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# STUDY OF GROWTH PARAMETERS FOR REFRACTORY CARBIDE SINGLE CRYSTALS



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CONTENTS

# I INTRODUCTION

Interest in the refractory carbides has increased recently in anticipation of many new applications requiring the use of superrefractories. However, during the research and development work on these materials, difficulties have been encountered in attaining and reproducing desired physical properties. Little is known about ultimate intrinsic physical properties or about the influences of stoichiometric changes, impurities, and grain boundaries on these properties. In obtaining this type of information, single crystals of various carbide compositions would be of great value. At present, the only crystals readily available are of titanium carbide, grown by the Verneuil process, and little is known of their structure and perfection.

Stanford Research Institute has been engaged by the National Aeronautics and Space Administration to investigate the application of new techniques and procedures to the growth of single crystals of tantalum carbide, hafnium carbide, and solid solutions of these carbides. Several techniques have been investigated: (1) induction plasma melting for Verneuil (fusion) crystal growth, (2) liquid metal solution growth of crystals, and (3) arc discharge heating for Verneuil growth of crystals. Of these methods, the arc-Verneuil technique is most promising and is presently being pursued. Tantalum carbide boules were produced free of grain boundaries for the first time this quarter.

Recent progress has been delayed owing to problems in obtaining carbide powders having the desired characteristics for crystal growth. As a result, Stanford Research Institute requested a three-month extension in time to complete the crystal growth studies. NASA has approved this request. This brief report is submitted in order to inform NASA of progress during the three-month period preceding the time extension.

Participating in the investigation during this period were J. W. Fowler (crystal growing experiments) and J. B. Saunders (X-ray analyses).

## II SUMMARY AND CONCLUSIONS

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Near the end of the quarter several tantalum carbide boules free of $Ta_2C$ and grain boundaries were grown. Elimination of grain boundaries in tantalum carbide had not previously been achieved. The yield of grain boundary-free boules was high enough to permit production of several boules on a fairly standarized basis for cutting and delivery to NASA - Lewis Research Center, Cleveland, Ohio.

Attempts to grow additional hafnium carbide boules free of grain boundaries were unsuccessful. However, this work preceded the successful tantalum carbide experiments and the prospects for growing hafnium carbide boules free of grain boundaries in the next quarter are good. High purity (spectrographic grade) hafnium carbide powder has been obtained for this purpose.

Float zone melting experiments with tantalum carbide were conducted early in the quarter using carbon arc heating. Although melting was achieved, crystal quality was inferior to that obtained with the Verneuil fusion method and further experiments were discontinued.

Author
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# III CRYSTAL GROWTH STUDIES

## A. Tantalum Carbide Boules Free of Grain Boundaries

Late in the quarter, tantalum carbide boules were grown in conjunction with a study of the affect of powder feed particle size on grain size in arc-Verneuil boules. Boules free of grain boundaries were grown in the powder size range 200 to 325 mesh. It was subsequently determined that a significant yield of grain boundary-free boules could be grown. The yield of boundary-free boules was somewhat higher for the -200+270 fraction than for the -270+325 fraction. Future growth experiments will employ -200+270 mesh tantalum carbide.

The changes in operating procedure that led to this improvement are minor. Boules are now grown at relatively fast rates. All -325 and +200 mesh particles are removed from the feed powder by double screening. The boule is kept as symmetrical as possible. The horizontal carbon electrodes are blunted and maintained within 1/16 inch of the boule. Although a 10% hydrogen - 90% argon gas mixture is used in the powder feed injection tube, additional argon is pumped into the furnace chamber from a port located some distance away from the boule. Consequently, the furnace atmosphere away from the melting area is essentially argon at one atmosphere pressure. No reduction in carbon stoichiometry has resulted from the addition of excess argon. The carbon content of these boules, determined by lattice parameter measurements, varies between 43.0 and 45.5 atomic percent. Single-crystal tantalum carbide boules have been grown from powder that had previously passed through the arc-Verneuil apparatus, been reclaimed from the bottom of the furnace chamber, and sieved.

Boules are still being initiated with a countersunk tantalum metal foot and consequently are polycrystalline at the base. The boules attain a single-crystal section after about one cm of growth.

In Table I, a spectrographic analysis of impurities in a typical tantalum carbide boule is compared with the analysis of the starting powder used to grow the boule.

Table I

ANALYSIS OF TANTALUM CARBIDE STARTING POWDER AND ARC-VERNEUIL BOULE

| Impurity | Powder[(1)] (ppm) | Boule (3/9/67)[(2)] (ppm) |
|---|---|---|
| Al | < 10 | 20 |
| B | < 1 | nil |
| Cb (Nb) | < 50 | 200 |
| Cd | < 1 | nil |
| Co | < 5 | 10 |
| Cr | 15 | 10 |
| Cu | < 10 | 10 |
| Fe | 70 | 80 |
| Mg | < 10 | 20 |
| Mn | < 10 | 40 |
| Mo | < 10 | 20 |
| Ni | < 10 | 70 |
| O | 179 | Not reported |
| Pb | < 5 | < 10 |
| Si | 30 | 60 |
| Sn | < 10 | 20 |
| Ti | < 10 | 300 |
| V | < 10 | 10 |
| W | Not reported | 100 |
| Zn | < 10 | < 50 |
| N | 132 | Not reported |
| Zr | < 10 | < 50 |

(1) Wah Chang Analysis of Lot SP106526B.

(2) Analysis by Metallurgical Laboratories, Inc., San Francisco.

Although these analyses were conducted by different laboratories, the agreement is good. With the possible exception of tungsten, nickel, and titanium, there is no evidence of an increase in impurity content. Since the content of other impurity metals with low vapor pressures, e.g., Mo and Cr did not show a corresponding increase, the quoted differences may be caused by analytical errors.

B. Hafnium Carbide Boules

In the previous Quarterly Status Report, growth of one hafnium carbide boule, free of grain boundaries, was reported. Ten attempts to duplicate this result in the present report period were unsuccessful. The starting powder was either -325 mesh or reclaimed powder. These hafnium carbide experiments preceded the successful tantalum carbide experiments. A new shipment of spectrographic grade hafnium carbide powder has been received and will be employed next quarter in hafnium carbide crystal growth experiments.

C. Arc-Float Zone Experiments

During this report period, the arc-Verneuil furnace was modified slightly to permit floating zone refining experiments using the horizontal electrodes for melting a zone of tantalum carbide or hafnium carbide. A Materials Research Corporation zone refiner was mounted in a vertical orientation above the arc-Verneuil apparatus in place of the powder feeder normally used for Verneuil fusion experiments. An extension arm from the boat carriage of the zone refiner entered the top of the arc-Verneuil furnace through the seal normally used for the powder feed tube. Inside the furnace, a 0.125-inch-diameter tantalum rod was connected to the zone refiner extension arm by an appropriate chuck. This arrangement, used in conjunction with the existing arc-Verneuil apparatus, permitted independent vertical motion at variable rates as well as independent rotation at variable rates for both the upper and lower sections of a zone refined "ingot." The upper section consisted of a hot pressed TaC billet or a TaC boule attached to the tantalum rod. The lower section was a TaC hot-pressed billet or boule inserted in the graphite seed holder. In principal, melting could be initiated in the center of a sample supported at both ends, or the separated upper section could be brought in contact with the lower section after striking the arc.

The results of six experiments are summarized in Table II. In some cases, melting of tantalum carbide and attachment of the tantalum carbide rods were achieved. However, the arc tended to discharge to the lower (grounded) section with the result that attachment was hard to maintain and the operation was highly unstable. The resulting samples were small and very irregular. Also, no decrease in the number of grain boundaries was obtained. Consequently, further experiments of this type are not planned.

Table II

SUMMARY OF ARC-FLOAT ZONE EXPERIMENTS

| Run Number | Bottom Section | Top Section | Rotation | Atmosphere (15 psia) | Results |
|---|---|---|---|---|---|
| 1 | TaC boule | Hot-pressed TaC billet | Yes | Argon | The top section would not melt, but small pieces of it were dislodged by the rotating boule. These fell into the boule. |
| 2 | HfC boule | Hot-pressed HfC billet | Yes | Argon | Similar to run 1. |
| 3 | TaC boule | Hot-pressed TaC billet | No | Argon | Melting and joining was established. The liquid was moved up and down by vertical translation of the sample. |
| 4 | Ta rod (0.125 in.) | Ta rod (0.125 in.) | No | 90% Argon-10% Hydrogen | The rod melted in the center and parted into the upper and lower sections. |
| 5 | Ta recessed in the graphite seed holder | Hot-pressed TaC billet | No | Argon | The TaC billet was drip-melted onto the hot pedestal where a boule formed similar to arc-Verneuil growth. |
| 6 | Ta recessed in the graphite seed holder | Hot-pressed TaC billet | No | Argon | The billet was joined to the seed holder and quickly lowered. The sample parted to leave a small lower boule. |

## IV FUTURE WORK

Production of tantalum carbide single crystals, including cutting, will continue through March and into April. Production of single-crystal hafnium carbide boules will commence in April and will continue into May.