Phase Relationship in the V-C-O Ternary System*

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The V-C-O ternary specimens placed in alumina or zirconia tubes were sealed in silica tubes under vacuum, annealed at 1000–1150°C, and then quenched into water. The phases in the specimens were identified and the lattice parameters of the phases having the *fcc* crystal structure were determined by X-ray diffraction analysis. It was confirmed that a continuous solid solution exists between the VC phase and the VO phase. The phase relationships of the V-C-O ternary system have been determined at temperatures in the vicinity of 1373 K (1100°C).

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I. Introduction

For a study of the carbothermic reduction of vanadium oxides, an exact knowledge of the phase relationship in the V-C-O system is of great help. The phase relationships in this system were reported first by Gurevich and Ormont⁽¹⁾, then by Worrell and Chipman⁽²⁾, and recently by Brauer and Reuther⁽³⁾. Both the phase diagrams given by Gurevich and Ormont (Fig. 1(a)) and by Worrell and Chipman (Fig. 1(b)) include broad VC-VO solid solutions, whereas the phase diagram shown by Brauer and Reuther (Fig. 1(c)) does not include any VC-VO solid solution and instead a V₂O₃-V₂C two phase region is drawn. In the course of the investigation of carbothermic reduction of V₂O₃ by X-ray diffraction, a question of the existence of the broad VC-VO solid solution and the V₂O₃-V₂C two-phase region was raised and the phase relationships of the V-C-O ternary system were reinvestigated.

II. Experimental Procedures

Specimens of the V-C-O ternary system were prepared from the following starting materials: vanadium(V) oxide, vanadium(III) oxide, vanadium oxides(VO_{1.273}, VO_{0.888}, VO_{0.589}, and VO_{0.527})[†], vanadium carbides(VC_{0.970}, VC_{0.576}, and VC_{0.537})[†], vanadium oxide carbide(VO_{0.190}C_{0.186})[†], and acetylene black. The vanadium(V) oxide, V₂O₅, was of a guaranteed reagent grade, and the vanadium(III) oxide, V₂O₃, was prepared by the hydrogen reduction of V₂O₅ at 800–900°C for 3 h. The vanadium oxides(VO_{1.273}, VO_{0.888}, VO_{0.589}, and VO_{0.527}) were prepared from V₂O₃ and vanadium metal(99.8% purity) by arc-melting with a tungsten electrode in an argon atmosphere. The vanadium carbides(VC_{0.970}, VC_{0.576}, and VC_{0.537}) and vanadium oxide carbide(VO_{0.190}C_{0.186}) were prepared by the reduction of V₂O₃ with acetylene black in a vacuum. The vanadium contents of the above starting materials were determined gravimetrically by the oxidation of finely powdered materials at 800°C for 2 h in air. The oxygen contents of the vanadium carbides(VC_{0.970}, VC_{0.576}, and VC_{0.537}) were determined by

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† VO_{1.273}, VO_{0.888}, VO_{0.589}, VO_{0.527}, VC_{0.970}, VC_{0.576}, VC_{0.537}, and VO_{0.190}C_{0.186} denote only the chemical compositions of the materials, and are not the chemical formulae of the materials.

Fig. 1 (a) Solid phases of the V-C-O system in the temperature range of 1253–2223 K by Gurevich and Ormont⁽¹⁾. (b) Solid phases of the V-C-O system above 1300 K and at 1 atm CO pressure by Worrell and Chipman⁽²⁾. (c) Isothermal section of the V-C-O system at about 1573 K by Brauer and Reuther⁽³⁾. (d) Phase diagram of the V-C system by Rudy, Windish and Brukl⁽⁴⁾. (e) Phase diagram of the V-O system by Alexander and Carlson⁽¹²⁾. (f) Phase relationships of the V-C-O system at temperatures in the vicinity of 1373 K (1100°C). I: V₂O₃+VC(O)+C, II: V₂O₃+VC-VO solid solution, III: VC-VO solid solution, IV: VC-VO solid solution+ζ, V: VO(C)+V₂C+ζ, VI: VO(C)+V₂C, VII: VO(C)+V₂C+V₂O, VIII: V₂O+V₂C, IX: V₂O+V₂C+V₄O, X: V₂C+V₄O, XI: V₂C+V₄O+V, XII: V₂C+V.

coulometric titration with an oxygen analyzer (Kokusai Denki Co., Coulomatic O, Model VK-2A), and were 0.02, 0.18, and 0.18 wt%, respectively. The carbon content of the vanadium oxide carbide (VO_{0.190}C_{0.186}) was determined by coulometric titration with a carbon analyzer (Kokusai Denki Co., Coulomatic C, Model VK-1C).

Specimens of the V-C-O ternary system were prepared in the following manner. Two or three kinds of the starting materials were

mixed at desired mixing ratios in an alumina mortar, and then compacted into cylinders of a 7.5 mm diameter and an about 20 mm height with a specific load of 270 MPa. These compacted bodies, each weighing 2.2–2.5 g, were placed in alumina tubes or zirconia tubes (sealed at one end) having an 8 mm inside diameter and a 40 mm length, and these tubes were plugged with zirconia disks. Specimen No. 48 in Table 1 was prepared by pressing the vanadium oxide carbide (VO_{0.190}C_{0.186}) in

Table 1 The compositions of the specimens, the phases before heat-treatment and after heat-treatment, and the lattice parameters of the phases having the *fcc* structure (VC, VO, and VC-VO solid solution).

No.	Composition(at%)			Phases before heat-treatment	Phases after heat-treatment	Lattice parameter(nm)
	V	C	O			
1	39.0	10.0	51.0	V ₂ C, V ₂ O ₅	FCC, V ₂ O ₃ , C	—
2	36.0	30.0	34.0	VC, V ₂ O ₅ , C	FCC, V ₂ O ₃ , C	0.4167
3	46.0	50.0	4.0	VC, V ₂ O ₅ , C	FCC, V ₂ O ₃ , C	0.4166
4	52.1	43.4	4.5	VC, V ₂ C, V ₂ O ₃	FCC, V ₂ O ₃	0.4165
5	52.0	42.0	6.0	VC, V ₂ C, V ₂ O ₃	FCC, V ₂ O ₃	0.4165
6	54.0	42.0	4.0	VC, V ₂ C, V ₂ O ₃	FCC, V ₂ O ₃	0.4153
7	54.0	40.0	6.0	VC, V ₂ C, V ₂ O ₃	FCC, V ₂ O ₃	0.4150
8	56.0	40.0	4.0	VC, V ₂ C, V ₂ O ₃	FCC	0.4143
9	56.0	38.0	6.0	VC, V ₂ C, V ₂ O ₃	FCC	0.4138
10	58.0	38.0	4.0	VC, V ₂ C, V ₂ O ₃	FCC, V ₂ C, ζ	0.4136
11	58.0	36.0	6.0	VC, V ₂ C, V ₂ O ₃	FCC, V ₂ C, ζ	0.4134
12	60.0	36.0	4.0	VC, V ₂ C, V ₂ O ₃	FCC, V ₂ C	0.4135
13	59.8	32.6	7.6	V ₂ C, V ₂ O ₅	FCC, V ₂ C	0.4135
14	58.0	34.0	8.0	VC, V ₂ C, VO	FCC, V ₂ C, ζ	0.4136
15	56.0	36.0	8.0	VC, V ₂ C, V ₂ O ₃	FCC, V ₂ C, ζ	0.4135
16	59.9	31.0	9.1	V ₂ C, V ₂ O ₃	FCC, V ₂ C	0.4134
17	58.0	32.0	10.0	VC, V ₂ C, V ₂ O ₃	FCC, V ₂ C	0.4135
18	56.0	34.0	10.0	VC, V ₂ C, V ₂ O ₃	FCC, V ₂ C, ζ	0.4135
19	56.0	32.0	12.0	VC, V ₂ C, V ₂ O ₃	FCC, V ₂ C, ζ	0.4134
20	56.7	26.1	17.2	V ₂ C, V ₂ O ₃	FCC, V ₂ C	0.4135
21	53.5	26.1	20.4	V ₂ C, V ₂ O ₅	FCC, V ₂ C, ζ	0.4134
22	54.6	24.9	20.5	VC, V ₂ C, V ₂ O ₃	FCC, V ₂ C, ζ	0.4135
23	53.9	21.6	24.5	V ₂ C, V ₂ O ₃	FCC, V ₂ C	0.4134
24	50.9	23.3	25.8	V ₂ C, V ₂ O ₅	FCC	0.4137
25	50.8	21.3	27.9	V ₂ C, V ₂ O ₅	FCC	0.4136
26	50.0	20.0	30.0	V ₂ C, V ₂ O ₅	FCC, V ₂ O ₃	0.4137
27	51.3	17.6	31.1	V ₂ C, V ₂ O ₃	FCC, V ₂ C	0.4134
28	50.1	15.8	34.1	V ₂ C, V ₂ O ₃	FCC, V ₂ C	0.4134
29	49.0	14.0	37.0	V ₂ C, V ₂ O ₃	FCC, V ₂ O ₃	0.4134
30	46.9	10.7	42.4	V ₂ C, V ₂ O ₃	FCC, V ₂ O ₃	0.4135
31	44.9	7.7	47.4	V ₂ C, V ₂ O ₃	FCC, V ₂ O ₃	0.4135
32	43.2	4.9	51.9	V ₂ C, V ₂ O ₃	FCC, V ₂ O ₃	0.4135
33	41.5	2.4	56.1	V ₂ C, V ₂ O ₃	FCC, V ₂ O ₃	—
34	44.0	2.0	54.0	V ₂ C, VO, V ₂ O ₃	FCC, V ₂ O ₃	0.4135
35	46.0	4.0	50.0	V ₂ C, VO, V ₂ O ₃	FCC, V ₂ O ₃	0.4133
36	46.0	2.0	52.0	V ₂ C, VO, V ₂ O ₃	FCC, V ₂ C	0.4133
37	48.0	4.0	48.0	V ₂ C, VO, V ₂ O ₃	FCC, V ₂ C	0.4135
38	48.0	2.0	50.0	V ₂ C, VO, V ₂ O ₃	FCC, V ₂ C	0.4114
39	50.0	4.0	46.0	V ₂ C, VO, V ₂ O ₃	FCC, V ₂ C	0.4109
40	50.0	2.0	48.0	V ₂ C, VO, V ₂ O ₃	FCC, V ₂ C	0.4088
41	52.0	4.0	44.0	V ₂ C, VO, V ₂ O ₃	FCC, V ₂ C	0.4085
42	52.0	2.0	46.0	V ₂ C, VO, V ₂ O ₃	FCC, V ₂ C	0.4070
43	54.0	2.0	44.0	V ₂ C, V ₂ O, V ₂ O ₃	FCC, V ₂ C, V ₂ O	0.4065
44	56.0	2.0	42.0	V ₂ C, V ₂ O, V ₂ O ₃	FCC, V ₂ C, V ₂ O	0.4034
45	58.0	2.0	40.0	V ₂ C, V ₂ O, V ₂ O ₃	FCC, V ₂ C, V ₂ O	—
46	67.0	10.0	23.0	V ₂ C, V ₂ O, V ₄ O	V ₂ C, V ₂ O	
47	70.8	10.0	19.2	V ₂ C, V ₂ O, V ₄ O	V ₂ C, V ₂ O, V ₄ O	
48	72.7	13.5	13.8	V ₂ C, V ₄ O	V ₂ C, V ₄ O	

FCC refers to the phases having the *fcc* structure (VC, VO, and VC-VO solid solution).

the same manner. Next, the alumina or zirconia tubes were placed in silica tubes and then the silica tubes were sealed under vacuum. The volumes of the silica capsules were made as small as possible in order to minimize the composition shift due to the evolution of CO gas during the subsequent annealing^{††}. The specimens placed in the silica capsules were annealed at the desired temperatures of 1000–1150°C for 50–835 h, and then quenched into water. The phases formed in the specimens were identified by X-ray diffraction analysis. The identification of the phases was made on the basis of the X-ray diffraction data given by the investigator listed in Table 2. The X-ray diffraction analysis was carried out by use of an X-ray diffractometer (Rigaku Denki, Model SG-7) with a Ni-filtered CuK α radiation. The lattice parameters of the VC and VO phases were determined with silicon as an internal standard. The free carbon contents of specimens Nos. 1, 2 and 3 after annealing were determined in the following manner: A portion of a sample was powdered finely, and dissolved in a mixture of hydrochloric acid and nitric acid in a volume ratio of 2:1, and undissolved carbon flakes were filtered off with a glass filter (Tokyo Roshi Co., No. GB 100), then washed

with water, and finally dried at 130°C in a dryer. The separated carbon flakes together with the glass filter were heated to red for the determination of the free carbon content.

III. Results and Discussion

The compositions of the specimens, the phases in the specimens before and after heat-treatment, and the lattice parameters of the phases having the *fcc* structure in the specimens after heat-treatment (hereinafter described as *FCC*) are summarized in Table 1. On the basis of the results of Table 1, the phase relationships of the V–C–O ternary system were determined as shown in Fig. 1. Specimens Nos. 8, 9, 24 and 25 gave the X-ray diffraction patterns of the single phase of *FCC*, as shown in Fig. 2. In addition, the lattice parameters of specimens Nos. 8, 9, 24 and 25 were 0.4143, 0.4138, 0.4137 and 0.4136 nm, respectively, thus, the lattice parameter of *FCC* decreased as the oxygen content increased. These two facts indicate that each of specimens Nos. 8, 9, 24 and 25 was a single phase of *FCC*, that is, a VC–VO solid solution. In the Ti–C–O system, the TiC phase and the TiO phase have the same *fcc* structure of the NaCl-type, and a continuous solid solution connecting the TiC phase and the TiO phase exists. The lattice parameter of this solid solution decreases as the oxygen content increases⁽¹⁵⁾. In the V–C–O system also, the VC phase and the VO phase have the same *fcc* structure of the NaCl-type, and the lattice parameter of the former increases from 0.4131 nm at VC_{0.75} to 0.4173 nm at VC_{0.89} with increasing carbon content⁽⁴⁾, while that of the latter increases 0.4027 nm at VO_{0.86} to 0.4138 nm at VO_{1.25} with increasing oxygen content⁽⁸⁾, so that the lattice parameter of the low-carbon VC phase is almost

Table 2 References adopted for the identification of the VC, V₂C, ζ , VO, V₂O, V₄O, and V₂O₃ phases.

Phase	Crystal structure	Investigators and references
VC	<i>fcc</i>	Rudy, Windisch and Brukl ⁽⁴⁾ , Storms ⁽⁵⁾
V ₂ C	hexagonal	Storms and McNeal ⁽⁶⁾ , Storms ⁽⁵⁾
ζ	rhombohedral	Yvon and Parthé ⁽⁷⁾ , Storms and McNeal ⁽⁶⁾
VO	<i>fcc</i>	Reuther and Brauer ⁽⁸⁾
V ₂ O	monoclinic	Hiraga and Hirabayashi ⁽⁹⁾ , Westman ⁽¹⁰⁾ , Cambini ⁽¹¹⁾
V ₄ O	<i>bct</i>	Alexander and Carlson ⁽¹²⁾ , Henry, O'Hare, McCune and Krug ⁽¹³⁾
V ₂ O ₃	rhombohedral	Hiraga and Hirabayashi ⁽¹⁴⁾ , ASTM card No. 1-1293

†† The volume of a silica capsule was about 10 cm³. The composition shift due to the evolution of CO gas is evaluated to be less than 0.13 wt%.

Fig. 2 X-ray diffraction pattern of specimen No. 24, (CuK α).

the same as that of the high-oxygen VO phase. Therefore, the formation of the continuous solid solution connecting the low-carbon VC phase and the high-oxygen VO phase is enough probable. The VC phase contains carbon vacancies, that is, carbon atoms are deficient against vanadium atoms, while the high-oxygen VO phase contains vanadium vacancies, that is, oxygen atoms are excess against vanadium atoms. Therefore, it is considered that the VC-VO continuous solid solution is formed in such a way that the excess oxygen atoms in the VO phase enter carbon vacancies in the VC phase, and excess vanadium atoms in the VC phase enter vanadium vacancies in the VO phase. Specimens No. 26 and No. 29 were composed of *FCC* and a small amount of the V_2O_3 phase, as shown in Fig. 3(b)†††. If the existence of the VC-VO continuous solid solution is accepted, the oxygen content of *FCC* in specimen No. 26 should be smaller than that in specimen No. 29, and as a result, the lattice parameter of *FCC* in specimen No. 26 should be larger than that of *FCC* in specimen No. 29. This is indeed the case: the lattice parameter of the former was 0.4137 nm and

that of the latter is 0.4134 nm. From the above results and discussion, it is reasonable to draw the conclusion that a continuous solid solution exists between the VC phase and the VO phase. Of the specimens on the line connecting the V_2O_3 phase and the composition of $VC_{0.576}$, specimens Nos. 16, 20, 23, 27 and 28 were composed of the V_2C phase and *FCC* as shown in Fig. 3(a), while specimens Nos. 29, 30, 31, 32 and 33 were composed of the V_2O_3 phase and *FCC* as shown in Figs. 3(b) and 3(c). Therefore, it is considered that the V_2C - V_2O_3 two phase equilibrium proposed by Brauer and Reuther is not set up at 1100°C. Also, it is found that the VC-VO continuous solid solution is very narrow in the high-oxygen region. At higher temperatures the solid solution might be broader as demonstrated by Worrell and Chipman, while at lower temperatures it might separate into the VC phase containing oxygen and the VO phase containing carbon. However, no data have been reported on the two-phase separation.

It has been reported that the ζ phase gives rise to very weak diffraction peaks even in the case of the V-C binary system because of the complexity of its crystal structure⁽⁷⁾. In the present study also, even though the strongest peak was weak, it was clearly detected in specimens Nos. 10, 11, 15, 18, 19 and 21 in region IV and specimens Nos. 14 and 22 in region V, but was not detected in specimens Nos. 27 and 28 in region IV and specimens Nos. 12, 13, 16, 17, 20 and 23 in region V. The reason why the ζ phase was not detected in these specimens is probably that its diffraction peaks are inherently weak and its contents were small. Yvon and Parthé⁽⁷⁾ have reported that it is not possible to obtain the ζ phase without the presence of the V_2C phase and/or the VC phase and that this phenomenon is probably connected with the intimate structural relationship among the V_2C , ζ , and VC phases. In the present study of the V-C-O ternary system also, the ζ phase was always found to coexist with the V_2C phase. This is believed to be due to the epitaxial growth of the ζ phase on the V_2C phase, as reported on the ζ phase by Yvon and Parthé.

The composition ranges of the vanadium

Fig. 3 X-ray diffraction patterns. (CuK α). (a) specimen No. 23, (b) Specimen No. 29, (c) Specimen No. 30, (d) V_2O_3 .

††† The contents of V_2O_3 in these specimens were estimated semi-quantitatively to be one to two mol% from the intensities of the diffraction peaks of the V_2O_3 phase.

phase, the V_4O phase and the V_2O phase shown in Fig. 1(f) are quoted from the phase diagram given by Alexander and Carlson⁽¹²⁾.

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REFERENCES

- (1) M. A. Gurevich and B. F. Ormont: *Zh. Neorg. Khim.*, **3** (1958), 403.
 - (2) W. L. Worrell and J. Chipman: *Trans. Met. Soc. AIME*, **230** (1964), 1682.
 - (3) G. Brauer and H. Reuther: *Z. Anorg. Allg. Chem.*, **402** (1973), 87.
 - (4) E. Rudy, St. Windisch and C. E. Brukl: *Planseeber. Pulvermet.*, **16** (1968), 3.
 - (5) E. K. Storms: *The refractory Carbides*, Academic Press, New York and London, (1967), pp. 53–55.
 - (6) E. K. Storms and R. J. McNeal: *J. Phys. Chem.*, **66** (1962), 1401.
 - (7) K. Yvon and E. Parthé: *Acta Cryst.*, **B26** (1970), 149.
 - (8) H. Reuther and G. Brauer: *Z. Anorg. Allg. Chem.*, **384** (1971), 155.
 - (9) K. Hiraga and M. Hirabayashi: *J. Solid State Chem.*, **14** (1975), 219.
 - (10) S. Westman: *Acta Chem. Scand.*, **17** (1963), 749.
 - (11) M. Cambini, G. Pellegrini and S. Amelinckx: *Mater. Res. Bull.*, **6** (1971), 791.
 - (12) D. G. Alexander and O. N. Carlson: *Met. Trans.*, **2** (1971), 2805.
 - (13) J. L. Henry, S. A. O'Hare, R. A. McCune and M. P. Krug: *J. Less-Common Metals*, **21** (1970), 115.
 - (14) K. Hiraga and M. Hirabayashi: *Trans. JIM*, **16** (1975), 431.
 - (15) H. Nishimura and K. Kimura: *J. Japan Inst. Metals*, **20** (1956), 528.
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