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STABILITY OF CrO_2 AT HIGH PRESSURES AND TEMPERATURES IN THE "BELT" APPARATUS

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ABSTRACT

An investigation of the decomposition of CrO_2 to Cr_2O_3 from 800° to 1580°C and 15 to 65 kb was made in the "belt" apparatus. CrO_2 can be held for at least 10 minutes without decomposition at temperatures to above 1500°C at pressures of 60 to 65 kb. These results indicate the feasibility of reacting other oxides with CrO_2 for the formation of new compounds.

Introduction

In order to carry out reactions at high temperatures for the synthesis of new compounds containing CrO_2, it is necessary to contain this material at high pressures to prevent the decomposition to Cr_2O_3. Since the "belt" apparatus is a convenient high-pressure unit for these kinds of reactions, a study was made to determine the stability limits of CrO_2 in that apparatus.

Kubota's original investigation (1) of the Cr-O system to pressures of about 1 kb and temperatures of about 600°C appears to have formed the basis for the selection of the 400° to 500°C

temperature limit for hot-pressing CrO_2 at higher pressures for the preparation of dense compacts. (2-6) Investigations by Goto and Kitamura, (7) by Somiya, Yamaoka, and Saito, (8) and particularly by White and Roy (9-11) have defined the equilibrium stability range to 5 kb and 650°C. Later data by these authors (11) to about 5 kb under probably very nearly equilibrium conditions are plotted in Fig. 1. Fukunaga (12) has recently completed an equilibrium study using a single-stage piston cylinder cell with sealed metal capsules to define the CrO_2-Cr_2O_3 P-T curve to 35 kb and 1400°C. He has very kindly made his results available prior to publication. The present study extends the data to 60 kb and about 1500°C (but not entirely at equilibrium) and are sufficiently interesting to warrant comparison of results from the two different experimental conditions.

Experimental

Two types of internally heated high-pressure cells were used: (1) a pyrophyllite cell with an Al_2O_3 liner, (13) and (2) a cell with an NaCl inner liner similar to that described by Hanneman and Strong. (14) Most of the data are from runs on the second cell and for which the starting material was CrO_2 (Table I). A few higher temperature runs were made in the first cell with either CrO_3, Cr_2O_5, or CrO_2 as the starting composition (Table II). All the compositions in the Al_2O_3-lined cell were wrapped with Pt foil while both wrapped and unwrapped samples were used in the NaCl-lined vessel with little or no difference in results. The starting materials were pressed into cylindrical pellet form (about 3 mm diameter by 3 mm height).

The procedure during a run involved first raising the pressure to the desired level and then raising the temperature. The sample was held at temperature up to 60 minutes in the NaCl cell and for about 1 to 5 minutes for very high temperature runs in the Al_2O_3 cell. The samples were rapidly quenched (about 400°C/sec) by turning off the power to the cell with the pressure still applied. The pressure was then released and the sample removed for examination.

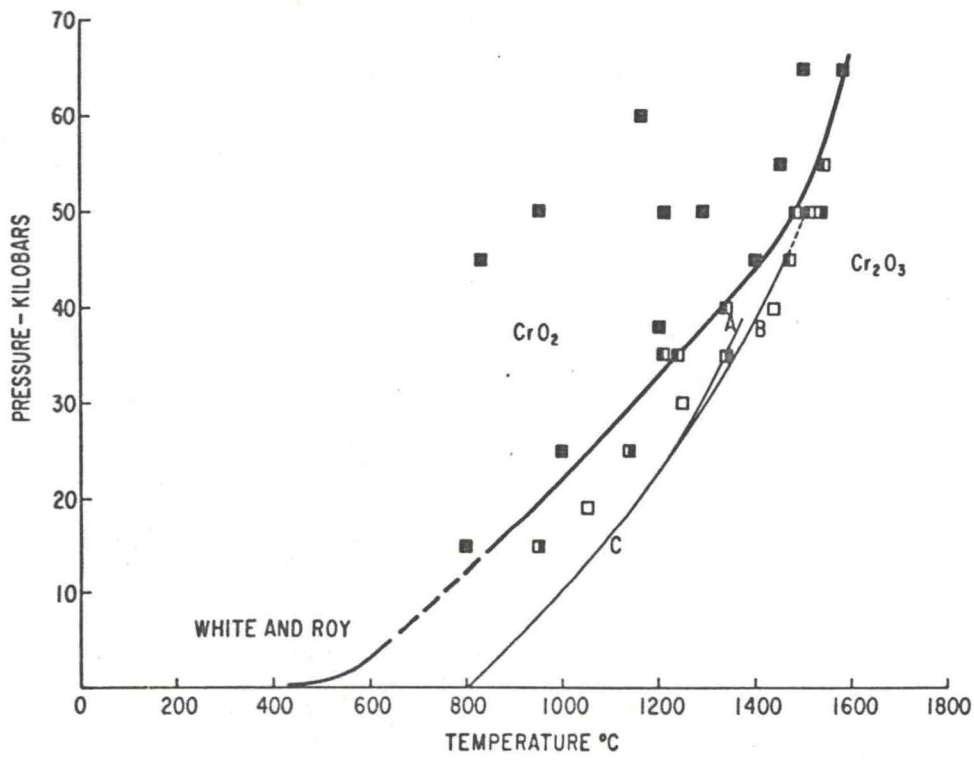

FIG. 1

P-T curve (heavy line) for the decomposition of CrO_2 to CrO_3 in the "belt" apparatus. Filled square, CrO_2; open square, Cr_2O_3; partially filled square, mixture of the two phases; all data for NaCl-lined cells; lower pressure data from White and Roy. (9-11) Melting curve for NaCl (light line): (A) from Pistorius, (15) (B) from Strong, (16) and (C) from Clark. (18)

The pressure calibration of the cell was made at room temperature at the 25.5 and 27.0 kb transformations of Bi and at the 58.0 kb transformation of Ba. Temperature was determined from a watts vs temperature plot which had been previously calibrated by inserting a Pt-Pt/10 Rh thermocouple in several runs in each type of cell. The highly reproducible electrical characteristics of the cells makes this a trustworthy and time-saving procedure.

TABLE I

Summary of Runs with CrO_2 in NaCl Cells

Press. (kb)	Temp. (oC)	Time (min)	
50	950	20	CrO_2
60	1160	11	CrO_2
45	830	12	CrO_2
25	1000	13	CrO_2
38	1200	15	CrO_2
50	1290	14	CrO_2
35	1240	15	CrO_2, Cr_2O_3
19	1050	10	Cr_2O_3
50	1210	60	CrO_2; c/a = 0.660
50	1480	10	CrO_2; (c/a = 0.659), Cr_2O_3
40	1340	16	CrO_2 (c/a = 0.659), tr. Cr_2O_3
40	1440	7	Cr_2O_3, tr. CrO_2
30	1250	8	Cr_2O_3
50	1510	9	CrO_2, Cr_2O_3
55	1540	10	CrO_2 (c/a = 0.660), Cr_2O_3
45	1470	10	CrO_2, Cr_2O_3
45	1400	12	CrO_2
35	1210	25	CrO_2, Cr_2O_3
35	1340	15	Cr_2O_3, CrO_2
25	1140	18	Cr_2O_3, CrO_2
50	1525	9	Cr_2O_3, CrO_2
15	800	20	CrO_2
15	950	20	Cr_2O_3, CrO_2
55	1450	15	CrO_2
65	1500	18	CrO_2
65	1580	11	CrO_2, tr. Cr_2O_3

TABLE II

Summary of Runs in Al_2O_3-lined Cells

Pressure (kb)	Temp (°C)	Time (min)	Starting Material	Results
50	1800	2	CrO_3	CrO_2
25	1800	1	CrO_3	CrO_2
25	1900	1	CrO_3	CrO_2
50	1300	3	CrO_3	CrO_2
50	1175	5	Cr_2O_5	CrO_2
50	2000	2	CrO_2	CrO_2

The phases in the quenched material were identified by x-ray and optical (both reflected and transmitted light) observation and by a qualitative magnetic check for CrO_2. The stoichiometry of the CrO_2 phase was checked by weight loss according to the reaction

$$2\ CrO_2 \rightarrow Cr_2O_3 + \tfrac{1}{2}\ O_2$$

and the deviation from stoichiometry was found to be negligible.

Results and Discussion

The results indicate that CrO_2 can be maintained without decomposition at temperatures up to 2000°C for short times (at least 2 minutes) and at temperatures to at least 1200°C for 60 minutes. Besides the characterization of CrO_2 structurally, chemically, and magnetically, another convincing proof for the stability of CrO_2 in the 1200°-1550°C temperature range was an increase in grain size of about one order of magnitude over that of the original approximately 5μ to 10μ powder without the formation of Cr_2O_3.

Direct evidence for the gas-containing ability of the particular cell used is shown in Fig. 1 where the CrO_2-Cr_2O_3 boundary curve becomes essentially coincident with the melting point of the salt liner as a function of pressure at about 1500°C. The portion of the CrO_2 decomposition curve which is dependent on loss of oxygen through the molten salt is in reasonable agreement with the NaCl melting data of Pistorius (15) and checks particularly well with the data of Strong (16) for equipment and cells very similar to that used here. The behavior of the salt liner with respect to gas containment can be observed directly in the form of bubbles in a quenched liner that has been above the melting point. Bubble formation means a rapid loss of oxygen and is accompanied by the rapid formation of Cr_2O_3. The conversion to Cr_2O_3 starts from the outer rim and a partial conversion showing an interface between Cr_2O_3 and CrO_2 is shown in Fig. 2. Conversion to Cr_2O_3 can also be seen along grain boundaries of the CrO_2.

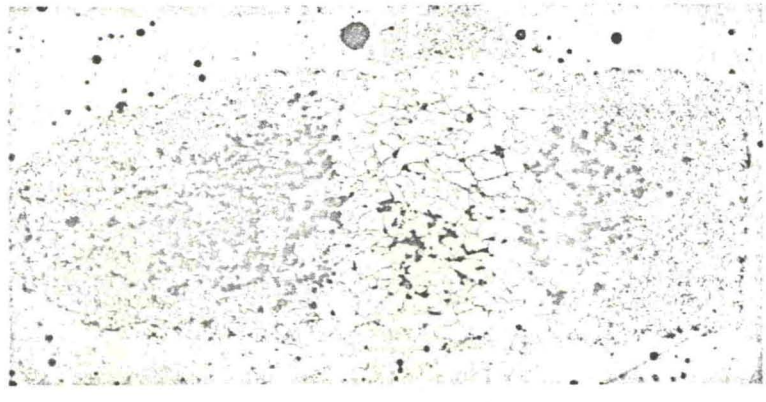

FIG. 2
Photomicrograph of cross section of a high-pressure run showing partial conversion of CrO_2 to Cr_2O_3 after 10 minutes at 1510°C and 50 kb. Bright field. Center part is primarily CrO_2 with Cr_2O_3 at grain boundaries; Cr_2O_3 predominates on both sides of the center section. 50X

In some of the short duration, higher temperature runs with alumina liners, CrO_3 was converted to CrO_2 and recovered as small whiskers about ¼ mm long (elongated along "c") after only 1 to 2 minutes at temperatures from 1800° to 1900°C. These runs were not considered to give equilibrium results, and there was some evidence of more rapid loss of gas from Al_2O_3 cells probably due to cracking of this more brittle material or to slower densification of during heating. Longer runs at very high temperatures were avoided primarily to prolong equipment life since the results with the salt-lined cells were completely adequate to show that CrO_2 could be maintained as the stable phase to moderately high temperatures.

The results with the salt-lined cells suggest that in spite of relatively short runs a close approach to equilibrium was attained as long as the melting point of the salt was not exceeded--i.e., along the portion of the curve below about 1500°C. This conclusion has now been supported by the quite good agreement with the more extensive results of Fukunaga, (12) who indeed approached the curve from both sides of the equilibrium reaction. An extrapolation of the present data to join the curve of White and Roy (9-11) appears to be justified.

Summary

It has been shown that CrO_2 can be maintained for at least several minutes without decomposition at temperatures to above 1500°C and pressures of 60 to 65 kb. The CrO_2-Cr_2O_3 decomposition curve as determined in NaCl-lined cells in the belt apparatus intersects the melting curve for salt at about 1500°C, and gas is released rapidly from the cell. These results have been

utilized in the preparation of a Cr^{4+}-containing perovskite, $PbCrO_3$. (17)

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References

1. B. Kubota, J. Am. Ceram. Soc., 44 (5), 239 (1961).
2. T.J. Swoboda, P. Arthur, Jr., N.L. Cox, J.N. Ingraham, A.L. Oppegard, and M.S. Sadler, J. Appl. Phys., Suppl., 32 (3), 374 (1961).
3. F.J. Darnell, J. Appl. Phys., 32 (7), 1269 (1961).
4. F.J. Darnell and W.H. Cloud, Proc. Colloq. Intern. CNRS, No. 149.
5. D.S. Chapin, J.A. Kafalas, and J.M. Honig, J. Phys. Chem., 69 (4), 1402 (1965).
6. N. Nakayama, E. Hirota, and T. Nishikawa, J. Am. Ceram. Soc., 49 (1), 52 (1966).
7. Y. Goto and T. Kitamura, J. Japan. Soc. Powder Met., 9, 109 (1962).

8. S. Somiya, S. Yamaoka, and S. Saito, Bull. Tokyo Inst. Technol., 66, 91 (1965).

9. W.B. White and R. Roy, Bull. Am. Ceram. Soc., 42, 203, 516 (1963).

10. R. Roy and W.B. White, Proceedings of an International Symposium on Paper in High Temperature Technology (IUPAC), Stanford Research Inst., September 8-11, 1963, Butterworths (1964).

11. R. Roy, Proc. Colloq. Intern. CNRS, No. 149, 99, Bordeaux (1964).

12. O. Fukunaga and S. Saito, submitted to J. Am. Ceram. Soc. (March 1966).

13. R. C. DeVries, J. Am. Ceram. Soc., 47 (5), 230 (1964).

14. R.E. Hanneman and H.M. Strong, Paper No. 64-WA/PT-20 at 1964 Symposium on High Pressure Technology, ASME Winter Annual Meeting, November 29-December 4, 1964, New York City.

15. C.W.F.T. Pistorius, J. Chem. Phys., 45 (10), 3513 (1966).

16. H.M. Strong, private communication (1966).

17. W.L. Roth and R.C. DeVries, GE Research and Development Center Rept. No. 66-C-428 (November 1966).

18. S.P. Clark, Jr., J. Chem. Phys., 31, 1526 (1959).