April 5, 1966

Report No. 8

Quarterly Status Report No. VIII/December 1, 1965 to March 1, 1966

STUDY OF GROWTH PARAMETERS FOR REFRACTORY CARBIDE SINGLE CRYSTALS

By: R. W. Bartlett

SRI Project No. FMU-4892

Prepared for:

National Aeronautics and Space Administration
Washington, D.C.

Contract No. NASr-49 (19)

Approved:

F. A. Halden

F. A. Halden, Director
Ceramics and Metallurgy Division

GPO PRICE $

CFSTI PRICE(S) $

Hard copy (HC) $1.00

Microfiche (MF) .50

ff 653 July 65

FACILITY FORM 602

N66 24118 (ACCESSION NUMBER)	(THRU)
15 (PAGES)	1 (CODE)
CR-74012 (NASA CR OR TMX OR AD NUMBER)	06 (CATEGORY)

Copy No. 4

CONTENTS

I INTRODUCTION

Interest in the refractory carbides has increased recently in anticipation of many new applications requiring the use of super-refractories. 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 application of new techniques and procedures to the growth of single crystals of tantalum carbide, hafnium carbide, and solid solutions of these carbides. The new techniques being investigated fall into two classes: (1) application of recently developed methods of liquid metal solution growth of crystals, and (2) utilization of a-c arc melting for Verneuil crystal growth.

II SUMMARY AND CONCLUSIONS

Arc-Verneuil crystal growth experiments were suspended during the quarter while the new crystal-growing furnace chamber was being constructed. Machining of the furnace parts was completed during the quarter, and delivery of the assembled furnace is expected early in the following quarter. Crystal growth experiments will be resumed after the furnace is installed.

Solution growth experiments were curtailed during part of the quarter in order to complete designs for the modified arc-Verneuil furnace. Some experiments were conducted using the thin-film, solution-crystallization method, which involves a narrow liquid zone of solvent metal and a steep temperature gradient between the nutrient and seed materials.

III CRYSTAL GROWTH STUDIES

A. Arc-Verneuil Growth

1. Apparatus Modifications

One of the major problems encountered in the growth of carbide crystals using the Verneuil technique is the feeding of powder to the boule at the required slow, well-controlled rates. The individual carbide particles are nearly equidimensional and have a high specific gravity. As a result, contrary to conditions encountered handling oxide materials, the carbide powders are too free-flowing. When conventional, mechanically activated screen feeders are used, it is necessary to restrict the screen area to such an extent that sensitivity of the powder flow rate to the tapping rate is nearly lost. The powder flow may stop completely or may greatly accelerate, with no apparent change in the feeder control system.

In order to gain improved control of particle feeding for the arc-Verneuil furnace, an audio-driven particle feeder was designed and constructed. This feeder employs the driver element of an audio speaker to pressure pulse the column of gas between the speaker and a bed of carbide particles resting on a metal sieve. As the particle bed expands and contracts during the audio pulsing, particles trickle through the sieve. The rate of flow is regulated by controlling the amplitude and frequency of the audio signal. Similar devices are being used for growing oxide crystals at the Insulation Laboratory of MIT.

The new feeder was tested in air, using tantalum carbide powder, -200+270 mesh. This powder consists of approximately spherical particles and is extremely free-flowing. Using a 200 mesh sieve with all but 1 cm^2 of the sieve area blinded, we found it possible to maintain the desired small particle feed rates. The feed rate is highly dependent on the height of the particle bed. As the height decreases, the particle feed rate increases, unless compensating changes in the frequency and amplitude of the audio signal are made. The increasing rate is caused by a decrease in damping of the audio signal by the particle bed as the total mass of particles is reduced. This effect is particularly prominent with tantalum carbide because of its high specific gravity, 14.5 g/cm^3. The audio feeder appears to work in air as well as, or better than, other feeders, and it will be tested with the new arc-Verneuil furnace as soon as assembly is complete.

The new arc-Verneuil furnace chamber is being fabricated by an outside machine shop. All parts to the furnace were completed and delivered to SRI in mid-February. However, the furnace was not in a sufficiently assembled condition to verify the critical tolerances for intersection of the three horizontal electrodes and the vertical seed holder. Consequently, the furnace parts were returned to the fabricator for assembly and specified tolerance verification prior to acceptance. Some minor corrections were also made, and the furnace was returned to SRI on March 7, 1966. The furnace was constructed in conformance with detailed drawings submitted by SRI, and it follows the description and sketches submitted in the seventh quarterly status report.

2. Future Work

The new furnace chamber will be installed in place of the previous arc-Verneuil furnace and will be tested. Connections must be made for water, electric power, vacuum and gas inlets, the particle feed tube, and both rotary and transverse motion for the three horizontal electrodes and the vertical seed holder. Crystal growth experiments will resume in conjunction with furnace testing, using tantalum carbide for the initial experiments. Bids on supplying mixed solid solution tantalum carbide-hafnium carbide powders have been received, and additional hafnium carbide powders and mixed solid solution powders will be secured in the near future.

B. Metal Solution Growth

1. Experimental Results

Some initial experiments were conducted with the thin-film, solution-crystallization method. These experiments involved an attempt to transfer tantalum carbide from a nutrient zone across a thin liquid metal zone, approximately ¼ inch thick, to a seed area for growth of tantalum carbide. All of the experiments involved transfer caused by a steep temperature gradient along the vertical axis. A small graphite heating element, 0.850 inch bore, was constructed that was capable of attaining temperatures to 2300°C. This particular heating element was much smaller than is normally used in the furnace for which this power supply was originally selected. Hence, some difficulties were encountered in designing an optimum heating element that was compatible with the low voltage-high current characteristics of the available furnace power supply. Yet it was necessary to design a small heating element that would be close to the crucible in order to provide the desired steep temperature gradient. Five test runs, each leading to modifications in the furnace design, were required before a suitable heating element was produced.

The first tantalum carbide transfer experiment used a graphite crucible with a tapered bottom. The crucible was partially filled with iron. A hot-pressed tantalum carbide billet immersed in the iron was used as the nutrient for transferring tantalum carbide to the cooler bottom of the crucible. This approach is similar to Stockbarger's method of melt growth. The experiment was unsuccessful because the tantalum carbide billet separated from the iron melt.

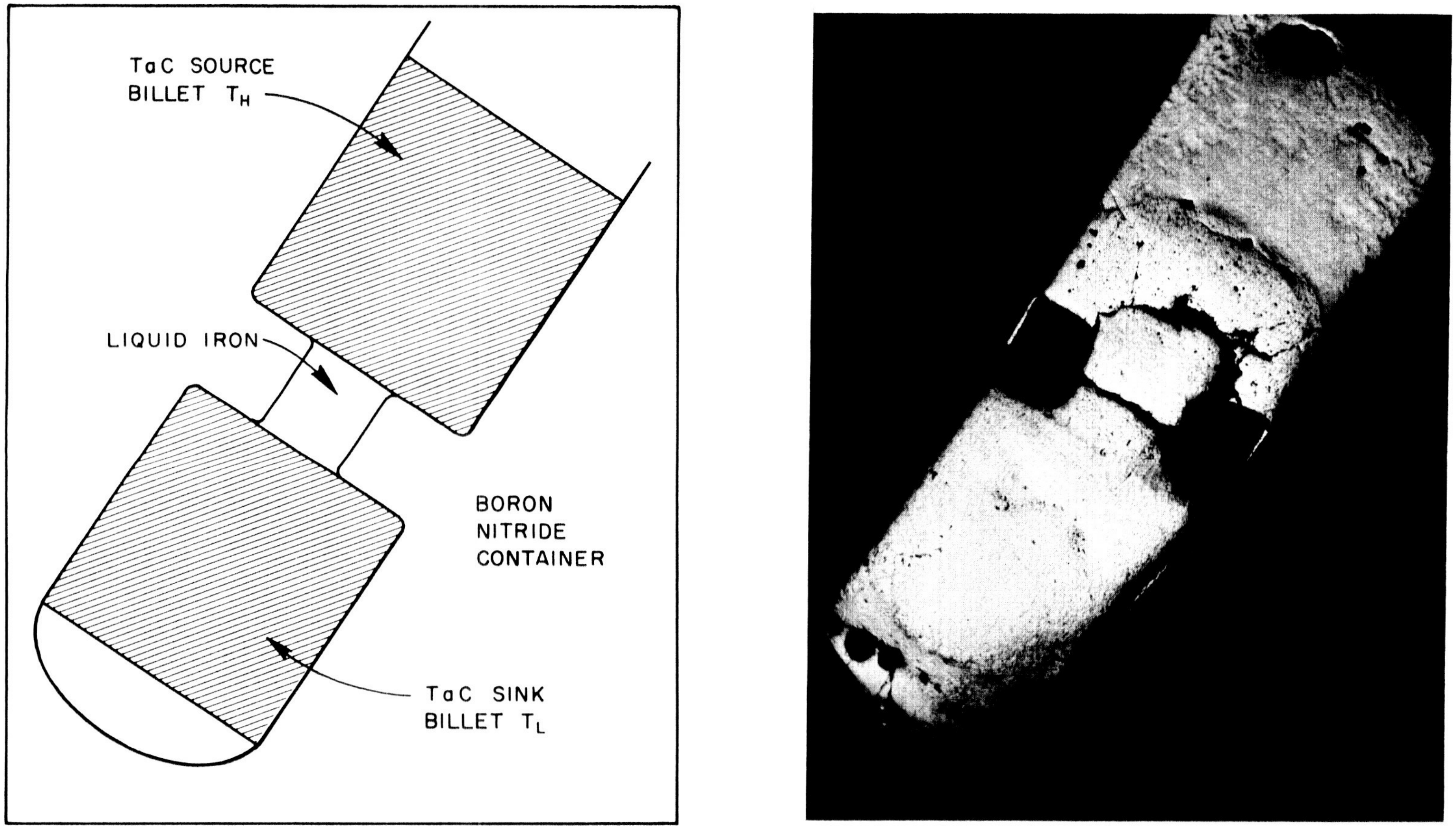
Another experiment conducted in a graphite crucible involved a tantalum carbide boule as the seed, separated from the tantalum carbide powder source by a liquid platinum zone. The tantalum carbide particles floated on the more dense platinum melt. This experiment was aborted because the graphite heater element failed. The experiment will be repeated.

A third transfer experiment employed a boron nitride crucible with two hot-pressed tantalum carbide billets separated by a boron nitride collar. Liquid iron was used to fill the region separating the tantalum carbide billets, and to fill the surrounding region. The billets were initially of equal size, and the temperature gradient was designed to transfer the tantalum carbide from the upper to the lower billet. A cross section of the tantalum carbide billets in the crucible, following the run, is shown in Fig. 1. The volume of tantalum carbide in the upper billet has been reduced, and tantalum carbide has been deposited in the intermediate zone between the two billets. This experiment will be repeated, using tantalum carbide boules in place of the hot-pressed polycrystalline billets, to determine whether tantalum carbide was transferred by a solution-precipitation mechanism as desired, or by liquid infiltration and separation of individual tantalum carbide grains from the hot-pressed billets.

Most of the recent crystal growing experiments in metal solutions have employed polycrystalline tantalum carbide as a nutrient for growth of single crystals of this material (reversible growth). On the other hand, tantalum and carbon dissolved in the menstruum in excess of the tantalum carbide solubility product will react irreversibly. If the reactant concentration in excess of the solubility product is large, nucleation and growth of many small crystals are expected to occur. However, if a menstruum is used in which the solubility of both tantalum and carbon is very low, growth of larger crystals may be possible.

Tantalum carbide was grown by two irreversible experiments in which tantalum metal and carbon were included with the aluminum melt in an aluminum oxide crucible. All of the components of the melt were premixed in powder form. These experiments were conducted at 1550°C and 1100°C. The tantalum carbide crystal yield at the lower temperature was much higher than the yield from the high temperature experiment. Average crystal size was 0.2 mm.

A mixed solid-solution crystal-growth experiment was performed using an aluminum menstruum with the primary goal of providing mixed crystals for the arc-Verneuil experiments. The crystals were grown at 1550°C. In addition to aluminum, the menstruum contained a 50-50 stoichiometric ratio of hafnium and tantalum, and carbon in excess of the amount required to



TA-4892-33

BEFORE

AFTER

FIG. 1 SPECIMEN CROSS-SECTION FROM TANTALUM CARBIDE MASS TRANSFER EXPERIMENT IN LIQUID IRON
Before. Sketch showing location of tantalum carbide source and sink billets prior to the experiment
After. Photograph of billets after the experiment, 5X

form the monocarbides. The hafnium was introduced to the crucible as sponge, and tantalum was introduced as -100 mesh powder. The experiment was conducted in a helium atmosphere.

After cooling the melt and dissolving the aluminum in hydrochloric acid, we obtained a purple residue of fine crystals. This residue was separated into the following sieve fractions: +48, -49+150, -150+325, and -325 mesh. Approximately equal amounts of material were retained in each fraction. The -325 mesh material was examined by X-ray fluorescence, and equal amounts of hafnium and tantalum were present. X-ray diffraction analysis of this material showed that an insignificant amount of free hafnium and large amounts of <u>two</u> separate carbide phases were present. These carbide phases had the face centered cubic structure of hafnium carbide and tantalum carbide, but their lattice parameters, a_0, were 4.519 Å and 4.586 Å. These values were determined in the back reflection region ($2\theta > 120^{\circ}$) by diffraction from (333) lattice planes, and they are intermediate values between the lattice parameters of tantalum carbide (a_0 = 4.456 Å) and hafnium carbide (a_0 = 4.640 Å). Thus, two solid solutions with distinct compositions were formed, suggesting partial solid immiscibility in these monocarbides. If we assume a linear relation between lattice parameter and mole fraction (Vegard's Law), the compositions of the two mixed solution compounds by atomic weight are:

(1) 34% HfC · 66% TaC
(2) 70% HfC · 30% TaC

If Rudy's data* for the relation between lattice parameter and mole fraction for these mixed carbides are used, the calculated compositions are:

(1) 50% HfC · 50% TaC
(2) 82% HfC · 18% TaC

This apparent immiscibility has not been previously reported.

---

*Rudy, E., "Ternary Phase Equilibria in Transition Metal-Boron-Carbon-Silicon Systems, Part I, Ternary Systems, Vol. 1, Ta-Hf-C System," Tech. Rept. No. AFML-TR-65-2, June 1965, Aerojet General Corporation, p. 36.

2. Future Work

Work on solution growth will be continued at a reduced level of effort, and will be restricted to (a) further exploration of the thin-film, solution-crystallization method, and (b) a limited number of irreversible long-time experiments conducted in aluminum oxide crucibles using aluminum-tin menstruums of various compositions to regulate tantalum and carbon solubility. Depending on the results of these experiments, work on solution growth may be terminated. Although crystalline perfection and growth of stoichiometric compositions have been quite encouraging using this technique, it appears doubtful that crystals of the desired size will be obtained within the remaining time on this project.