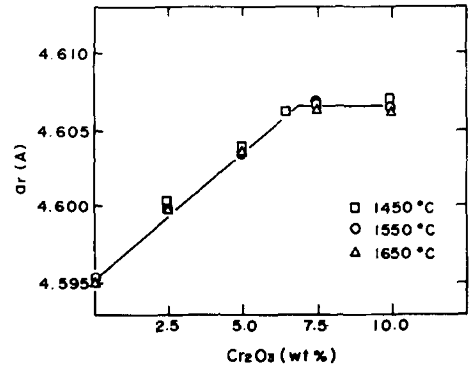

FIG. 8. Changes in the lattice parameter a_r of rutile as a function of Cr_2O_3 content.

spots were continuously reoriented as the chromia content decreased until 14 wt% Cr_2O_3. Therefore, the present results suggested that a continuous solid solution existed in the composition range of 14 to 22 wt% Cr_2O_3 below 1425°C. This continuous solid solution coexisted with rutile in a range of less than 14 wt% Cr_2O_3.

Rutile and Chromia

Both rutile and chromia existed as solid solutions. The lattice parameter of chromia decreased with the addition of rutile above 1550°C and the region of chromia solid solution increased as the temperature was raised. Figure 8 showed the change of the lattice parameter a_r of rutile as a function of a chromia content at several temperatures. The slight increase of a_r was observed up to 7 wt% Cr_2O_3, at which the solid solubility of rutile was limited to a temperature range of 1450 to 1650°C.

High-Temperatures Phases n and n'

The continuous solid solution was transformed to the high-temperature phase *n'* above 1425°C. This transformation occurred reversibly as suggested by Flörke *et al.* (*5*). The high-temperature form *n'* existed at temperatures between 1425 and 1520°C and the region of the *n'* phase became narrow and the other high-temperature phase *n* appeared as the temperature was raised. Both *n* and *n'* phases gave X-ray patterns similarly to one another and they were clearly different from those of the continuous solid solution, but some lines of the *n* phase were strongly diffused as shown in Fig. 9.

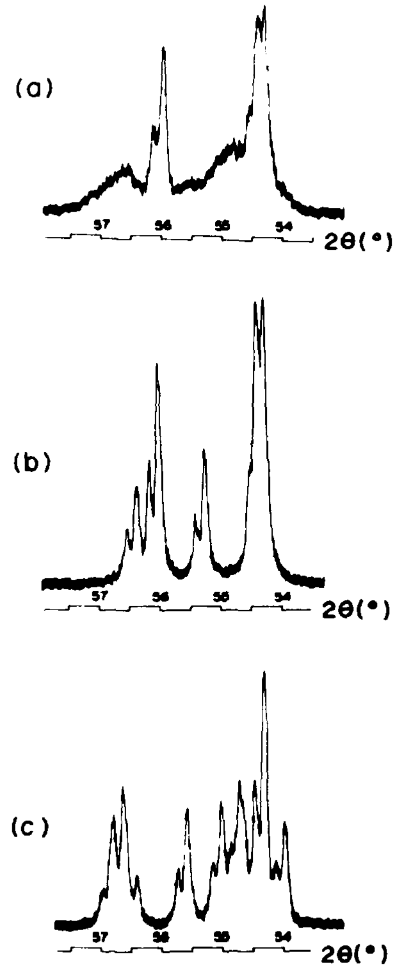

FIG. 9. X-ray powder diffraction patterns of the specimens containing 17.50 wt% Cr_2O_3. (a) *n* phase, (b) *n'* phase, (c) the continuous solid solution.

Discussion

Åsbrink *et al.* (*13*) first reported that a very small amount of the compound based on the V_3O_5-type structure appeared after arc melting of the sample with $Cr_2O_3{\cdot}TiO_2$ composition. They presumed the compound was Cr_2TiO_5 which had neither pseudobrookite nor Ti_3O_5-

type (*18*) structure. However, the conditions were far from those at equilibrium in the sample of Åsbrink *et al.* Kwestroo *et al.* heat-treated the sample with $Cr_2O_3 \cdot TiO_2$ composition at 1300°C and reported that the compound corresponding to Cr_2TiO_5 was never formed without stabilization by the addition of Fe (*11*). Hamelin also found an unknown phase *W* to be analogous to the V_3O_5-type structure in the ternary Al_2O_3–Cr_2O_3–TiO_2 system (*19*). In this work, the existence of the compound Cr_2TiO_5 above 1660 ± 10°C as a single phase and also the stability region of the compound Cr_2TiO_5 which decomposed to the *E* phase and chromia below 1660°C were made clear. The results led to the conclusion that failure to form Cr_2TiO_5 below 1660°C was not simply due to the kinetic problem but rather due to its thermodynamic stability. More recently, the authors reported the existence of another unknown phase *A* showing the solid solubility in the Cr_2O_3–MgO–TiO_2 system (*20*). The *A* phase lay on the tie line between $MgTi_2O_5$ and Cr_2TiO_5 at 1400°C. All of these results may suggest that Cr_2TiO_5 has the structure based on the V_3O_5-type structure and is stabilized by Mg as well as by Fe or Al.

The *E* phase had the homogeneity range as determined in the present study by the precise measurement of the changes of *d*-spacing with the composition over a wide temperature range. X-ray diffraction patterns of the *E* phase were related to those of series of $(Cr,Fe)_2Ti_{n-2}O_{2n-1}$ derived from the α-PbO_2 structure. Further studies on the structure of the *E* phase are proceeding from the viewpoints of whether the region of the *E* phase is composed of a number of closely related phases based on either V_3O_5-type structure or the continuous intergrowth phases.

The earlier X-ray diffraction studies reported the existence of the series of oxides with $Cr_2Ti_{n-2}O_{2n-1}$ ($n = 6$, 7, 8 and 9) and found these phases to be the members of $(121)_r$ CS family (3). Recently, Philip and Bursill (*9*, *10*) revealed the fine structural aspects on a rutile with up to 24 wt% Cr_2O_3 at 1300°C using an electron microscope. They found that crystallographic shear planes cooperatively reoriented from $(253)_r$ to $(121)_r$ around the $[1\bar{1}1]_r$ zone axis for 8 to 24 wt% Cr_2O_3 and claimed that the highest member of the $(121)_r$ CS family was not $n = 9$ but $n = 8$. The present X-ray work could not solve the question on the existence of $Cr_2Ti_7O_{17}$ ($n = 9$) because of its insufficient resolving power. The present electron diffraction studies, however, showed results similar to Philp *et al.*, that is, the specimen with stoichiometric $Cr_2O_3 \cdot 7TiO_2$ composition gave no characteristic super lattice spots along to $(121)_r$, but only the CS phase with high index close to $(121)_r$. The results suggest that the continuous solid solution, reoriented from $(253)_r$ to $(121)_r$ CS phase, proposed by Philp *et al.* would be retained at least up to 1425°C. Further electron microscopic studies on these phases are in progress.

The continuous solid solution were transformed to the *n'* phase above 1425°C, and again to another high-temperature form *n* as the temperature was raised. First, the effect of quenching process on the phase changes of the *n* and *n'* was taken into account. After quenching quickly in cold water, the *n'* phase gave sharp X-ray diffraction lines which were obviously different from those of the continuous solid solution, while another high-temperature *n* phase showed characteristic diffused X-ray lines. On the other hand, both *n* and *n'* showed almost the same X-ray diffraction patterns, both of which showed further diffused X-ray diffraction lines especially at low angles after cooling down slowly in air. Thus, one could still distinguish between *n* and *n'* phases from the X-ray diffraction patterns of rapidly quenched samples. The present results did not show the existence of the diphasic region of the high-temperature phase and the continuous solid solution as reported by Werner (*8*). The transformation between the continuous solid solution and the high-temperature phases was confirmed to be reversible. Both *n* and *n'* were transformed completely to the continuous solid solution after reheat-treatment in a sealed capsule even after 2 hr at 1390°C.

Preliminary examinations of the *n* phase with an electron microscope showed that it consisted of a variety of features, in particular disordered twin lamella over the whole thin crystal fragment. The disordered features in the microstructure of the *n* phase are presumably considered to be responsible for making the X-ray diffraction lines diffusive. Recently, Bursill *et al.* (*21*) found a new CS phase in the Fe_2O_3–TiO_2 system above 1450°C mainly using an electron diffraction technique. They reported that the compounds in the range of 14 to 16 wt% Fe_2O_3 may be described as $(020)_r$ CS phase and transformed reversibly to the $(121)_r \sim (132)_r$ CS family based on an ordered rutile structure below 1450°C. The present phase analysis and preliminary electron microscopic studies indicate that the similar transformation might also occur in the Cr_2O_3–TiO_2 system. However, the effect of quenching process on the concentration of the strain in the high-temperature *n* and *n′* phases should be taken into account by applying the *in situ* electron microscopic observation method at high temperatures. The studies on the transformation of the phases at high temperatures and the structural analysis of the phase are undertaken using the high-temperature X-ray diffraction and electron microscopic techniques.

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