STANFORD RESEARCH INSTITUTE
MENLO PARK, CALIFORNIA
SRI

UNPUBLISHED PRELIMINARY DATA

April 26, 1965

Report No. 4

Quarterly Status Report No. IV/December 1, 1964 to March 1, 1965

STUDY OF GROWTH PARAMETERS FOR REFRACTORY CARBIDE SINGLE CRYSTALS

By: F. A. Halden and W. E. Nelson

SRI Project No. PMU-4892

GPO PRICE $ ____________

OTS PRICE(S) $ ____________

Hard copy (HC) $1.00

Microfiche (MF) .50

Prepared for:

National Aeronautics and Space Administration
Washington, D.C.

Contract No. NASr-49 (19)

FACILITY FORM 602

N65 23835 (ACCESSION NUMBER)
(THRU)
19 r (PAGES)
1 (CODE)
CR-62727 (NASA CR OR TMX OR AD NUMBER)
17 (CATEGORY)

Approved:

A. E. Gorum
A. E. Gorum, Director
Material Sciences Division

Copy No. 24

[redacted]

CONTENTS

ILLUSTRATIONS

TABLES

I INTRODUCTION

Interest in the refractory carbides has increased greatly in recent years in anticipation of many new applications requiring the use of super refractories. In the course of research and development work performed, several problem areas have also become apparent. In processing difficulties are encountered in attaining and reproducing desired properties. Little is known of ultimate properties or influences of changes in stoichiometry, impurities, and grain boundaries.

To get this type of information, which will certainly be needed soon, single crystals of various carbide compositions would be of great value. At the present time, 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, therefore, been engaged by the National Aeronautics and Space Administration to investigate the application of several new techniques and procedures for the growth of single crystals of tantalum carbide, hafnium carbide, and solid solutions of the two.

II SUMMARY AND CONCLUSIONS

X-ray lattice measurements and examination of polished sections of arc-melted, high purity tantalum carbide boules confirmed that a single phase can be maintained during melting and that the stoichiometry can be varied by control of the gaseous environment. On the basis of these studies, the final arc-melting furnace has been designed and is presently being constructed. The furnace will consist of three rotating carbon electrodes spaced at 120°, each powered by an independently controlled saturable reactor providing 5 to 30 volts and up to 100 amps. The three in-phase arcs will attach directly to the rotating crystal boule. The graphite resistance after-heater will be powered by a 20-kw variac-transformer source. Construction should be completed during the next quarter.

Melting studies conducted in the induction-coupled plasma on tantalum carbide and hafnium carbide were unsuccessful. A molten cap could not be obtained at power levels that could be maintained continuously in the water-cooled quartz plasma tubes. Work on this crystal growth technique has been terminated.

Very small crystals of tantalum carbide have been grown in aluminum and iron alloys. Lattice constant measurements for all crystals grown show a_0 values of 4.455 ± 0.001 Å--corresponding to the high carbon boundary of the TaC stoichiometry range. Studies are continuing to improve material transport conditions during crystal growth.

III CRYSTAL GROWTH STUDIES

A. Melt Growth

1. Arc Fusion

During this period a number of arc-melting tests were performed on bars hot pressed from Wah Chang reactor grade TaC powder. The supplier's analyses of this material and of HfC powder were presented in Status Report III. Lattice constant measurements gave a value of 4.456 ± 0.001 Å, compared with the literature value for stoichiometric TaC of 4.456 Å.[1] In addition, the following weak diffraction lines were not identified: 2.83 Å, 2.46 Å, 2.05 Å, and 1.13 Å.

The lattice constant of the starting HfC powder was found to be 4.633 ± 0.005 Å, compared with the literature value of 4.641 Å, indicating, possibly, a slight deficiency in combined carbon. In addition, the following unidentified lines were observed: 2.94 Å, 2.55 Å, and 2.47 Å.

Melting was performed by striking an a-c arc from two electrodes, diametrically opposed, to the carbide bar, which was placed upon a water-cooled support rod. Power to the arc was maintained for several minutes at a level providing a molten cap sufficiently large for crystal growth, using the Verneuil technique. Compositional changes observed for tantalum carbide in various environments are shown in Table I. These results are consistent with values reported in Status Report III for less pure carbide compositions.

It appears that the highest carbon concentrations are maintained in pure hydrogen and when small hydrogen additions are made to argon. In pure argon and when large hydrogen additions are made to the argon, carbon removal increases. The addition of small amounts of acetylene to the environment does not appear to be of value.

Polished sections of all of these melts revealed only a single phase grain structure. Indeed, the only conclusion that appears justified as yet is that a single phase can be maintained during melting and that the stoichiometry can be varied to some extent by control of the gaseous environment.

---

[1] Santoro, G. J., Magnetic Susceptibilities of Compositions in Tantalum-Tantalum Carbide Systems, NASA TN D-2638, 1965

Table I

LATTICE PARAMETERS OF ARC-MELTED TaC[a]

Gaseous Environment (percent)	a_0 (Å)	Carbon-Tantalum Molar Ratio $\left(\frac{C}{Ta}\right)^b$
(Starting powder)	(4.456 ± 0.001)	(0.99)
95A : 5H_2	4.451 ± 0.002	0.92
90A : 10H_2	4.437 ± 0.002	0.84
80A : 20H_2	4.434 ± 0.002	0.82
60A : 40H_2	4.433 ± 0.002	0.82
20A : 80H_2	4.424 ± 0.002	0.77
100 H_2	4.449 ± 0.002	0.91
85A : 10H_2 : 5C_2H_2	4.428 ± 0.005	0.79

[a] Each specimen was held molten for 5 minutes

[b] Taken from curve by Santoro[1]

The trends in compositional variations observed may be significant or may just result from the limited control over melt uniformity that can be maintained in the test furnace. For these tests, only two electrodes were used and the pedestal was not rotated. In addition, the saturable-core reactors used in these tests did not provide the desired degree of control. Consequently, in order to obtain a complete molten cap, parts of the cap may have been considerably superheated.

Figure 1 shows a polished section of a boule cut approximately in the plane of the carbon electrodes. Here, the regions directly under the electrodes are seriously affected by superheating. Under high

FIG. 1 VERTICAL SECTION OF A TANTALUM CARBIDE ARC-MELTED BOULE — heavily etched to show grain structure (26 X)

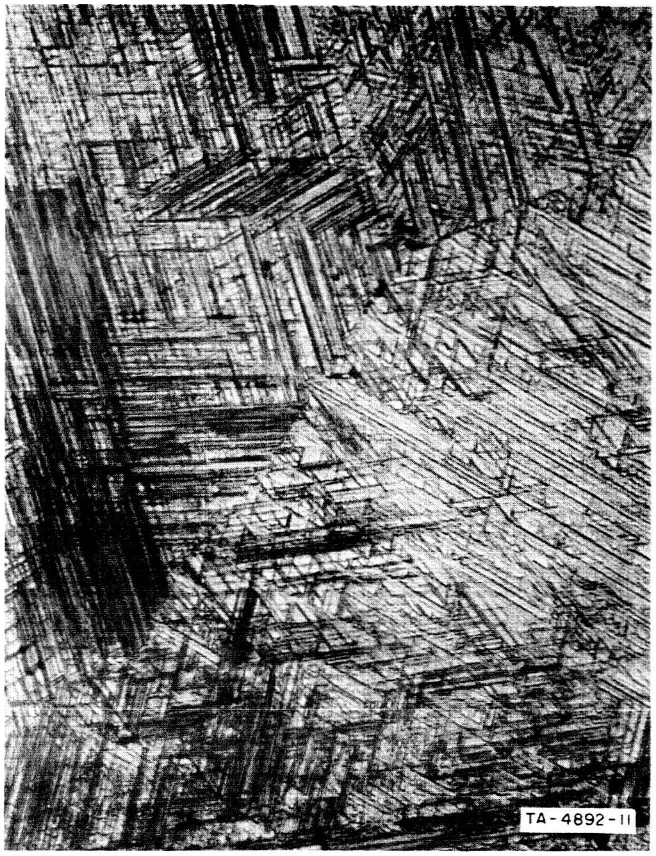


FIG. 2 STRUCTURE OF ARC MELTED
TANTALUM CARBIDE BOULE
NEAR ELECTRODE (500 X)

magnification, Fig. 2, these areas are seen to have the Widmanstatten structure typical of Ta_2C precipitation from TaC.[2]

Based on the results obtained, the final furnace configuration and power supply were fixed, and the needed components were ordered. The a-c arc power supply will consist of three separately variable saturable-core reactors operating from a single phase line and delivering 5 to 30 volts to each electrode. The three electrodes will arc directly to the seed crystal. Final construction of the furnace chamber is also in progress. Additional thermal protection will be required for the electrode insulators, and each electrode will rotate at approximately 10 rpm. The resistively heated furnace to be used for annealing and slow cooling of boules is also being assembled.

2. Plasma Fusion

Work using the induction-coupled plasma as a heat source for Verneuil growth was directed toward forming a stable molten cap on a crystal pedestal. Use of a water-cooled quartz tube for the plasma eliminated all problems of tube breakage when operating an argon plasma at 10 kw. It was anticipated that the addition of diatomic hydrogen to the plasma would greatly increase the enthalpy and heat transfer of the plasma in a manner similar to that obtained with the addition of oxygen. A considerable increase in temperature was observed, but neither tantalum carbide nor hafnium carbide, nor for that matter, tantalum metal, could be melted in a plasma containing up to 100 percent hydrogen. In fact, the temperature of the seed rod did not appear to increase significantly with hydrogen additions above about 20 percent.

The power level was then increased to 20 kw while maintaining a 20 percent hydrogen level. It was still not possible to melt a tantalum metal rod, much less the carbides.

At this point, measurements were made of the temperature of the seed tip at various positions in the plasma, using an optical pyrometer, in order to establish the hottest point. Such measurements are comparative only, absolute values of temperature being meaningless without

---

[2] Santoro, G. and H. B. Probst, An Explanation of Microstructures in the Tantalum-Carbon System, Proceedings of the 12th Annual Conference on Applications of X-ray Analysis, Aug. 7-9, 1963, Plenum Press, New York

extensive calibration of optical absorption by the plasma and the water-cooled walls. While it might be assumed that the plasma absorption is not significant since it is not optically dense, this is not the case. To illustrate the magnitude of this effect, the temperature of a tungsten ribbon lamp was measured directly, through the water-cooled plasma tube walls, and through an argon plasma operating at 12 kw. The temperature of the lamp was 2435°C. A 320° drop was obtained by sighting through the water-cooled walls. A 755°C drop was recorded with the plasma in operation. From such measurements, and allowing for the fact that the seed is in the center of the plasma, an effective constant for Wien's law* of 61×10^{-6} can be calculated. However, this value is a strong function of both the plasma composition and the power level. Thus, the measured temperature of the seed tip was frequently observed to decrease as the plasma power was raised. In addition, as the power was increased, boiling was initiated in the cooling water, which further affected temperature reading.

With the seed tip positioned in the hottest part of the plasma, several variations in coil design and oscillator frequency were evaluated to see if improved heating could be obtained. By changing from a 5-turn cylindrical coil approximately three inches in height to a "pancake" coil, the plasma was shortened considerably but the seed temperature at the hottest point was not changed significantly. Oscillator frequency changes from 4.8 to 5.6 megacycles did not seem to affect the temperature as long as the circuit was well tuned.

With these factors optimized, the plasma enthalpy was again increased to see if melting could be attained. At 21 kw, using a pure argon plasma, melting was just started on a tantalum metal rod (mp, 3000°C). Tantalum carbide was unaffected at this power level even with hydrogen additions up to 20 percent by volume.

At this enthalpy level, problems began to arise with the water-cooled quartz plasma tube. The tube was 2 inches in inside diameter and had a double wall to permit high-velocity, vortex-flow water cooling. At the higher power levels the water boiled at the inside surface, but not in excess of that frequently observed in water-cooled furnace walls. At 21 kw and 20 percent hydrogen, if the plasma was only slightly deflected to one side of the tube, either by a slight misalignment of the sheath tube or by a slight tilting of the coil, a brown reaction layer formed on the side quartz wall. Once this layer formed, heat absorption in the wall increased rapidly and the tube failed within

---

[*] $A = \frac{1}{T_{\text{measured}}} - \frac{1}{T_{\text{true}}}$

a few minutes. This reaction apparently was between the hot plasma and the quartz, since it occurred even when the seed rod was removed. At higher power levels, it occurred with decreasing hydrogen additions.

During one run the power level was increased fairly rapidly to see just where tantalum carbide could be melted. Melting was initiated at the seed tip at 36 kw and 20 percent hydrogen. The power had to be lowered almost immediately, however, so no idea of melt stability could be obtained. This behavior can be contrasted with that of aluminum oxide (mp, 2050°C), where a large molten cap can be maintained, using the same plasma equipment, at 10 kw in pure argon and at 3.5 kw with 50 percent oxygen added to the argon.

One of the major limiting features in heating uninsulated solids at temperatures above 2500°C is the large amount of energy lost by radiation. Based on the temperature calculations made for the seed rod in an argon plasma at 12 kw, it appears that the temperature attained may be very near 2500°C. At this temperature, considering the seed and support geometry, the maximum radiation loss would be about 2 kw. This is a significant fraction of the power transferred to the plasma. Using the same geometry, one can calculate that the radiation losses, under anticipated crystal growth conditions, will fall between 7 and 10 kw under crystal growth conditions. If we could in some way reduce these losses, it is possible that melting could be obtained under more reasonable operating power levels.

Previously, at the Institute, it was found that a vapor-deposited metal film applied to the quartz tube acted as a reflector and assisted in raising the plasma enthalpy at a fixed power level. One of the plasma tubes was therefore coated with a thin chromium plate (vacuum evaporated) to see if such reflections would significantly alter previous findings. The coating was placed on the outside surface of the tube, although in a final application one would hope to reduce absorption in the walls by coating the inside surface. No induction coupling to such a thin film was observed. However, the high velocity water flow over the coated surface did cause removal of flakes after several minutes of operation. The carbides of interest still could not be melted under plasma conditions which could be maintained for extended periods.

At the initiation of this program, it appeared that the induction-coupled plasma was particularly suited for Verneuil growth of refractory crystals because of its similarity in many respects to the torches that have been well established in commercial crystal growth. Indeed, these advantages still appear attractive. However, as a result of the difficulties encountered in constructing a torch that can operate reliably at the required energy levels, it does not appear that a useful crystal growth facility will soon be forthcoming. There are still numerous design features and chemical systems to be explored which may make this device of great value in carbide crystal growth. Such developments will probably be quite costly and time-consuming and are not considered to be of sufficient immediate value to the objectives of this program to permit recommendation of additional study. Therefore, work on the use of the induction-coupled plasma will be terminated.

B. Solution Growth

Additional work to establish suitable solvent systems for solution growth of tantalum and hafnium carbide was directed toward aluminum and tin melts. Both are low-melting metals--tin apparently dissolving almost no carbon and thus of interest as an alloying metal and a diluent, and aluminum dissolving somewhat more carbon but forming an aluminum carbide which, fortunately, is quite soluble in dilute acids. The results of carbon solubility studies on these metals are shown in Table II, which shows that tin, as anticipated, dissolves very little carbon. The behavior of aluminum, on the other hand, appears quite erratic. The analytical problem of getting "complete burns" is quite difficult, and repeat measurements did nothing to clarify the results.

Table II

CARBON SOLUBILITY IN TIN AND ALUMINUM

Sample No.	Solvent	Sampling Temperature (°C)	Carbon (ppm)
1	Tin	825	< 20
2	Tin	825	20
3	Tin	1000	30
4	Tin	1004	20
5	Tin	1300	20
6	Tin	1610	40
7	Tin	1663	30
8	Aluminum	1000	> 400
9	Aluminum	1000	110
10	Aluminum	1300	> 400
11	Aluminum	1000	< 20
12	Aluminum	1000	< 20

A number of crystal growth experiments were run in a Czochralski-type furnace, using a "double-chamber" graphite crucible. Hot-pressed tantalum carbide rods were placed in the lower "hot chamber" to serve as the nutrient in most of these experiments, and the cooler upper chamber was filled with either tin or aluminum alloys as the solvent media.

No attempts were made during these very preliminary experiments to grow crystals on a "seed" suspended in the upper chamber. Instead, the crystals were allowed to nucleate spontaneously and grow on the graphite walls.

A summary of significant crystal growth runs is presented in Table III.

In runs 18 and 19, the small amount of tantalum was added to the solvent in order to precoat the large crucible surface with tantalum carbide. When the tin melt was removed, the crucible surface was indeed gold-colored over most of the area. However, absolutely no crystals were observed anywhere in the melt, indicating no carbide transfer even with a temperature gradient of almost 600°C. A thin cryptocrystalline "scum" recovered from the surface of the melt was found to consist primarily of TaC ($a_0 = 4.445 \pm 0.005$ Å), with some Ta_2C also present. This material probably formed from the excess tantalum in the solvent and any loose carbon powder from the crucible walls.

Pure aluminum melts could not be maintained for extended periods in graphite crucibles. An example of the type of breakage experienced in these runs is shown in Fig. 3. However, significant yields of small tantalum carbide crystals were obtained from the lower chamber in each of these runs. The crystals are gold in color and many appear under the microscope to be perfectly formed octahedrons as is shown in Fig. 4. Back reflection lattice constant measurements give $a_0 = 4.455 \pm 0.001$ Å, indicating nearly stoichiometric TaC.

The addition of tin to the aluminum melts seems to have eliminated crucible breakage problems as can be seen in runs 22 and 23, which were held at temperatures for 48 hours with no noticeable deleterious effects.

In run 23, tantalum alloyed with the Sn-Al solvent was used as a nutrient, with the carbon being supplied by the crucible. It was anticipated that the presence of excess tantalum might shift the crystal stoichiometry toward Ta_2C. However, only TaC crystals were obtained and the measured lattice constant was 4.456 ± 0.001 Å.

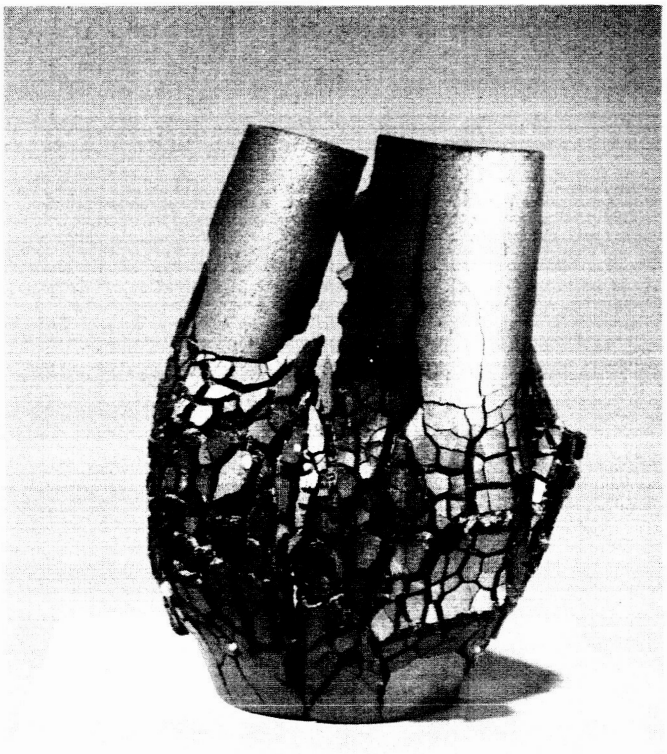
Table III

SOLUTION CRYSTAL GROWTH CONDITIONS AND RESULTS

EXPERIMENT NUMBER	SOLVENT [a]	NUTRIENT	SURFACE TEMPERATURE (°C)	BASE TEMPERATURE (°C)	THERMAL GRADIENT (°C)	STATIC GROWTH (hr)	COOLING GROWTH (hr)	RESULTS
18	Sn + 0.1 % Ta	TaC	1075	1650	575	6	1	No crystals
19	Al + 0.1 % Ta	TaC	1075	1650	575	2	Crucible broke	Small octahedral TaC crystals plus transparent plates of Al_4C_3
20	Al	TaC	1100	1155	55	~6	Crucible broke	Larger yield of smaller octahedral TaC crystals and more Al_4C_3
21	Sn + 10 % Fe	TaC	1435	1530	95	48	5-1/2	Small TaC cubes and prismatic FeC_3 crystals
22	Sn + 50 % Al	TaC	1435	1530	95	48	5-1/2	A few small, thick TaC laths, small TaC octahedrons, and large numbers of relatively large transparent plates of Al_4C_3
23[b]	Sn + 50 % Al	Tantalum + Carbon	1475	1570	95	48	5-1/2	Large yield of relatively large subhedral crystals of TaC plus large amounts of Al_4C_3

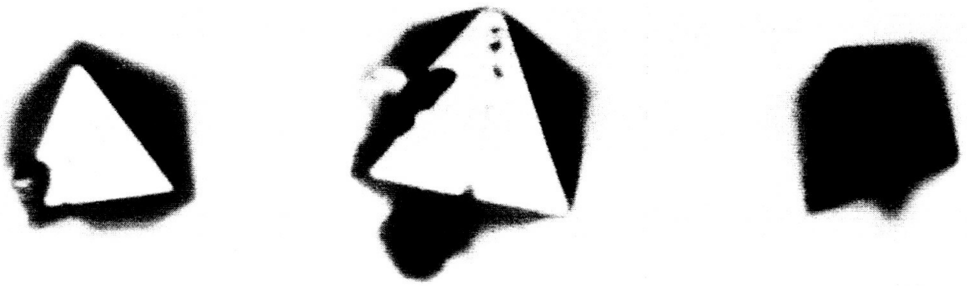
[a] Compositions on atomic basis.

[b] Run in single chamber crucible.



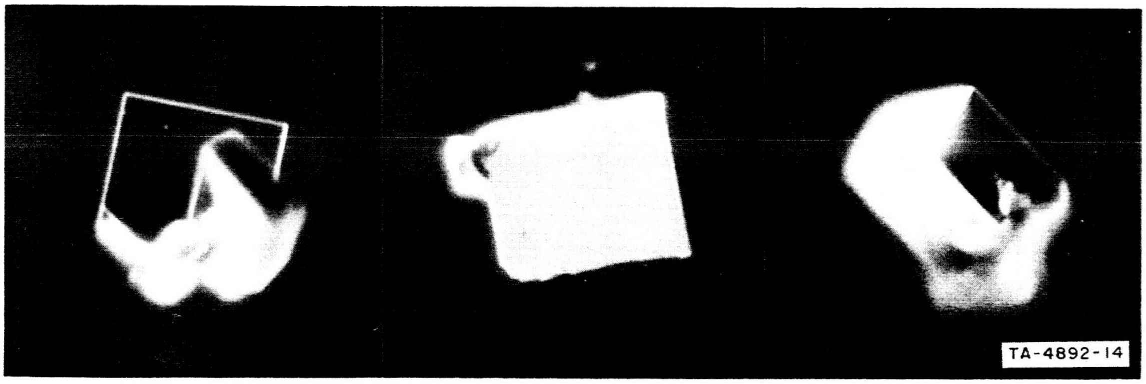
TA-4892-12

FIG. 3 CRUCIBLE FAILURE FROM ATTACK BY MOLTEN ALUMINUM



TA-4892-13

FIG. 4 TANTALUM CARBIDE CRYSTALS GROWN USING ALUMINUM SOLVENT (400 X)



TA-4892-14

FIG. 5 TANTALUM CARBIDE CRYSTALS GROWN USING AN IRON-TIN ALLOY SOLVENT (400 X)

In run 21, a 10 percent iron addition was employed to increase the solubility of tantalum carbide in tin. As in the aluminum-tin runs, gold-colored TaC crystals were obtained having a lattice constant of 4.455 ± 0.001 Å. In this case, however, the crystal morphology was predominantly cubic as is shown in Fig. 5. In addition, grey, prismatic iron carbide crystals grew about one-half inch above the TaC crystals, replacing the Al_4C_3 crystals found in all of the aluminum-base alloys.

The fact that all of the TaC crystals in these runs grew in the hot lower chamber, while iron carbide or aluminum carbide crystals grew in the upper chamber, demonstrates a lack of the desired convection stirring within the melt. Design studies are in progress to determine the most promising crucible configuration to promote the formation of strong convection currents capable of transporting dense TaC-saturated solution from a hot zone to a cooler crystal growth zone. Mechanical stirring by a graphite propellor may be employed if studies indicate that increased convectional stirring will not be sufficient.