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Single-Crystal Growth of VO_2 by Isothermal Flux-Evaporation

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Single crystals up to 1 cm × 5 mm × 5 mm of VO_2 have been grown by utilisation of the isothermal flux-evaporation principle. The "flux" used is V_2O_5 which results in the formation of a low-melting eutectic with a composition between V_2O_5 and VO_2. Best growth was achieved at 1210° C at a pO_2 of $10^{-3.8}$, yielding crystals up to 2 × 2 × 0.5 cm. The formation of a new oxy-carbonate of vanadium is reported and serves as an illustration of the dangers involved in contamination from "controlled atmospheres".

1. Introduction

At the International Conference on Crystal Growth [1], one of the authors reported on the general applicability of the technique of evaporation of a flux to the growth of refractory oxide crystals. During the same year, other papers, such as that by Tsushima [2], appeared reporting the use of the same method in general. In the paper by Roy, however, reasons were given for the various special advantages of this method, among them, the growth of crystals of a variable valence metal oxide. This paper reports the results on the application of the IFE methods to the growth of VO_2.

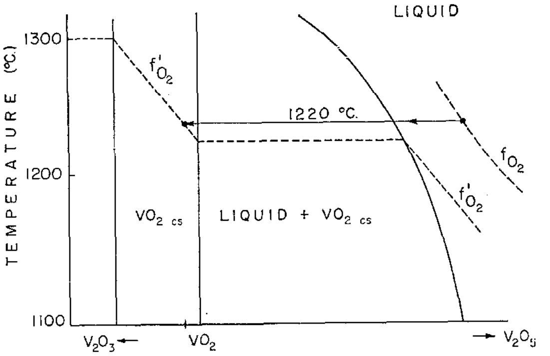

Figure 1 Part of the system V/O, showing liquidus, solidus (after Kachi and Roy) and schematic oxygen fugacity isobars. A liquid is stable at 1220° C and f_{O_2}. If the system is reduced to f'_{O_2} at the same temperature, VO_2 crystals begin to precipitate from the liquid and finally all the liquid is converted to a VO_2 crystalline solution.

Crystals of this phase have been grown previously by various methods, most recently by a melt technique by Sasaki and Watanabe [3] to a maximum dimension of 3 to 4 mm. The most recent equilibrium diagram for the high oxygen end of the system V/O is that of Kachi and Roy [4] reproduced in fig. 1. Examination of this diagram shows that in this particular case, not only can we use the IFE method, but in principle it should be possible to use it without any flux other than the high oxygen melts in the system itself. These circumstances therefore offer us a unique opportunity to test the usefulness of the method. Part of the equilibrium phase diagram of the system V/O is shown in fig. 1. Two schematic oxygen fugacity isobars are also given in the figure (labelled as f_{O_2} and f'_{O_2}). If the starting material with a composition of V_2O_5 is held at a certain temperature, say, 1220° C, it is completely liquid when in equilibrium with a gas phase with an oxygen fugacity of f_{O_2} (fig. 1). When the oxygen fugacity is decreased to f'_{O_2} by use of appropriate gas mixtures, the composition of the liquid will move across the isotherm till it encounters the liquidus. At this temperature, as more oxygen is removed, VO_2 precipitates from a liquid of fixed composition. This is the desired condition for growth. Finally, the whole batch may be converted to crystalline VO_2. The whole process takes place at a constant temperature, and the composition of the final solid solution of the VO_2 precipitating is fixed by the temperature and f_{O_2} as shown in fig. 1. By selecting the f_{O_2} and temperature the equilibrium solid solution can be made to approach the precipitating phase quite closely.

2. Experimental

A platinum-wound vertical quench furnace with a mullite muffle 25 mm in inner diameter was used. In most runs the charge was put in a cylindrical container of platinum with a diameter ranging from 5 to 19 mm and suspended near the hot point of the furnace with a Pt-Pt90Rh10 thermocouple placed very close to the crucible. (It was found that when the thermocouple was exposed to vanadium oxide vapour, it became contaminated very rapidly and the emf increased considerably. To avoid contamination, the thermocouple was sealed in mullite tubing wrapped with platinum foil.) The top of the platinum container was covered with platinum foil leaving only a small opening (2 to 3 mm) in order to avoid too rapid evaporation of the liquid. To obtain the desired oxygen fugacity, pure CO_2 was found to be nearly ideal. The CO_2 gas was fed through a flow-meter from the bottom of the furnace and let out at the top. The starting material used was powder of Baker's analysed V_2O_5.

3. Results

More than 30 runs were made in order to determine the optimum conditions for growth. The best yield was obtained with the following set of conditions.

Size of container:	cylinder 19 mm in diameter
Temperature:	1210 to 1220° C
f'_{O_2}:	$= 10^{-3.8}$ atm
Flow-rate of CO_2:	$5 \sim 8$ cm^3/sec
Duration of run:	$30 \sim 50$ h

The VO_2 single crystals usually formed on the bottom of the container; the best of these is shown in fig. 2. Its upper surface, in contact with the liquid, is smooth and convex upward. For the runs lasting 30 to 50 h, maximum thickness obtained was about 5 mm with a 2 cm diameter. A few fine cracks which filled up with a film of quench crystals of V_2O_5 were unavoidable in most runs and the dimension of usable single crystals is smaller than the size of the whole crystal.

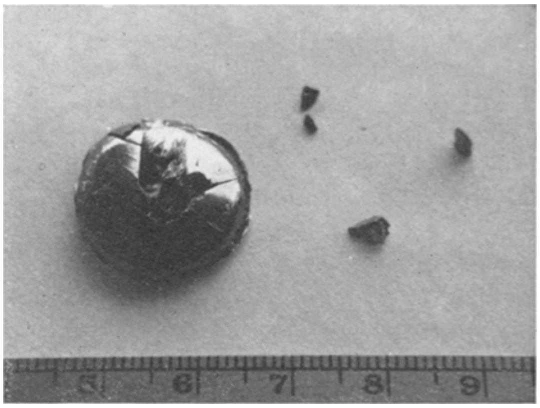

Figure 2 Typical single crystal of VO_2 grown in the smaller crucibles. If no precautions are taken to avoid thermal shock, the crystals develop fine cracks and break into smaller pieces as shown.

The liquid coexisting with the VO_2 crystal is converted upon quenching into a mixture of V_2O_5, VO_2 and sometimes a small amount of V_6O_{13} (see Aebi [5], and Kachi and Roy [4]). The quench crystals of V_2O_5 and VO_2 both show a very marked prismatic habit (as also noted by Sasaki and Watanabe [3]). X-ray powder patterns of VO_2, V_2O_5 and V_6O_{13} obtained from this study compared closely with earlier data from this and other laboratories [5], except that the V_6O_{13} showed a very strong preferred orientation so that no hkl reflections appeared.

To separate the VO_2 crystals the "quench crystals" of V_2O_5 were dissolved by treating with dilute aqueous solutions of Na_2CO_3 after the procedure of Sasaki and Watanabe. In an attempt to produce much larger single crystals of VO_2, the same technique was tried with a large vertical furnace with a mullite muffle 88 mm in inner diameter, with platinum containers up to 40 mm in diameter. None of the 14 runs tried so far produced any larger single crystals of VO_2. The nucleation of VO_2 started at the upper edges of the container and resulted in the growth of many individual grains. In the large-furnace runs, the container was supported from below, instead of being suspended from above as in the runs with a small furnace. This may have produced unfavourable temperature gradients in the container thus preventing a single VO_2 crystal from growing slowly from the bottom of the container.

3.1. Formation of a Vanadium Oxy-Carbonate

Among the quench products of many of the runs described above, a small amount of an unidentified phase was repeatedly and consistently recognised by its set of sharp peaks in the X-ray powder patterns (shown in table I) which are not assignable to any of the phases in the system V/O so far reported. This phase occurs in the form of an aggregate of fine rather soft black crystals, and dissolves more slowly than V_2O_5 in a dilute aqueous solution of Na_2CO_3. Under the reflection microscope, it shows much lower reflectivity than VO_2 and strong anisotropy. It consists of randomly oriented, poorly formed stout prisms about 10 μm wide and 50 μm long.

Chemical analysis using an ARL electron microprobe with VO_2 and V_2O_5 as standards indicated that it contained only 53 ± 0.8% by weight of vanadium which suggested that it was a higher oxide than V_2O_5. However, after considerable study, contamination was suspected. Electronprobe analysis then confirmed the presence of considerable amounts of carbon present in the phase. Hence it appears that this phase is a vanadium carbonate or oxycarbonate. Its appearance here, highlights again one of the dangers of CO/CO_2, and H_2/H_2O gas mixtures in the control of oxygen fugacity: that these gases become real components in the system when liquids are involved is quite apparent, this danger seems to have received insufficient attention in recent work in silicate systems.

TABLE I X-ray powder data for vanadium oxy-carbonate phase. This powder pattern was obtained from the best crystallised sample of this phase using a Norelco diffractometer, smeared glass slide mount, Si internal standard. 2θ values ±0.02°, except for the peaks with *, which are ±0.04°.

I	CuK_α 2θ°	d	I	2θ°	d
23	9.30	9.51	26	41.44	2.1789
100	12.15	7.284	4	43.82*	2.0659
12	17.66	5.022	2	44.32*	2.0437
31	18.69	4.748	2	45.04*	2.0127
12	23.12	3.847	12	45.88	1.9778
13	24.52	3.630	6	48.72*	1.8690
14	25.60	3.480	9	50.53*	1.8062
18	26.38	3.378	4	52.17	1.7532
4	26.70	3.339	3	54.81	1.6748
5	27.83	3.201	4	58.21	1.5849
87	29.11	3.068	6	60.0	Broad
48	30.64	2.918		60.7	peak
11	33.88	2.646	7	62.17	1.4931
3	34.14	2.626	6	63.81	1.4586
2	34.50	2.600	5	64.21	1.4505
10	35.62	2.520			
4	36.67	2.451			
7	37.80*	2.380			
2	38.57*	2.334			
3	39.82*	2.264			

3.2. Characterisation of VO_2

Spectroscopic analysis of typical products shows no impurities above the 10 ppm range, with Mg, Si, Fe, Al and Ti in the 10 ppm range, mostly originating in the starting material, Laue patterns taken in various parts of the crystal confirm its single character. The VO_2 crystals show weak cleavage in three directions roughly perpendicular to each other. Two of them are approximately perpendicular to and the third is parallel to the bottom face of the container. With application of moderate pressure, a conchoidal fracture with strong vitreous lustre is easily formed.

Acknowledgement

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