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STUDY OF GROWTH PARAMETERS FOR REFRACTORY CARBIDE SINGLE CRYSTALS

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I INTRODUCTION

Interest in the refractory carbides has increased in recent years in anticipation of many new applications requiring the use of super-refractories. In the course of research and development work on these materials, however, difficulties have been encountered in attaining and reproducing desired physical properties. Little is known of ultimate intrinsic physical properties or the influences of changes in stoichiometry, 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 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 application of new techniques and procedures to growth of single crystals of tantalum carbide, hafnium carbide, and solid solutions of the two. The new techniques being investigated fall into two classes: first, application of recently developed methods of liquid metal solution growth of crystals, and, second, utilization of a-c arc melting for Verneuil crystal growth.

II SUMMARY AND CONCLUSIONS

Crystal growth experiments were conducted with the arc-Verneuil furnace early in the quarter to explore the influence of various atmosphere compositions, during melting, on crystal stoichiometry. While some indications were obtained that single-phase compositions can be maintained, a number of experimental problems were encountered. Difficulties in maintaining uninterrupted growth experiments of long duration were partly caused by power limitations. Consequently the power supply was returned to its manufacturer and modified to provide a 70% increase in power. While experimental operations were suspended to modify the power supply, the arc-Verneuil furnace was extensively redesigned. Major changes were required, based on previous experiments; these could not be made by modifying the existing furnace. Design drawings for the new arc-Verneuil furnace were completed and construction bids will be secured in the near future.

The solution growth experiments emphasized attempts to determine the tantalum solubility in several carbon-saturated liquid metals and crystal-pulling experiments using a cold probe or single crystal tantalum carbide seed. In both cases, it was found that nucleation and growth of many small tantalum carbide crystals in the cool region of the melt cause a uniform dispersion of small tantalum carbide crystals and prevent both growth of a large single crystal and sampling of the liquid phase exclusive of solid tantalum carbide. Work was initiated on a thin-film, solution-crystallization method involving a narrow liquid zone and a steep temperature gradient between the nutrient and seed materials.

III CRYSTAL GROWTH STUDIES

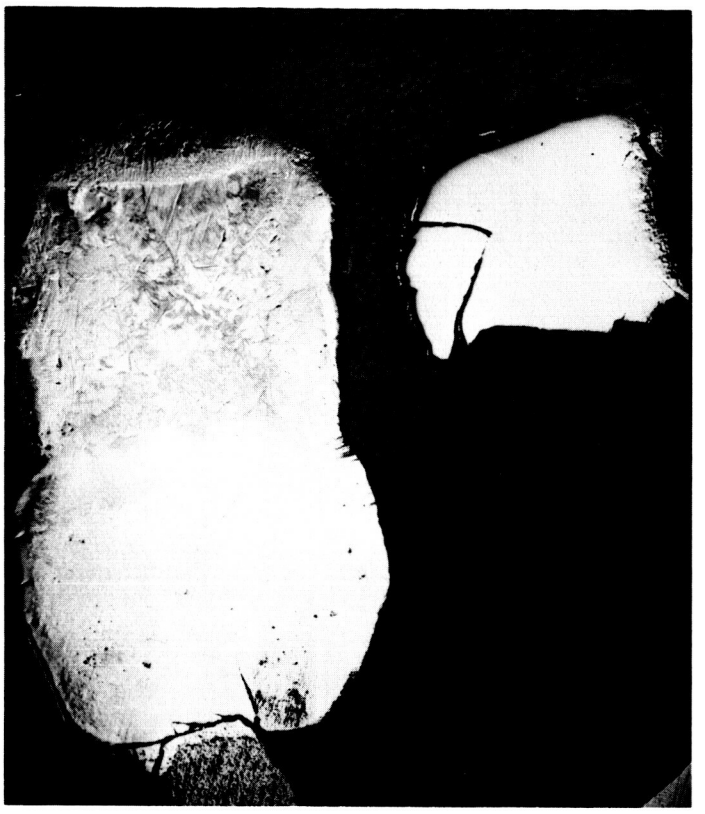
A. Arc-Verneuil Growth

During the early part of the quarter, Verneuil growth experiments were continued in the three-electrode, single-phase, a-c arc furnace. Some changes were made in the seed-rod train in an attempt to reduce the eccentricity of the seed during rotation. Although the total movement of the seed in the horizontal plane is less than 0.100 in., a more precise location during rotation is desired for single crystal growth. Additional difficulties were encountered in maintaining a stable arc for a significant period of time, particularly when hydrogen was introduced into the furnace atmosphere. Arc instability seemed to increase as the graphite electrode tips were blunted. The saturable core reactor power supply was operating near or at peak power output, 100 amperes for each of three electrodes. After consulting with the manufacturer of the power supply, a decision was made to modify the power supply in order to increase the current output. This decision was made midway in the quarter and prevented further experimental runs. A decision was also made to redesign and construct a new model arc-Verneuil furnace. Down time will be minimized by undertaking these changes concurrently.

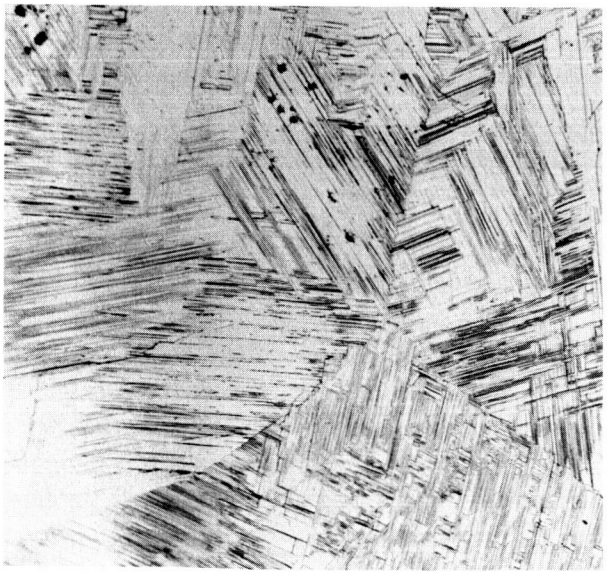
1. Experimental Results

Crystal growth runs made during this quarter were directed primarily toward reducing carbon losses in the molten carbide by altering the gaseous environment in accordance with the early results reported in Quarterly Report No. III. All of the boules grown in pure argon showed extensive carbon loss with the appearance of large quantities of Ta_2C and even in some cases tantalum metal.

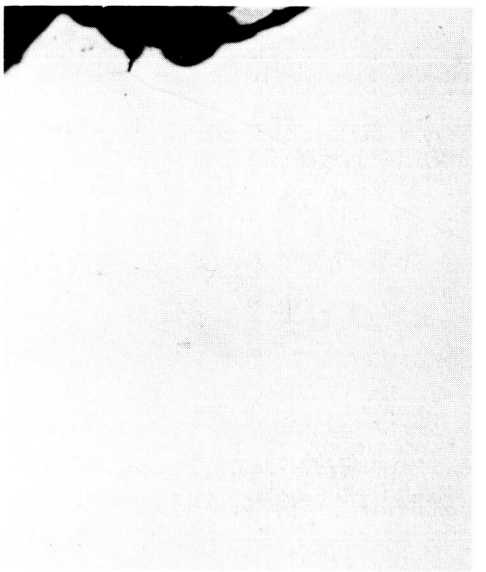
In Fig. 1(a) a typical argon-grown boule is shown, illustrating the structures observed. This specimen has been etched very heavily with hot $HF-HNO_3$ and with boiling aqua regia. A clearer picture of



(a) ARGON (left), ARGON-HYDROGEN (right) – 8X



(b) ARGON – 100X



(c) ARGON – HYDROGEN – 100X

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FIG. 1 POLISHED AND ETCHED SECTIONS OF TANTALUM CARBIDE BOULES GROWN IN ARGON AND ARGON-HYDROGEN ENVIRONMENTS

the extent of second-phase precipitation can be seen in the higher-magnification view of Fig. 1(b).

The problems encountered in maintaining stable crystal growth conditions in the arc increased greatly with increasing additions of hydrogen to the furnace environment. At high hydrogen contents, nearly all runs were terminated by extinguishment of the arc or by failure to maintain proper melting conditions. Polished sections of boules usually showed continued carbon loss. However, polished sections of some of the boules showed areas of single phase material; thus, it is possible that much of the difficulty arose from changes in growth conditions during formation of the boule. At high hydrogen contents (>60% H_2) the coloration of the boule surfaces shifted from silver to the yellow "brassy" color typical of TaC.

In one run, the furnace chamber was first evacuated, flushed, and back-filled with argon. During crystal growth, pure hydrogen was employed as the powder carrier gas. In this way, a high hydrogen concentration was probably maintained in the molten region. This boule was yellow, and neither X-ray diffraction nor examination of a polished section showed any indication of the presence of a second phase. The section of the upper portion of this boule is shown in Figs. 1(a) and 1(c). The boule was mounted with an argon-grown boule in order to assure that the etching procedure would reveal any substructure if it were present. Only a single grain boundary was observed. The lattice constant was measured as 4.427 $\mathring{A}$ which places it well within the single phase region according to the calibration curve presented in Quarterly Report No. III. Microhardness readings of 2760, 2760, and 2330 kg/mm^2 were obtained using a 50 g load.

2. Apparatus Modifications

Experiments were conducted early in the quarter in which a Metco Model MP vibrating type of powder feeder was used to feed TaC powder to the boule. The performance of this feeder was somewhat better than the performance of the centrifugal-capillary particle feeder previously employed, particularly when acicular rather than equidimensional particles

were used. Particle feeding is still not ideal and design of a system for feeding particles using a pulsed air column driven by an audio speaker was initiated.

In conversations with the manufacturer of the saturable core reactor power-supply, it was determined that the current output to each of three electrodes could be increased from the maximum of 100 to 170 amperes without rewinding the saturable core reactors. The required modifications were completed by the manufacturer and the power supply was returned on December 1, 1965. A larger voltage step-down transformer on the primary side and larger current-monitoring coils and ammeters were installed. Since the voltage is fixed by the arc characteristics, current output from the power supply limits the amount of power which can be supplied to the arc melting process at the seed. This 70 percent power increase was the maximum value consonant with the present saturable core windings and a further increase in power would have caused a considerable greater expenditure.

Drawings for the new model of the arc-Verneuil furnace have been completed and bids for its manufacture will be secured in the near future. In outward appearance this furnace is similar to the previous model. It involves an 8-in.-diameter brass cylindrical shell in lieu of the 6-in.-diameter shell used previously. Three single-phase, a-c electrode ports are located on the same horizon at 120^{0}. The electrode holders are 1/2 in. in diameter rather than 1/4-in. previously used. The common electrode holder, which supports the seed, has been increased from 1/2-in. to 1-in. diameter. These larger electrode sizes will permit conducting more current into the system without appreciable resistance heating. The system of arc-discharging three single-phase, a-c horizontal electrodes to the seed is retained.

Both the horizontal and vertical (seed train) electrode holders have been completely redesigned. The design is intended to provide for accurate positioning control of the seed during rotation, ± 0.015 in. It permits viewing of each electrode through three windows, each located at right angles to one of the horizontal electrodes. This should provide for more

precise control of the electrode standoff distance and better control of the arc. The design also provides for rotation of the horizontal and vertical electrodes. Previously, the horizontal electrodes could not be rotated without loosening the water seals enough to permit water leakage into the system. In the new system, copper-graphite brushes will be used to conduct electricity and some heat out of each electrode. Copper-graphite sleeve bearings will also be used to support and align the electrodes and conduct heat from the system. The sturdier design, particularly in the electrode support areas, and the electrical brush design will accommodate larger power loads without electrode misalignment. The new design also provides for consumption of three linear inches of the graphite horizontal electrodes before replacement is required. This furnace will be a vacuum-tight system sealed with O-rings or quad-rings.

A partial assembly view of the furnace is shown in Fig. 2. The rotational drive mechanism for the horizontal and vertical electrodes presently used will be retained, and the powder feed tube presently in use will also be employed in the new furnace. Consequently, these details are not shown in Fig. 2. Although the graphite resistance heater for annealing the crystals is not shown, its terminal connectors are shown. A horizontal view of the furnace showing the electrode and window alignment is presented in Fig. 3.

Critical lead time materials for the construction of this furnace have been ordered. These include boron nitride raw stock, graphite raw stock, vacuum fittings, and V-band clamps for attaching the furnace shells. It is anticipated that construction will be completed late in the next quarter.

Mixed tantalum carbide/hafnium carbide crystalline powders are required for the arc-Verneuil growth of mixed solid-solution single crystals. Although feeding a mechanical blend of tantalum carbide and hafnium carbide powders may suffice, it is expected that this practice may lead to variations in stoichiometry in the resulting crystal. Therefore, techniques for readily synthesizing solid solutions of tantalum carbide and hafnium carbide in particle form are required. Some preliminary attempts have been made to do this by solution growth in liquid metals. A 50/50

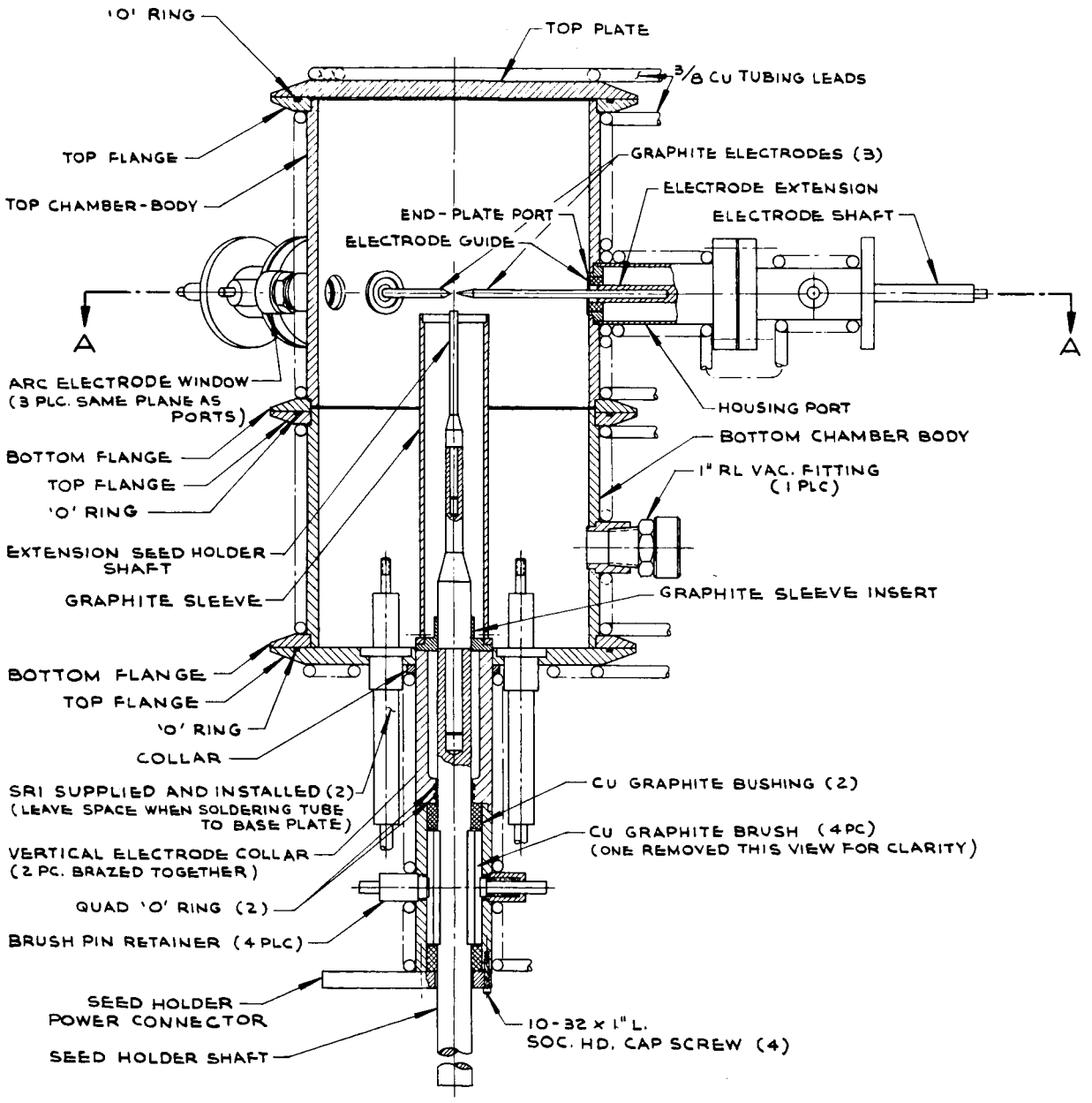

FIG. 2 FRONT VIEW OF ARC-VERNEUIL FURNACE MOD 2 ASSEMBLY

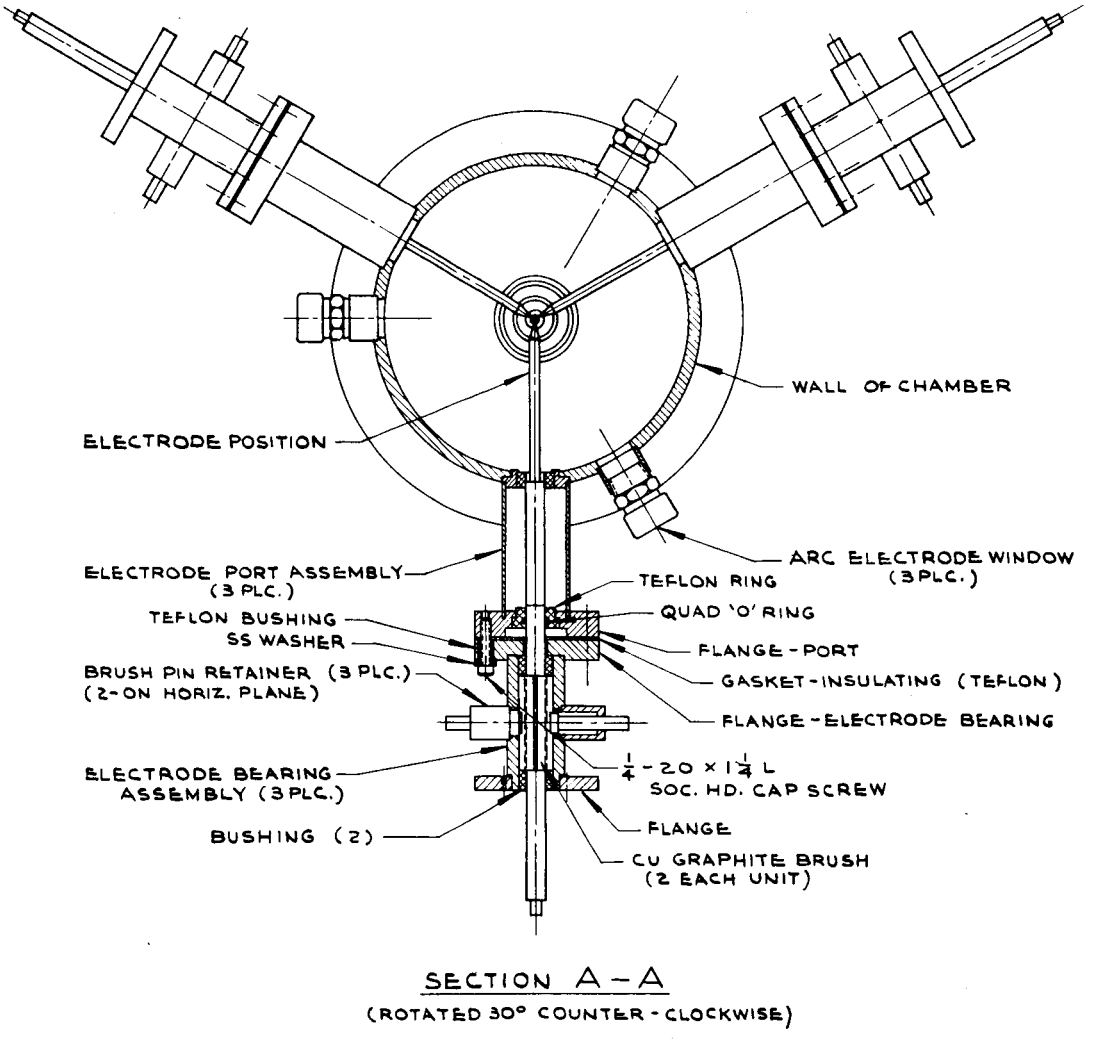

FIG. 3 TOP SECTION VIEW OF ARC-VERNEUIL FURNACE MOD 2 ASSEMBLY SHOWING THREE HORIZONTAL ELECTRODES

atomic mixture of hafnium and tantalum, with the required stoichiometric amount of carbon, was added to an iron alloy contained in an alumina crucible. Carbide crystals were formed but could not be effectively separated from the cooled melt or analyzed because of the presence of excessive quantities of iron carbide. A second experiment has been conducted using an aluminum melt in an alumina crucible. A 50/50 mixture of hafnium and tantalum metal powders and an excess of carbon were added to the melt. The results of this experiment will be presented in the next quarterly report.

3. Future Work

The new arc-Verneuil furnace must be constructed, delivered, and assembled to the existing power supply and electrode rotary-drive components before further experimental work can be conducted. It is expected that this work will occupy the next quarter, and that crystal growth experiments will resume in the following quarter. In the meanwhile, the pulsed-bed particle feeder will be constructed and tested.

B. Metal Solution Growth

1. Experimental Results

A number of modified Czochralski experiments were made in which a cold probe was introduced into a saturated tantalum carbide solution. Iron was used as the solvent; both alumina and graphite were used as crucible materials. With alumina crucibles, stoichiometric mixtures of tantalum and carbon powders were added to the melt. With the carbon crucibles, an excess of tantalum powder was added to the melt. The experiments in alumina crucibles were conducted at $1650^{\circ}C \pm 25^{\circ}$. Most of the experiments with the graphite crucible were conducted at $2000^{\circ}C$. The probe was inserted just below the melt meniscus and withdrawn slowly, eventually removed from the melt, and examined. The following materials were used for probes: hot-pressed polycrystalline tantalum carbide, tantalum carbide originating from arc-Verneuil experiments, graphite, alumina, tantalum wires or rods, and boron nitride. The diameters of the tantalum rod and wires were 0.125, 0.062, and 0.032 in. The larger tantalum rods and the carbon and boron nitride probes were machined to form sharp tips on their ends.

Introduction of only the sharp tip of a large diameter probe into the melt caused very large temperature gradients at the melt-probe interface and usually resulted in freezing of the solvent on the tip at temperatures below $1650^{\circ}C$. The solidified iron usually contained small dispersed crystals of tantalum carbide. Thin tantalum wires were usually dissolved. The intermediate size tantalum wires also dissolved, but a few tantalum carbide crystals were attached to the tip of the 0.062-in. wire withdrawn

from the iron melt in an alumina crucible. These crystals were small and little significance is attached to them. The graphite probes withdrawn from an iron melt at 2000°C contained some very small black crystals which were later found by X-ray analysis to be the lower carbide of iron, FeC.

A number of experiments were made to secure data on the activity of tantalum in various liquid metals saturated with carbon. These experiments were performed in graphite crucibles. The initial series involved iron, nickel, aluminum, and a ferrochrome alloy. The experiment involving ferrochrome was unsuccessful because of a violent carbon boil causing ejection of much of the melt. In these experiments 1.5 wt percent of tantalum carbide in the form of hot-pressed polycrystalline chips was added to the melts. The experiments were conducted in isothermal baths at a temperature of 1650°C. The unsuccessful ferrochrome experiment was conducted at 1750°C. Aliquot samples were withdrawn periodically for subsequent semiquantitative emission spectrographic analysis. Results are shown in Table I.

Table I

TANTALUM CONTENT BY SEMIQUANTITATIVE EMISSION SPECTROGRAPHIC ANALYSIS OF CARBON-SATURATED LIQUID METALS IN CONTACT WITH TaC

Run No.	Initial TaC Addition (wt %)	Liquid Metal	Equilibration Period (hours)	Ta Content of Sample (wt %)
38	1.5	Iron	1 1 6 24	2.0 1.5 2.5 2.5
39	1.5	Nickel	1 1 6 24	1.25 2.0 2.5 2.5
43	1.5	Aluminum	1	nil

With the exception of aluminum, where the tantalum solubility is known to be very low, the reported tantalum analyses were much higher than expected, and in all cases equalled the amount of tantalum added in the initial mixture, within experimental error. These data suggest that all of the tantalum carbide chips had dissolved and that either the tantalum solubility was high, in spite of the presence of carbon, or that tantalum carbide had re-precipitated as small crystals, uniformly dispersed in the melt by convective mixing. As a consequence of these results, another series of experiments was conducted in which larger amounts of tantalum were added to the melts. The larger amounts of tantalum exceeded the maximum analytical limits for the emission spectrographic technique, and X-ray fluorescence spectrographic methods were used for the analyses. A calibration curve of X-ray intensity versus weight percent present was made for each metal solvent system, using standard samples prepared in our laboratory by mixing tantalum carbide and metal powders.

The results, given in Table II, show that the amount of tantalum present in the withdrawn samples is again approximately equal to the amount of tantalum added to the melt charge. X-ray diffraction analyses were also conducted and, although the results were not reliable enough to permit quantitative analysis, they did indicate that most of the tantalum was present as tantalum carbide. This suggests that the tantalum

Table II

TANTALUM CONTENT BY X-RAY FLUORESCENT SPECTROGRAPHIC ANALYSIS OF CARBON-SATURATED LIQUID METALS IN EQUILIBRIUM WITH TaC

Run No.	Initial Ta Addition (wt %)	Liquid Metal	Equilibrium Period (hours)	Ta Content of Sample (wt %)
46	13.8	Iron	1 6 24	12.2 12.5 12.5
47-2	15	Nickel	1 3 6 24	15.3 13.5 21.1 12.8

carbide nutrient is dispersed uniformly in the bath because of convective mixing and does not settle to the bottom as has been previously assumed. This also explains much of the difficulty in growing tantalum carbide single crystals from metal solutions using a modified Czochralski method. Tantalum carbide dissolved in the hotter regions of the bath precipitates on small tantalum carbide particles suspended in the cooler regions of the bath, even at very low temperature differences, rather than growing on the surface of a single-crystal-seed or cold probe. In order to circumvent this problem, crystal growing methods which reduce either the amount of convection, the amount of solvent, or the distance between the nutrient and growth interfaces are required.

As a consequence of the tantalum activity experiments, in which it was found that tantalum carbide nutrient is dispersed uniformly in the crucible bath, an investigation of other modifications of the solution growth method was initiated. A thin-film solution-crystallization experiment was designed in which a large thermal gradient is maintained between the tantalum carbide polycrystalline nutrient and a seed crystal through an intervening thin zone of liquid metal solvent. This is a modification of zone-melting techniques for crystal growing. The initial experimental configuration employs a carbon resistance-heated ring in close proximity to a thin graphite crucible containing a 1/4-in.-diameter tantalum carbide charge and an approximately 3/16-in.-long solvent zone. The apparatus allows for differential movement of the heater and crucible. Five preliminary experiments have been made to establish the ideal graphite heater design compatible with the voltage and amperage characteristics of the power supply. This work will continue and will include an attempt to use boron nitride as the crucible material in order to control the carbon and tantalum solubility.

2. Future Work

Work will continue with the thin-film solution-crystallization method described in the preceding section. Some irreversible growth experiments with an aluminum solvent will also be undertaken in an attempt to grow larger crystals than were previously grown by this approach. Some previous work on irreversible growth of tantalum carbide from aluminum melts was described in the Quarterly Report No. V (Experiment 35).