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TITLE: "The Problems of Growth of Single Crystals of Rhenium and Iridium Dioxides."

FINAL REPORT

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Prior to the work of this final year, most construction of equipment was completed. The final year plus one-half year extension on the work of this research grant was concerned almost entirely with the actual growth of crystals, under a wide variety of crystal growth conditions. The results of this work were presented in a paper given at The Second National Conference on Crystal Growth, sponsored by the American Association for Crystal Growth, at Princeton University, Princeton, New Jersey, from July 30 to August 3, 1972. A copy of the abstract of the paper, as written in the Program of the conference, is included in this report. In addition, a short article has been submitted for publication by the Journal of Applied Physics. A copy of that article, as submitted, is also attached to this report.

(NASA-CR-133213) THE PROBLEMS OF GROWTH OF SINGLE CRYSTALS OF RHENIUM AND IRIDIUM DIOXIDES Final Report (Tuskegee Inst.) 6 p HC $3.00 CSCL 20B

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Abstract of paper presented at the Second National Conference for Crystal Growth, Princeton, New Jersey, July 30 to August 3, 1972.

Growth of IrO_2 and ReO_x by Vapor Phase Method*

Fred M. Reames
Physics Department
Tuskegee Institute, Alabama 36088

Iridium dioxide and various rhenium oxides have been grown by the vapor phase method. Crystal growth has been accomplished by the continuous flow method, in which a measured flow of oxygen gas carries the vapor products of the pure metals from a "hot" zone to a "cold" zone, in a two temperature zone furnace. The pressures under which growth has been attempted range from $\frac{1}{2}$ atmosphere to 5 atmospheres for IrO_2, and from 1/10 atmosphere to about 2 atmospheres for the rhenium oxides.

In the case of IrO_2, the basic crystal growth results of Butler and Gillson (1) have been reproduced. However, a new growth form, of "chunk" growth, rather than the usual rod-like growth, has been found, when the oxygen pressure is between 3 and 4 atmospheres.

Two of the many possible rhenium oxides have been produced, Re_2O_7 and ReO_3, as determined by powder pattern x-ray identification. Growth of optically clear yellow-green Re_2O_7 crystals has been accomplished in growth zone temperatures of 150°C under a range of pressure conditions. Further work on the growth of rhenium oxides will be reported.

*Work supported by National Aeronautics and Space Administration, Grant No. NGR-01-005-003.

(1) S. R. Butler and J. L. Gillson, Mat. Res. Bull., 6, 81 (1971).

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Growth of IrO_2 and Re_2O_7 Single Crystals*

F. M. Reames and H. L. Jacocks,** Physics Department

Tuskegee Institute

Tuskegee Institute, AL 36088

ABSTRACT

Single crystals of IrO_2 larger than previously reported in the literature have been obtained by the chemical vapor transport method, under conditions of elevated gas vapor pressures. In addition, a new growth form of IrO_2 has been found. Attempts to grow rhenium oxides other than Re_2O_7, using this same method, have failed; however, two different growth forms of Re_2O_7 are reported.

Growth of IrO_2 and Re_2O_7 Single Crystals

In the recent literature, various experiments on IrO_2 have been described. Butler and Gillson[1] have reported x-ray diffraction and electrical resistivity measurements, Ryden, Lawson and Sartain[2] have reported resistivity and Hall effect measurements, and Ryden and Lawson[3] have described magnetization measurements[3]. In all cases, the crystals used were quite small (about *1/2x1/2x2* mm). Crystals of IrO_2 grown by methods described here have been considerably larger (*1x1x5* mm), and the ultimate size does not appear to be limited by growth conditions. In addition, single crystals in a new growth form, more gem-shaped, have been produced. Ryden and Lawson do not describe the growth form of the crystals used in their magnetization experiments, but the gem-shaped crystals grown in our laboratory would allow more complete data to be obtained than the needle-shaped crystals used in their electrical properties measurements with Sartain. Small spheres large enough for magnetization experiments could be shaped out of our crystals.

The basic method of growth of IrO_2 has been described by Schafer[4]. A flow of pure oxygen gas over iridium metal powder at about 1150°C oxidizes the iridium to IrO_3, a gas. The IrO_3 carried to a lower temperature, about 1000°C, then dissociates to IrO_2 and oxygen. The work reported here has been an investigation of growth habits under various conditions of pressure and flow rate of the oxygen gas. The gas pressure was measured on Bourdon gauges and was controlled by a regulator similar to that described by Walker[5]. This regulator has proved most useful, since it has an effective operating range of pressures as low as

1 mm Hg and as high as structural limitations allow. The highest pressure used in this work, 5 atmospheres, was determined by the strength of the quartz growth tubes (2 cm diameter and 2 mm walls) at 1150°C. Gas flow rates were controlled with a needle valve and measured with a Matheson Mass Flowmeter.

Growth of IrO_2 at 1 atmosphere pressure and lower produced crystalline growth similar to that described by Butler and Gillson[1]: "many small crystals grew in intergrown masses." But at pressures from 2 to 2 1/2 atmospheres, less nucleation occurred, and a small number of larger sword-shaped crystals was produced. All crystals examined by Laue x-ray diffraction techniques grew along (0,1,1) crystallographic directions. Furthermore, these larger crystals were produced in growth runs of only 4 days, as compared to the 10 to 20 day runs reported by Butler and Gillson. At pressures of 3 1/2 to 5 atmospheres, the sword or needle growth of lower pressures did not occur. Instead, crystals of a more compact gem shape appeared, of size up to approximately 3x3x2 mm, and mass of up to 150 mg. In all these experiments, the flow rate of oxygen seemed to be optimum at about 10 cc/min. Slower flow rates reduced the growth rate, while higher flow rates seemed to produce more nucleation in the crystal growth zone, and hence more and smaller crystals were produced.

Growth of Re_2O_7 was undertaken to determine whether any of the other rhenium oxides could be produced, under the various conditions of pressure, temperature, and gas flow obtainable in the apparatus. The only major difference in the growth of Re_2O_7 was temperature: the rhenium metal powder was placed in temperatures ranging from 350°C to 500°C. No significant evidence of oxides other than Re_2O_7 was obtained, other than residues of ReO_3. But the growth habits of Re_2O_7 changed, under different conditions of oxygen pressure. At low pressures of about 0.1 atmosphere, large single crystals of approximately 1 cm. on a side were produced, in growth runs of about 1 day. At high pressures of 5 atmospheres, platelet growth became evident. Optimum conditions of gas flow were not found.

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**Now in graduate school at North Carolina State University, Raleigh, North Carolina.

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4. Harald Schafer, Chemical Transport Reactions, Academic Press, New York, (1964), p 48.

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