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STUDY OF GROWTH PARAMETERS FOR
REFRACTORY CARBIDE SINGLE CRYSTALS

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CONTENTS

ILLUSTRATIONS

TABLES

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

A number of experimental runs, made with the arc-Verneuil furnace, produced tantalum carbide boules. These experiments provided operating experience and indicated several apparatus modifications, each of which was made as its need became evident. Although the boules were polycrystalline, they consisted of only a few large TaC grains and were free of cracks. These results are very encouraging with respect to the growth of TaC single crystals by this method. Better control of the effective carbon vapor pressure will be required to control the tantalum carbide stoichiometry and prevent precipitation of Ta_2C on cooling. Difficulties with controlling particle feed rates and maintaining a steady experimental run longer than 15 minutes are the major current problems.

Attempts to grow large TaC crystals by pulling hot pressed TaC seed material from iron melts have been unsuccessful. An equilibrium or reversible approach was used. In general these failures were caused by mechanical problems or what is believed to be an inadequate control of the atmosphere, causing oxidation of carbon present in the melt. Further seed pulling (Czochralski) experiments are planned later. Presently, a search for a better solvent system is being made by experimentally determining the activity coefficient of tantalum in dilute tantalum alloys of several carbon-saturated liquid metals.

III   CRYSTAL GROWTH STUDIES

A.   Arc Verneuil Growth

During most of the quarter, alterations were made in the three-electrode, single-phase, a-c arc furnace constructed for Verneuil growth of refractory carbide crystals. During this period, molten caps were achieved on tantalum carbide seeds. The first actual growth of a boule involving the addition of significant amounts of tantalum carbide powder to the molten cap occurred early in August. Since then a number of experiments have been performed to improve the apparatus and gain operating experience. Several additional boules have been grown, and those shown in Fig. 1 are typical. None of the boules grown thus far are single crystals.

1.   Apparatus Modifications

A number of apparatus modifications have been made to improve the control of the growth process. These constitute relatively minor changes that were indicated from the initial operating experience, and could not have been anticipated in the original design. These "shakedown" operations are still in progress, with most of the effort being devoted to achieving a steadier growth rate.

Precise control of the carbide-particle feed rate is a major problem in Verneuil crystal growth generally. The problem is aggravated in this instance because of strong thermal convection currents of gases in the region of the arc and boule. A gas envelope surrounding the boule must be maintained at an appreciable pressure in order to stabilize the arc and retard evaporation of carbon. A number of tantalum carbide particle sizes were tried. Because of the thermal convection currents, a fairly coarse particle size fraction, -200 +270 mesh, was found to be optimum, and this size is now being used in all of the experiments.

The particles are fed through a water-cooled, 18-inch feed tube. The initial tube had an inside diameter of .042 inch.. A new feed tube with an inside diameter of .020 inch has been constructed and is now being employed. Because particle dispersion is less with the smaller tube, a larger percentage of the powder feed now reaches the
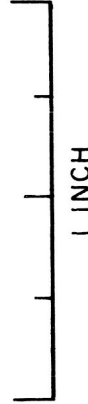
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FIG. 1   TYPICAL TaC BOULES GROWN BY THE ARC-VERNEUIL PROCESS

boule. The particles are accelerated within the feed tube by using a carrier of gas of the same composition as that in the furnace chamber. Thus far, argon has been the only gas used and only at the pressure of 300 millimeters, where a stable arc is achieved. Terminal velocity calculations for the particles at this pressure confirm that a significant fraction of the particle feed should strike the boule.

Three types of feeders were tried: a vibrating screen, a rotating gate or chopper device, and a capillary tube, centrifugal feeder. The desired properties of a feeder are a continuously variable feed rate from a small positive value down to zero, and a reproducible relationship between the controller setting and the feed rate. No particle feeder used to date meets these requirements to the desired degree, but the capillary tube, centrifugal device is the most effective of those tried and has been used on all of the boule growth experiments. In this device particles flow out of a rotating container similar to a thistle tube and through a capillary tube that is bent slightly upward at an angle of about 20° with the horizon. Particles are discharged when a critical rotating speed is reached where the centrifugal force balances the gravity force on a particle. An analysis of the behavior of this type of feeder is given in the Appendix.

A number of other alterations were made to the crystal growing furnace during the period, including:

1. The feeder motor drive mechanism was changed to reduce vibration.
2. The armature brush assembly, used to establish electrical contact with the seed rod, was redesigned and changed to prevent localized arcing.
3. The saturable core power supply wiring was changed to prevent overheating.
4. A new vacuum pumping system was installed.
5. A powder trap was installed at the bottom of the furnace to collect powder that had not deposited on the boule.
6. The heat-shielding over the electrodes and boule was redesigned and raised to prevent a partial current discharge to the furnace walls and loss of electrical efficiency.

5

2. Experimental Results

During the arc-Verneuil growth experiments, variations in particle size and powder feed rate were made. Experiments were usually terminated because of equipment difficulties or unsatisfactory process control. These initial experiments were performed without using the graphite auxiliary heater. It is encouraging to note that, in spite of these variable growth conditions and large temperature gradients, there is no evidence of cracking in any of the boules. Metallographic examination of a sectioned boule usually indicates four to eight approximately equiaxed grains of tantalum carbide.

Because all of the runs to date have been conducted in argon there is dissociation and evaporation of carbon from the molten TaC. A Widmanstätten structure is observed in a region of the boule adjacent to its surface. This structure results from the precipitation of Ta_2C from a carbon deficient tantalum carbide (γ) phase during cooling. A very small amount of Ta_2C precipitation is observed in the interior of these boules. The Ta_2C precipitate occurs as platelets along the (111) plane of TaC.[1] The precipitation occurs preferentially at sub-grain boundaries in tantalum carbide. This effect is shown in Fig. 2. The etchant consists of 25 ml HNO_3, 8 ml HF, 25 ml H_2O, 15 ml lactic acid. Some porosity has been observed at very fast growth rates.

X-ray analyses of the boules are consistent with the metallographic examinations. Using a Debye-Scherrer camera, Ta_2C was detected and estimated to be present in amounts of ten to fifteen percent. The lattice parameter of tantalum carbide in the boules was 4.417 a.u. Using the calibration curve[2] based on data of Bowman and Lesser, the carbon content in the tantalum carbide (γ) phase was calculated. A carbon/tantalum ratio of 0.74 was determined, which approximates the lower limit of carbon content within the defect range of TaC at low

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[1] 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.

[2] Halden, F. A. and H. J. Eding, Quarterly Status Report No. III/September 1 to December 1, 1964, Contract No. NASr -49(19).
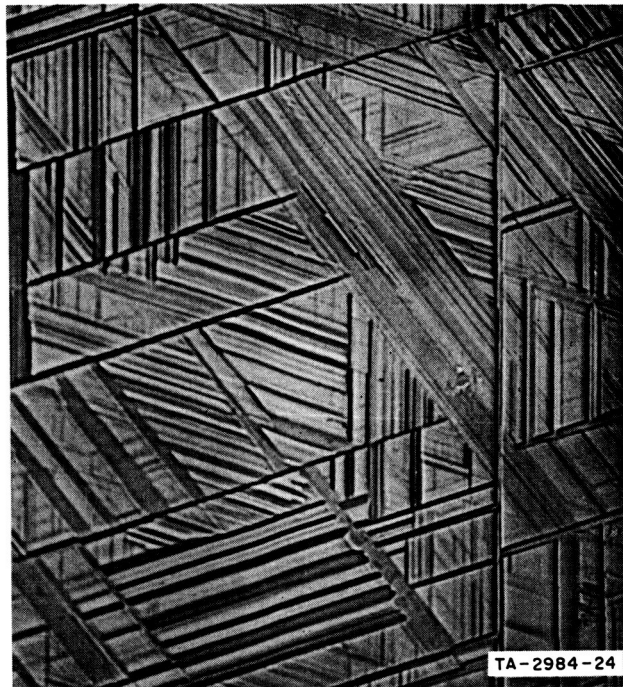
(a)
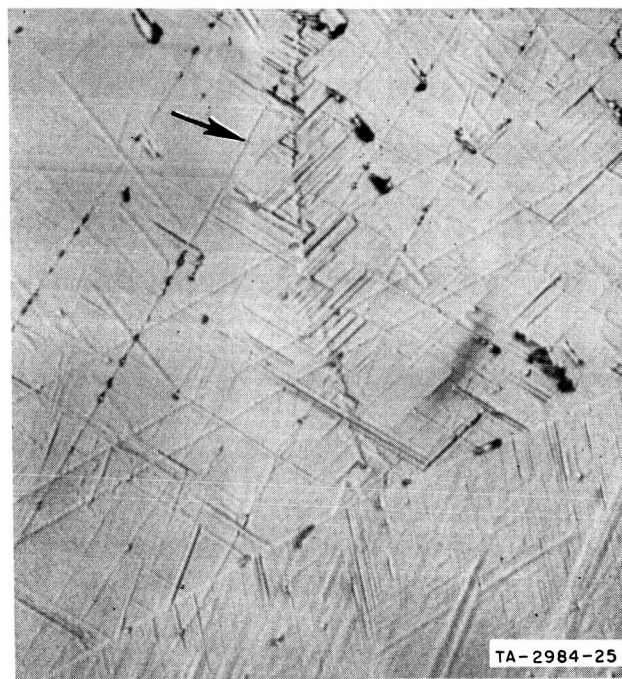
(b)

FIG. 2 HEAVY Ta$_2$C WIDMANSTÄTTEN PRECIPITATION
NEAR SURFACE OF BOULE (a); AND LIGHT Ta$_2$C
PRECIPITATION IN THE INTERIOR OF THE BOULE
(b) WITH PREFERRED PRECIPITATION ALONG SUB
GRAIN BOUNDARIES (arrow); ETCHED, 1600 X

7

temperatures (below $2400^\circ C$). This result is also consistent with the appearance of the Ta_2C phase. Because diffractometer techniques do not provide precise parameter determinations or allow detection of low levels of Ta_2C, camera methods are being used for the X-ray analyses of arc-Verneuil boules.

3. Future Work

Some changes in the seed-rod train will be made in an attempt to reduce the eccentricity of the seed and boule during rotation of the seed. Several crystal-growing experiments will be made in various atmospheres containing either hydrogen, acetylene, or hydrogen-acetylene mixtures in order to determine the effect of atmosphere on the carbon content in TaC during crystal growth. These experiments will be guided by the experimental and theoretical work reported in the third and fourth quarterly status reports. A number of methods for synthesizing mixed TaC-HfC feed powders will be considered. Solution and recrystallization methods will be considered initially in attempting to produce mixed powders. Hot pressing and arc melting will only be employed if other techniques are unsuccessful.

B. Metal Solution Growth

Most of the experimental work conducted during the quarter was devoted to attempts to grow tantalum carbide on tantalum carbide seeds pulled from the melt. These experiments employed tantalum carbide as the only nutrient, with a thermal gradient to induce dissolution and recrystallization. No large single crystals were obtained in these experiments. Small crystals, similar to those grown and reported previously, were obtained. This lack of success is believed to have been caused by inadequate solubility at the temperatures employed in the experiments. A consideration of thermodynamic and kinetic factors that affect the solubility of tantalum and carbon in the solution, and the rate of growth of tantalum-carbide crystals, respectively, was continued. Liquid metals usually form extremely nonideal solutions. An extended search for activity coefficients for tantalum and carbon in various liquid metals was made but very few data were obtained. Activity coefficients for dilute concentrations of carbon in iron and

8

several iron alloys are available. The implications of these data and the requirements for additional activity coefficients that must be determined experimentally are discussed in the following paragraphs.

1. Thermodynamic and Kinetic Considerations

In the previous quarterly status report, thermodynamic factors affecting solution growth of TaC were considered. From the thermodynamic viewpoint, two general experimental methods are available, (1) an equilibrium or reversible method based on dissolution and re-growth of TaC in a thermal gradient and (2) an irreversible precipitation of TaC from a metal solution in which separate sources of tantalum metal and carbon, usually the crucible wall, are present.

Although TaC crystals have been grown by both methods, it is more likely that excessive nucleation can be prevented with the equilibrium approach. Some further consideration of tantalum carbide thermodynamics in metal solution, in particular the relationship between tantalum and carbon solubilities and crystal growth kinetics, is needed.

a. Kinetics of Crystal Growth

The rate of crystal growth can be no greater than the rate of transport of tantalum and carbon in the metal solution. If fluid mixing, caused by either thermal convection or mechanical stirring, is neglected, the transport rate J is given by Fick's first diffusion equation:

$$J = D \frac{dC}{dx}, \qquad (1)$$

where D is the solute diffusion coefficient in the liquid metal solution, C is the solute concentration, and x is the diffusion distance. Under steady state crystal growth the diffusion equation is:

$$J = \frac{D (C_h - C_1)}{\delta_c} \qquad (2)$$

where C_h is the concentration at the higher temperature source, C_1 is the concentration in the liquid adjacent to the growing crystal, and δ_c is the distance between the source and the crystal. For the equilibrium growth of TaC in a chemically inert crucible, the source is usually TaC chips lying on the crucible bottom while the crystal is

9

located near the melt meniscus. Thus, δ_c is equal to the liquid depth. When concentration C is expressed in atomic percent, the diffusion coefficient D in cm^2/sec and the transport rate J in cm/sec, for dilute solutions equation (2) is approximately

$$J \ (cm/sec) = \frac{D \ (C_h - C_l)}{100 \ \delta_c} \ \left(\frac{M}{\rho}\right) \ soln \ \left(\frac{\rho}{M}\right) \ TaC \qquad (3)$$

Some reasonable estimates of most of the parameters in Eq. 3 can be made. Diffusion coefficients in liquids at high temperatures are similar, $D \approx 10^{-4} \ cm^2/sec$. The diffusion distance is limited by free convection (without stirring) to $\delta \approx 1$ cm, even though actual melt depths are slightly greater than 1 cm. On this basis the TaC crystal growth rate dependence on the concentration difference from source to crystal can be estimated using Eq. 3:

$$J \approx 10^{-6} \ (C_h - C_l) \ cm/sec$$

$$0.86 \ (C_h - C_l) \ mm/day. \qquad (4)$$

Forced stirring will increase the growth rate considerably, but this is not always convenient and there may be undesirable chemical reactions with the stirrer.

b. Equilibrium Concentrations of Tantalum and Carbon

The concentration differences $(C_h - C_l)$ can be determined for tantalum and carbon at specified temperatures, using the equilibrium constant for the formation of TaC,

$$Ta + C \ \underset{\longleftarrow}{\overset{K}{\longrightarrow}} \ TaC \qquad (5)$$

provided activity coefficients are known. This is done with the following relations:

$$(a_{Ta}) \ (a_C) = (1/_K) \qquad (6)$$

$$a_{Ta} = \gamma_{Ta} \ c_{Ta} \qquad (7a)$$

$$a_C = \gamma_C \ c_C \qquad (7b)$$

where a is the chemical activity and γ is the activity coefficient. For equilibrium dissolution and regrowth of TaC, stoichiometric considerations require the carbon and tantalum concentrations in the solution to be equal:

$$C_C = C_{Ta} \equiv C_l \qquad (8)$$

This requirement assumes that there are no chemical side reactions, in the melt or with the crucible or atmosphere, that remove either tantalum or carbon. Equations 6-8 provide the following relation:

$$\gamma_{Ta} \, \gamma_C \, C_l^{\,2} = K^{-1}$$

and

$$C_l = (K \, \gamma_{Ta} \gamma_C)^{-\frac{1}{2}} \, . \qquad (9)$$

The temperature dependence of the equilibrium constant is based on the free energy of formation ΔF of TaC:

$$K = e^{-\Delta F/RT} \, . \qquad (10)$$

Activity coefficients usually vary slightly with temperature, but vary considerably with concentration. These effects are shown in Fig. 3 for carbon in liquid iron.

Plots of equilibrium concentration C_l versus the activity coefficient product $(\gamma_{Ta}\gamma_C)$ based on Eq. 9 are shown for various temperatures in Fig. 4. In order to maximize the carbon and tantalum concentration and the crystal growth rate, a liquid metal solution that provides the lowest value of $(\gamma_{Ta}\gamma_C)$ is sought. Superimposed on the concentration curves of Fig. 4 are two curves representing the values of $(\gamma_{Ta}\gamma_C)$ required to achieve the indicated crystal growth rates at these temperatures. These curves are based on a $100^\circ C$ temperature difference between source and crystal.
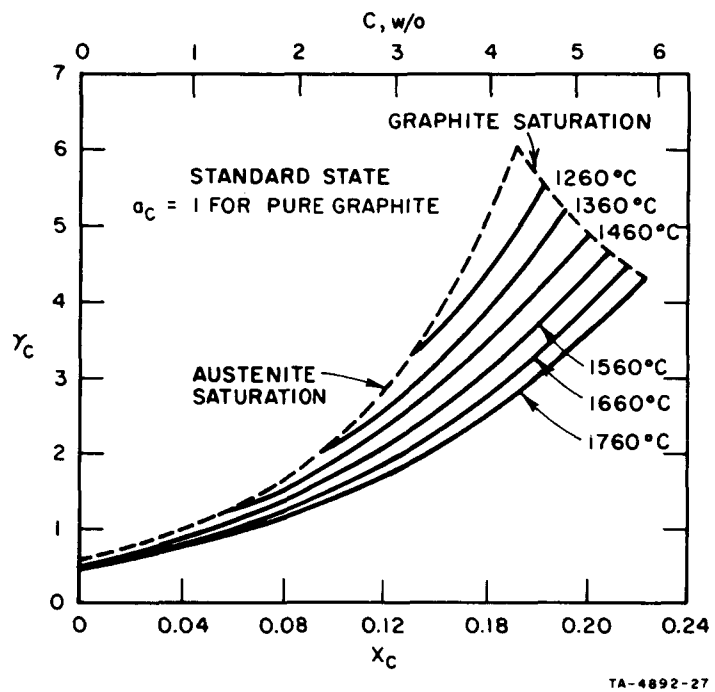
FIG. 3 ACTIVITY COEFFICIENT (γ_C) OF CARBON IN
LIQUID IRON. From Elliott, et al, Thermochemistry
for Steel Making Vol. 2 p. 499, Addison Wesley,
Reading, Massachusetts, 1963.

c. Activity Coefficients and Predicted Growth Rate

Unfortunately, tantalum activity coefficients (or activities) in dilute solutions are unknown for any liquid metal solvent, and part of our current experimental program is directed toward providing this information. In the meanwhile, a very crude estimate for the activity of tantalum in liquid iron was made in the previous quarterly status report by assuming that it had the same activity coefficient as zirconium in liquid iron, 0.011. Since then, more literature has been received and activity coefficients for dilute solutions of several metals in liquid iron are presented in Table I. The arrangement of metals in this table corresponds to the arrangement of metals in the periodic chart. A revised order of magnitude estimate of γ_{Ta}^{Fe} is 0.1. When this is combined with the $\gamma_C^{Fe} = 0.6$ for dilute solutions, an estimate of $\gamma_{Ta}^{Fe}\gamma_C^{Fe} = 0.06$ is obtained. On this basis it would take a crystal growing temperature of 1800°C with a 1900°C source temperature to grow TaC at the rate of 1 mm/day; see Fig. 4. Although these temperatures exceed the capabilities of Al_2O_3 crucibles somewhat, it does appear reasonable to expect that some improvements in solvent or crucible can be developed that will permit solution growth of TaC crystals at this rate, using the Czochralski method.

It is expected that the lowest values of $\gamma_{Ta}\gamma_C$ will be found in those liquid metals that have a high solubility for both carbon and tantalum. This consideration and the need to avoid formation of other carbides point to the third period transition metals, vanadium through nickel. Although most of these metals form carbides, they can be used at least partially in alloys at crystal growing temperatures without carbide formation. The carbide forming tendency decreases when going from vanadium to nickel. With the exception of iron, little is known about the carbon activity in dilute solutions of carbon in these liquid metals. However, predictions as to whether the carbon activity coefficient is more or less than the carbon activity coefficient in liquid iron can be made from the effect of these metals as alloying elements on the activity coefficient of carbon in liquid iron alloys. These data are shown in Fig. 5. Vanadium and chromium additives have the desireable effect of decreasing the activity coefficient of carbon.
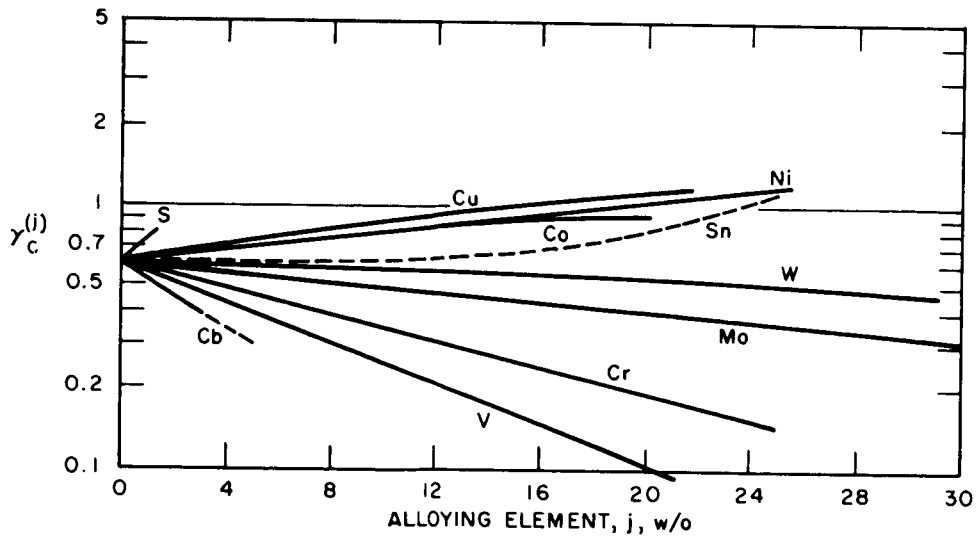
13

Table I

METAL ACTIVITY COEFFICIENTS IN BINARY INFINITELY DILUTE
SOLUTIONS OF LIQUID IRON

Ti $\gamma = 0.011$	V $\gamma = 0.18$	Cr
Zr $\gamma = 0.011$	Nb	Mo
Hf	Ta	W $\gamma = 0.3$
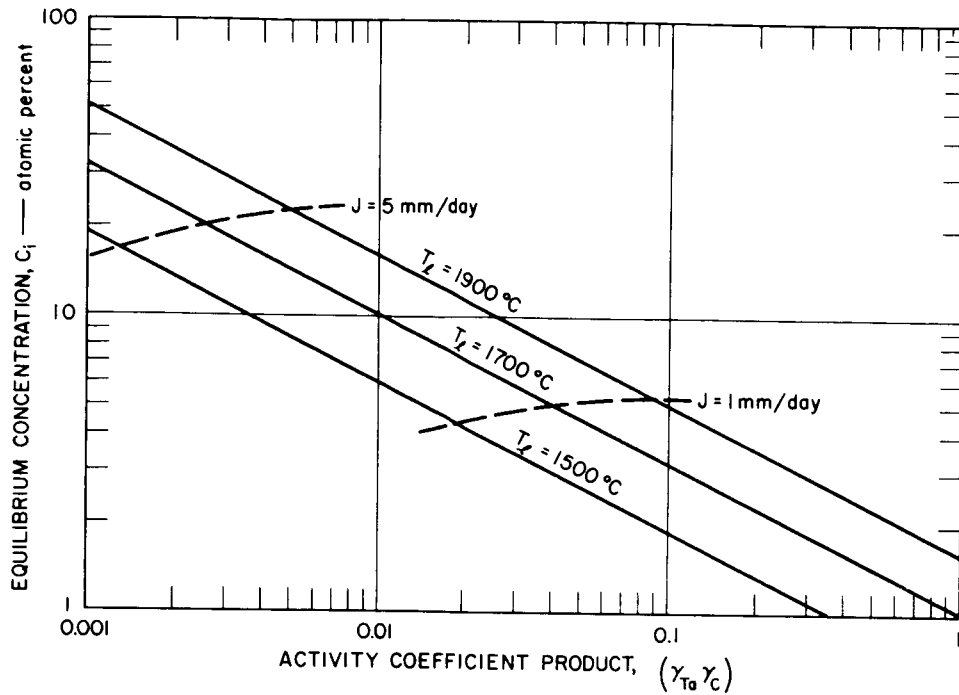
FIG. 4 EQUILIBRIUM CONCENTRATION OF Ta AND C AS A FUNCTION
OF THEIR ACTIVITY COEFFICIENT PRODUCT

FIG. 5 EFFECT OF ALLOYING ELEMENTS ON ACTIVITY COEFFICIENT
OF CARBON IN LIQUID IRON AT 1560°C FOR DILUTE
SOLUTIONS OF CARBON IN IRON. After Elliott.

15

Experimental determinations of the tantalum activity coefficients in
these liquid alloys are planned.

2. Experimental Results

Several solution growth experiments were conducted in an attempt
to grow tantalum carbide on a hot pressed tantalum-carbide seed insert-
ed in the melt. In this modified Czochralski method the seed was
rotated and withdrawn at a controlled rate. Iron was used as the solvent
in these experiments because the activity coefficient of carbon in
liquid iron and the estimated activity coefficient of tantalum in liquid
iron appeared favorable for practical growth rates.

In the initial experiment, the hot pressed tantalum carbide seed
was held by a graphite rod, using a threaded clamp. During insertion
of the seed in the melt, the seed broke at the point of contact with
the clamp. In a second experiment the seed and holder were heated
slowly before insertion in the melt in order to lessen thermal-shock
fracture of the seed. However, the seed fell off a second time and
this holder method was abandoned. In a later experiment the seed
was attached to tantalum wire which was braided and connected to a
graphite pull-rod. This arrangement provided for a more secure
attachment of the seed without excessive sacrifice of the stiffness
required to rotate the seed. After a short period of time the seed was
withdrawn from the melt. Subsequent weight and size measurements
indicated that tantalum carbide had dissolved from the seed rather than
grown upon it. This result was not explained until a subsequent
experiment in which the tantalum wire holding the seed became carburized.
We now believe that the rapid carburization of the tantalum wire and
the appearance of Al_2O_3 whiskers above the seed were caused by the
presence of carbon monoxide in the furnace chamber. Any oxygen that
leaks into the furnace will rapidly react with carbon in the melt to
form carbon monoxide. Such a depletion of carbon near the meniscus of
the melt would cause dissolution rather than growth of tantalum carbide
in this region. The carbon monoxide thus formed would also account for
the rapid carburization of the tantalum wire at high temperatures. In
the equilibrium growth experiments just described, Al_2O_3 was used as the

crucible material. The melts contained 1.4 weight percent aluminum in order to minimize chemical attack of the crucible.

An irreversible type of experiment was also performed, using an iron melt and a graphite crucible. In part, this experiment was performed to test a pyrolytic graphite heat shield as an aid in attaining extremely high temperatures. In this respect the experiment was successful since a base temperature of 2125^{0}C and a meniscus temperature of 1925^{0}C were attained. A chemically inert crucible suitable at these temperatures was not available. A hot pressed tantalum carbide seed was inserted in the melt and rotated until the tantalum holder wire became carburized, dropping the seed into the melt. Subsequent examination of the seed after etching did not indicate any tantalum carbide regrowth.

The experiments performed since then have involved an attempt to determine the tantalum activity coefficients in several liquid metals. The procedure is to run isothermal experiments in graphite crucibles. Tantalum carbide is dissolved in the carbon-saturated liquid. At equilibrium the tantalum activity is controlled by the equilibrium constant for formation of tantalum carbide, Equation 5. Samples of the liquid are being withdrawn for analysis at 1 hour, 6 hours, and 24 hours to insure attainment of equilibrium. These samples will be analyzed for tantalum content, using emission spectroscopy. From this measured tantalum concentration in the liquid and the thermodynamically calculated tantalum activity, the tantalum activity coefficient at that temperature can be calculated. Since carbon-saturated solutions are being used, the tantalum concentration will be very low and it is hoped that valid activity coefficients for dilute solutions of tantalum in the metals will result. From these determinations of tantalum activity coefficients and from what is already known about carbon activity coefficients, see Figs. 3 and 5, the optimum solvent system will be selected. Furthermore, from the activity coefficient product $(\gamma_{Ta} \gamma_{C})$, and Fig. 4 it should be possible to determine the diffusion limitations on the crystal growth rate of tantalum carbide. Experiments have been performed with iron, nickel, and aluminum solvents.

17

Chemical analyses are not yet available. Additional experiments will be performed on chromium, iron-chromium, and iron-vanadium melts.

An extensive delay occured when one of the crucibles broke, depositing liquid aluminum in the bottom of the crystal growth apparatus. Repairs to the furnace are in progress.

3. Future Work

The experiments aimed at determining tantalum solubility and tantalum activity coefficients in other liquid metals will be continued. Further Czochralski type seed pulling experiments are planned, using iron or a more optimum solvent if such is determined. Additional steps have been taken to prevent oxygen contamination in the furnace chamber. An experiment to grow mixed HfC-TaC crystals by an irreversible (precipitation) approach, using tantalum metal, hafnium metal, and a graphite crucible, is planned. The primary purpose of this experiment is to provide mixed crystal powder for the arc-Verneuil experiments.

Appendix

ANALYSIS OF CENTRIFUGAL CAPILLARY PARTICLE FEEDER

The feeder in current use has the configuration shown below.
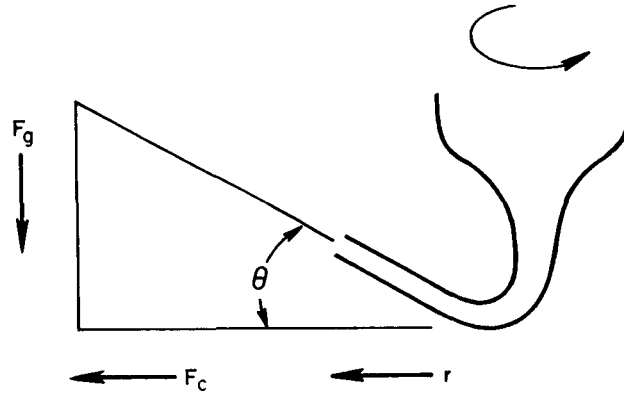
The centrifugal force F_c and gravity force F_g on a spherical particle, and their vector components along the exit capillary, are given by the following equations.

$$F_c = \left(\frac{\pi D^3}{6} \right) \frac{\rho v_t^2}{r}$$

$$F_c \, \theta = \left(\frac{\pi D^3}{6} \right) \frac{\rho v_t^2}{r} \cos \theta$$

$$F_g = \left(\frac{\pi D^3}{6} \right) \rho g$$

$$F_g \, \theta = \left(\frac{\pi D^3}{6} \right) \rho g \sin \theta$$

where D is the particle diameter, ρ is the particle density, r is the feeder radius, and v_t is the tangential velocity. If friction is neglected, particles will flow when

$$F_{g_\upsilon} \leq F_{c_\theta}$$

This condition is satisfied when

$$\frac{v^2_t}{r} \geq g \tan \upsilon$$

Since $v_t = \frac{2\pi r \Omega}{60}$, where Ω is the rotary speed of the feeder in rpm, the critical speed (Ω_c) in rpm for particle flow is

$$\Omega_c > \frac{60}{2\pi} \sqrt{r\, g \tan \upsilon}$$

The effective acceleration in gravity equivalents, g_e, experienced by a particle is given by the following equation.

$$g_e = \left(\frac{v_t^2 - r\, g \tan \theta}{r} \right) \cos \upsilon$$

The rate of particle flow depends on g_e and the friction between particles and the capillary wall. For small particle flow rates, g_e must be small.