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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 superrefractories. 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. To get 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 the application of new techniques and procedures for the 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, the application of recently developed methods for liquid metal solution growth of crystals and, second, the utilization of new heating methods for Verneuil crystal growth. The latter new heating methods include r-f plasma heating and a-c arc melting. After an extensive feasibility investigation, including considerable experimental work, the r-f plasma heating method has been dropped. Work continues on the solution growth and arc melting Verneuil methods.

II SUMMARY AND CONCLUSIONS

Construction of the triple-electrode arc melting furnace was essentially completed during this period. This includes fabrication and assembly of the arc melting furnace proper and the connecting graphite resistance heater for controlling the cooling rate of the boule. The power supply and other major components were received and assembled. As a result of start-up tests, several modifications and adjustments were made. Remaining modifications will be completed early in the next period.

Thermochemical factors affecting the solution growth of TaC were considered in detail. It was concluded that moderately low-solubility solvents (high activity coefficients) are desired when both excess free carbon and excess free tantalum are present in the melt system. This is necessary in order to limit the degree of supersaturation with respect to equilibrium with TaC. Excessive supersaturation is believed to cause uncontrolled nucleation and leads to rapid precipitation of many small crystals rather than growth of a few large crystals. The use of elemental carbon and tantalum metal sources for nutrients has been termed irreversible or nonequilibrium solution growth. A thermal gradient is not required.

When excess free tantalum and carbon are absent from the melt system and another sample of TaC is used as the nutrient, the chemical activities of carbon and tantalum in the solution in equilibrium with the nutrient are considerably diminished. Solvents with low activity coefficients are required in order to compensate for the very low activities and keep the concentration of carbon and tantalum at an adequate level. If the reactant concentrations are too low, solution diffusion will be too slow and crystal growth rates will be retarded. Thus, high solubility solvents are desired when free carbon and free tantalum are excluded. This latter type of melt system is termed reversible or equilibrium solution growth of TaC and requires a thermal gradient in the melt. It is worth noting that the slowest growth rates are expected when a TaC nutrient is combined with a separate high activity source of only one of the reactants (either tantalum or carbon).

Small tantalum carbide crystals were grown in several solution growth experiments. Many of these experiments were initial investigations of new solvent systems. Some experiments were performed in which polycrystalline TaC was used as the only nutrient by employing Al_2O_3 crucibles in lieu of graphite and omitting additions of free tantalum metal to the melt.

III CRYSTAL GROWTH STUDIES

Most of the work during this period was concentrated on: (1) assembling and testing the three-electrode a-c arc melting furnace for melt growth of crystals, (2) analyzing thermodynamic and kinetic factors affecting the selection of systems for solution growth of TaC, and (3) performing crystal growth experiments and solubility experiments for solution growth of TaC.

A. Melt Growth

Experimental work on the application of plasma fusion for melt growth of crystals was terminated at the end of last quarter. The plasma method had not shown sufficient promise for attaining the required high temperatures. During this quarter, the three-electrode a-c arc furnace, including the graphite resistance after-heater used to control cooling of the boule and the powder feed system, was assembled. Major auxiliary components and power supply units were received and installed. A photograph of this furnace and some of its associated apparatus is shown in Fig. 1.

In early tests of the arc melting furnace, it became apparent that several alterations would have to be made in the system. These alterations were almost impossible to predict until actual operation of the complete unit had been accomplished. The resistivity of the 12-segment graphite after-heater element was slightly high for the 14-volt, 1500-ampere power transformer available, so the desired temperature of 2300-2500°C could not be reached. A new thinner-walled graphite element, consisting of 8 segments instead of 12, was designed. Upon testing, it was found that the desired temperatures could be reached easily within the limitations of the power supply.

During this period, it was also found that the existing water cooling system could not dissipate all of the heat being conducted to the walls of the furnace when operating at full power. This problem was solved by placing flow control valves on each cooling circuit so that maximum flow could be maintained in the hottest zones. The interior

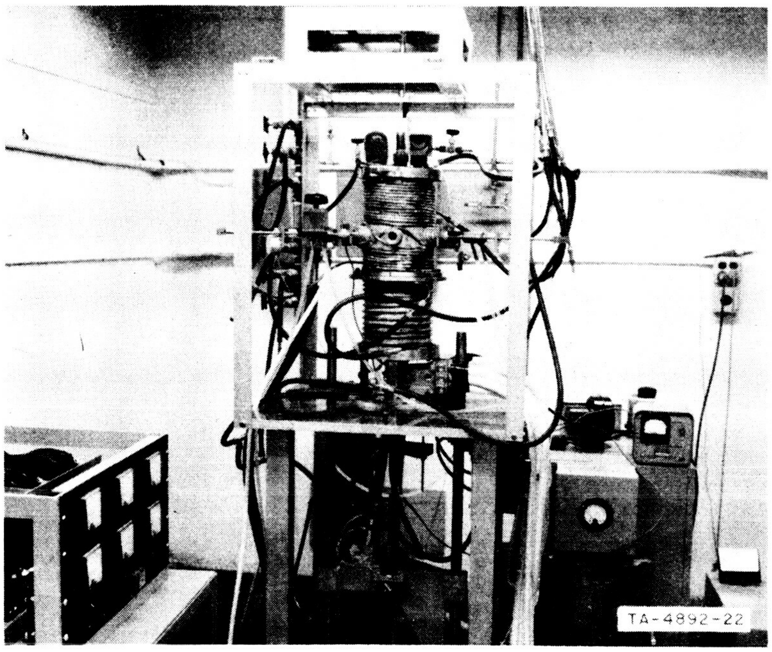

FIG. 1 TRIPLE ELECTRODE a-c ARC MELTING FURNACE FOR VERNEUIL CRYSTAL GROWTH

shielding of the system was also modified to provide greater insulation of the furnace walls from the graphite element. These alterations enabled operation of the furnace for long periods at maximum temperatures without overheating any part of the system.

The power supply for the triple-electrode arc-melting system has been installed and is operating satisfactorily. This a-c arc power supply consists 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 arc directly to the seed crystal.

The powder introduction system has been installed and tested and seems to be operating satisfactorily. Some modifications to the system were made so that the furnace could be evacuated with the powder system in place and ready for operation.

A more efficient vacuum system for the furnace is in the process of being installed. With this new system, it will be possible to bake out the new graphite element and the graphite blanket insulation more completely to clean out the furnace system in preparation for crystal growing.

Several test runs were made, but only with the objective of testing and evaluating furnace and powder feed systems. Crystal growth was not attempted.

B. Solution Growth

During this quarter and previous quarters, a number of liquid-metal and alloy compositions were found to be solvents for tantalum and carbon, permitting growth of TaC. During this quarter, additional consideration was given to thermodynamic and kinetic factors affecting solution growth of TaC, with particular emphasis on increasing crystal size. This work included a literature survey of thermodynamic properties, and directed solution growth experiments.

1. Thermodynamic Considerations in System Selection

A discussion of some thermochemical factors that may affect the growth of TaC crystals follows. The argument is limited to TaC in order to gain clarity by using a specific system. However, the general conclusions and qualitative results should be valid for HfC.

Most of the solution growth experiments conducted thus far have involved (1) a solvent metal, (2) excess tantalum metal, and (3) carbon from a graphite container, as the starting materials. In general, this is not a sufficiently specified system to be in equilibrium, and reaction will proceed irreversibly at elevated temperatures, dissolving tantalum and carbon and precipitating TaC. Provided that the graphite crucible is large, the reaction will continue until an insignificant amount of tantalum, dissolved in the solution, remains.

Tantalum carbide crystals can also be grown under equilibrium (reversible) conditions if a TaC nutrient and thermal gradient are employed. Equilibrium growth requires elimination of either the excess tantalum metal from the melt charge or substitution of an inert crucible for the graphite crucible. When a separate source of either reactant is excluded from the melt system, the chemical activity of that reactant in the liquid metal solution will depend on the TaC equilibria:

$$\mathrm{TaC}\ (s)\ K_1 \rightleftharpoons \mathrm{Ta}\ (\mathcal{L}) + \mathrm{C}\ (\mathcal{L}) \tag{1}$$

and

$$(a_{Ta})(a_C) = K_1 \tag{2}$$

where "a" is the chemical activity. If tantalum metal is not included in the melt charge but a carbon crucible is used, then $a_{Ta} = K_1$ and $a_C = 1$. If tantalum is not included in the melt charge and an inert crucible is used, the carbon and tantalum activities will be intermediate between $a_i = 1$ and $a_i = K_1$. In the unlikely condition that the activity coefficients (γ) are equal, $\gamma_{Ta} = \gamma_C$, then $a_{Ta} = a_C = K_1^{1/2}$. Variations in equilibrium constants or activity products with temperature (free energy data) are shown for several carbides[1] in Fig. 2. As can be seen in Fig. 2, the tantalum and carbon activities are several orders lower when TaC is used as the nutrient in lieu of a free tantalum or a free carbon source, respectively. The value of K_1 for TaC at 1500°C is 3.5×10^{-5}.

Tantalum and carbon activities maintained during growth of TaC at 1500°C under several conditions are shown in Table I. The purpose of this table is to indicate the wide variation in activities that will occur depending on whether separate tantalum and carbon sources are

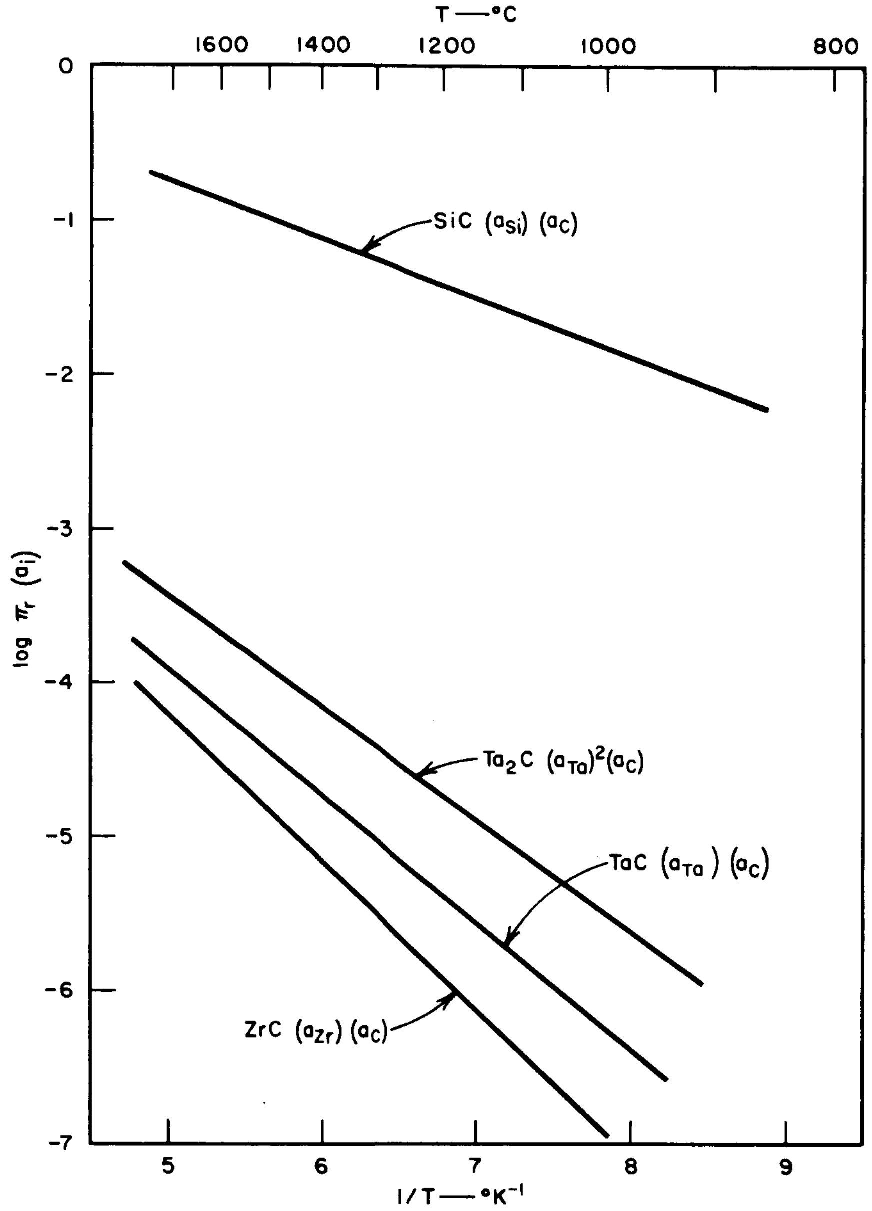

FIG. 2 FREE ENERGY OF FORMATION OF SEVERAL REFRACTORY CARBIDES, PLOTTED AS THE LOG OF THE REACTANT ACTIVITY PRODUCT VERSUS RECIPROCAL TEMPERATURE

Table I

TANTALUM AND CARBON ACTIVITIES DURING GROWTH
OF TaC AT 1500°C

Melt System	Carbon Activity		Tantalum Activity		Growth Condition
	Initial	Equilibrium	Initial	Equilibrium	
Excess tantalum and carbon crucible	1	1	$1 \geq a_{Ta} \gg 3.5x10^{-5}$[‡]	$3.5x10^{-5}$	irreversible
TaC nutrient and carbon crucible	1	1	$3.5x10^{-5}$	$3.5x10^{-5}$	reversible (thermal gradient)
TaC nutrient and inert crucible	$5.9x10^{-3}$[*]	$5.9x10^{-3}$[*]	$5.9x10^{-3}$[*]	$5.9x10^{-3}$[*]	reversible (thermal gradient)

[‡] If enough tantalum metal is added to the melt to saturate it, than $a_{Ta} = 1$. The tantalum activity will be reduced for smaller additions.

[*] Provided that $\gamma_{Ta} = \gamma_C$.

present or are not present in the melt system. Although activity coefficients are unknown for tantalum in any liquid metal, the concentrations of tantalum and carbon are related to their activities,

$$c_i = a_i/\gamma_i, \tag{3}$$

and a corresponding large difference in concentrations of tantalum and carbon will occur between the melt systems with and without separate tantalum and carbon sources.

Since the goal of this investigation is to grow large crystals, it appears desirable to limit the supersaturation (excess concentration) of tantalum or carbon with respect to TaC in order to prevent excessive nucleation. If both excess tantalum and excess carbon are present in the melt system (irreversible case), a solvent with low solubility of one or both reactants is required to prevent excessive supersaturation. Conversely, if a TaC nutrient is used without a tantalum source (reversible case), a solvent with a high tantalum solubility (low activity coefficient) is required to increase the tantalum concentration to a high enough level to secure adequate mass transport rates in the solution. A further increase in the tantalum concentration in solution can be secured by substituting an inert crucible for the carbon crucible (see Table I). In effect, as the carbon activity is lowered, the tantalum activity, and concentration, are increased to maintain the equilibrium constant K_1. This extreme difference in tantalum solubility is required to compensate for the large difference in tantalum activities, ca 10^{-5}, between the equilibrium and nonequilibrium melt systems. What is desired in both melt systems is a reactant concentration that is very low but not too low to permit growth at practical rates.

Some additional considerations for the growth of TaC crystals irreversibly from dilute solutions and reversibly using a TaC nutrient are contained in the following sections.

a. Low Solubility Solvents for Irreversible Growth of TaC

Almost without exception, higher temperatures favor higher solubilities. This is because the entropy of the solution is greater than that of the segregated solid phases. Therefore an increase in temperature causes a decrease in chemical potential of the solute, which can only be offset by increased solution of the solute component. Since, for the irreversible case, moderately low solubilities are being sought, an examination of tantalum and carbon solubilities near the melting points of several liquid metals provides a guide to useful solvent systems.[2-4] Tantalum solubility data are presented in Table II, and carbon solubility data are shown in Table III.

It appears that the transition metals are either too refractory or have high solubilities for tantalum and carbon. Lower solubilities are expected in metals from groups IB, IIB, IIIA, IVA, and VA. In most cases the solubility will probably be too low. This condition has already been observed with tin. The effective solvent properties obtained with a binary melt containing a solvent inactive metal, e.g., tin, and a solvent active metal, e.g., iron, are probably too complex for analysis or even speculation without experimental data. We have observed experimentally that the 10% iron and 90% tin alloy is an active

Table II

TANTALUM SOLUBILITIES NEAR MELTING POINTS OF LIQUID METALS[2-4]

Solvent	Temperature	Tantalum Solubility (Wt %)	Tantalum Source
Aluminum	2680°C	0.15	$TaAl_3$
Iron	1534°C	>20	$TaFe_2$
Nickel	1453°C	>40	$TaNi_3$
Silicon	1405°C	> 6	$TaSi_2$
Tin		Unknown low	

Table III

CARBON SOLUBILITIES IN LIQUID METALS[2-4]

Solvent	Carbon Solubility (Wt %)	Eutectic Temperature (°C)
Chromium	3.0	1498
Cobalt	2.9	1300
Copper	<.001 (1400°C)	--
Iron	4.26	1153
Molybdenum	~ 3.5	2200
Nickel	2.1	1318
Silicon	3-4 (2300°C) 2.5×10^{-3} (1413°C)	1413
Aluminum	Unknown low	--
Tin	Unknown low	--

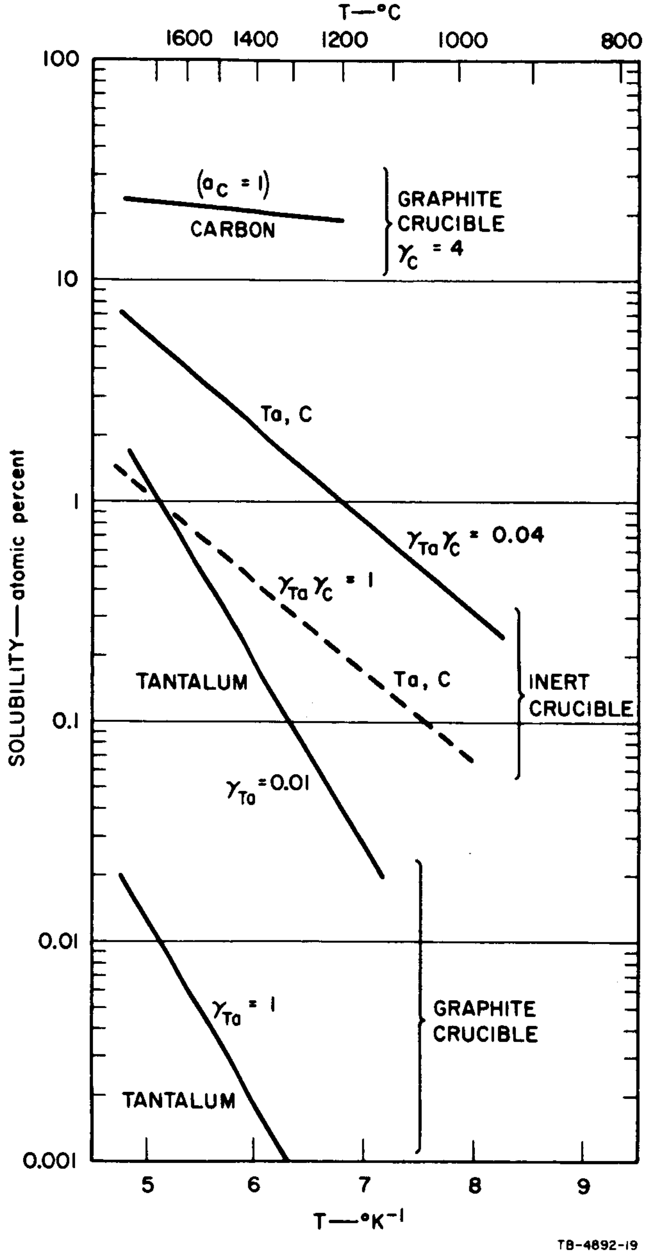

FIG. 3 CONCENTRATION OF TANTALUM AND CARBON IN EQUILIBRIUM WITH TaC IN AN IRON SOLVENT, WITH AND WITHOUT A CARBON CRUCIBLE; TANTALUM ACTIVITY COEFFICIENTS ARE ESTIMATED

solvent for carbon and tantalum. Review of the literature is continuing in order to gain any available additional information on carbon and tantalum solubilities in liquid metals.

b. Equilibrium Growth, Using a TaC Nutrient and a Thermal Gradient

If TaC is the sole source for both tantalum and carbon in solution, then their concentrations must be equal in order to maintain a mass balance regardless of differences in their respective activity coefficients. The corollary to this is that their activities need not be equal. The activity product (a_C) (a_{Ta}), and not the individual activities, is governed by the TaC equilibrium constant K_1. Activity coefficients of carbon in several liquid metals have been determined, but no activity coefficient data for tantalum or hafnium were found during a literature search. The activity coefficient of zirconium[5] in liquid iron is $\gamma_{Zr} = .011$. The activity coefficient of carbon in liquid iron is $\gamma_C = 4$. If one ignores interactions in the ternary iron-carbon-tantalum system and predicts $\gamma_{Ta} = \gamma_{Zr}$, then concentrations of tantalum and carbon in liquid iron can be calculated. This was done and the results are graphed in Fig. 3. Calculated values based on use of an inert crucible are compared with values based on using a graphite crucible; $a_C = 1$. The upper and lower curves represent the carbon solubility and tantalum solubility, respectively, when a graphite crucible is employed. This is the equilibrium situation without free tantalum additions. Two values of the tantalum activity coefficient are used, $\gamma_{Ta} = .01$ and $\gamma_{Ta} = 1$. In both cases the tantalum solubility is below 1% at practical melt temperatures. Our experience with SiC crystal growth[6] has shown that a solubility approaching 1% is desirable to obtain reasonable growth rates with the thermal gradient method.

Higher tantalum solubilities can be obtained by eliminating the graphite crucible. Assuming $\gamma_{Ta} = .01$ or $(\gamma_{Ta}\ \gamma_C = .04)$, solubilities well over 1% are obtained at reasonable temperatures. Consequently, the use of iron as a solvent for TaC appears feasible, provided that a nongraphitic crucible is used.

A review of the literature disclosed studies of the effect of additional metals on carbon solubility in iron ternary systems. Data on cobalt,[7] manganese,[8] chromium,[9] and silicon,[10-12] have been reported. The results are summarized in Table IV. The chromium study was conducted using a solid phase, austenite, but it indicates that chromium probably increases the carbon solubility in liquid iron. Manganese does increase the carbon solubility in liquid iron, as is shown in Fig. 4.

Table IV

EFFECT OF ADDITIONAL METALS ON CARBON SOLUBILITY IN LIQUID IRON

Ternary Alloys	Effect of Additional Metal on Carbon Content
Fe-C-Co (solid)	For a fixed carbon activity cobalt decreases the carbon content
Fe-C-Mn (liquid)	For a fixed carbon activity manganese increases the carbon content
Fe-C-Cr (solid)	For a fixed carbon activity chromium increases the carbon content in austenite (1000°C)
Fe-C-Si (liquid)	For a fixed carbon activity silicon decreases the carbon content

c. Inert Crucibles for Equilibrium Growth of TaC

Nitrides and borides, particularly BN, AlN, and $BN-TiB_2$, are being considered as inert crucibles for liquid metals. The stabilities of some nitride crucible materials are compared with those of TaN and Fe_4N in Fig. 5. These values indicate that only AlN could be considered further as a crucible material, because of the favored formation of TaN. Because of the high cost of nitride crucibles, oxide crucibles, particularly of Al_2O_3 are being used for initial studies. A detailed analysis of the chemical reaction between Al_2O_3 and the proposed iron-tantalum-carbon melt is necessary. Consider the situation at 1727°C (2000°K), which is higher than temperatures at which melt experiments are likely to be conducted. The likely reactions are:

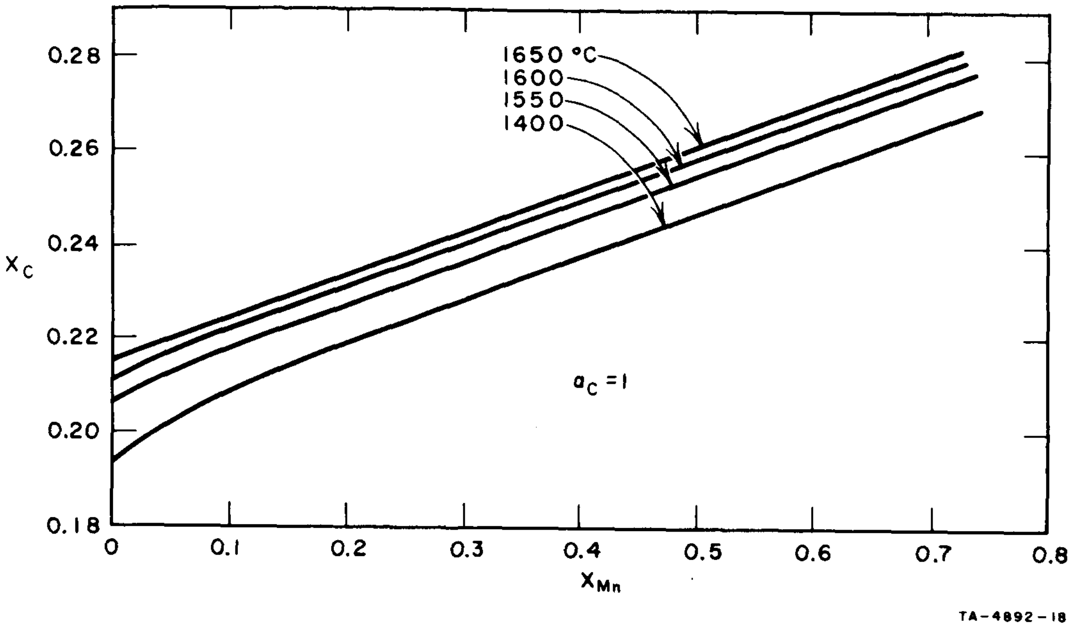

FIG. 4 SOLUBILITY OF CARBON IN IRON–MANGANESE ALLOYS
(After Chipman and Coworkers[10])

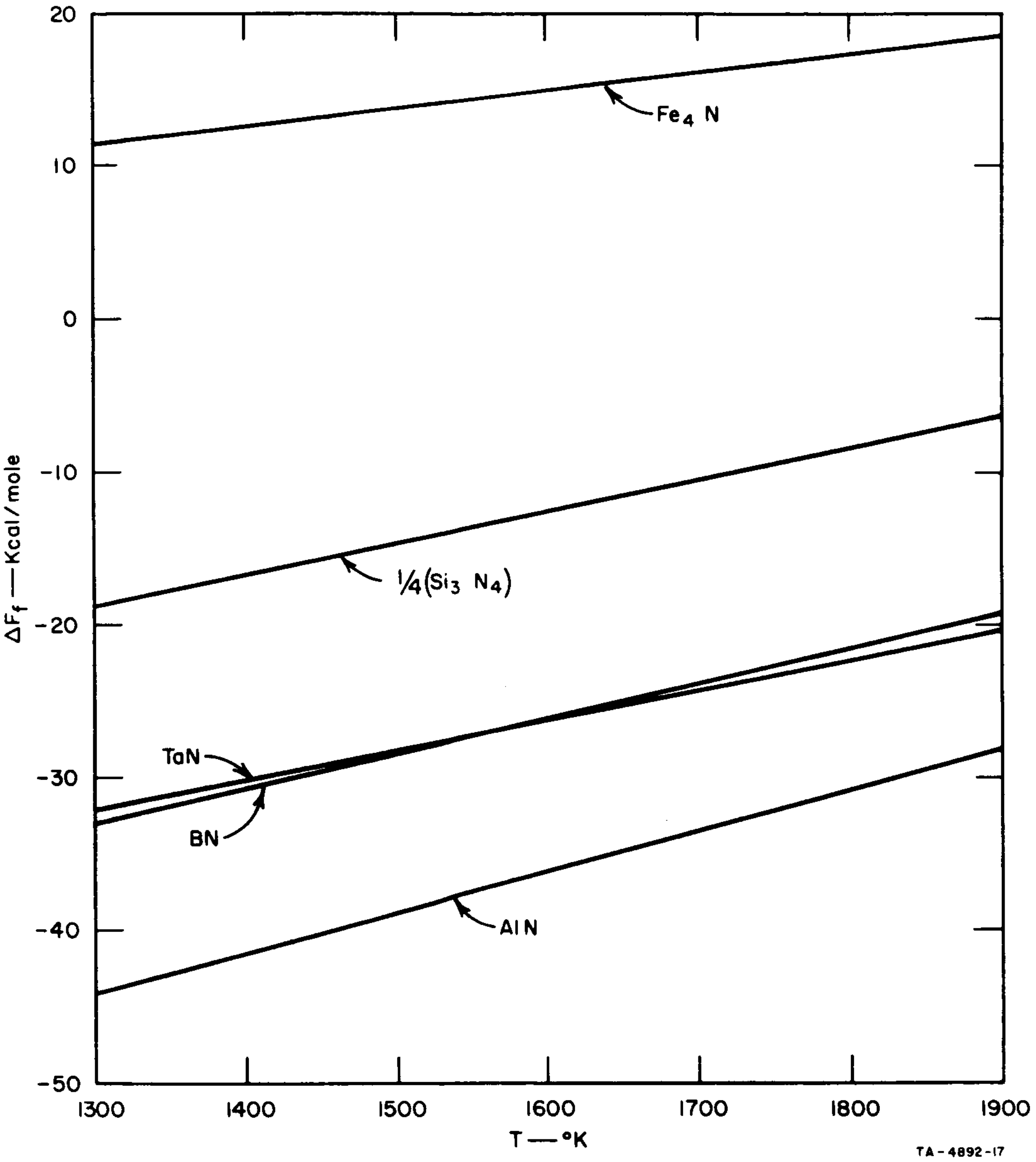

FIG. 5 COMPARISON OF THE CHEMICAL STABILITIES OF NITRIDE CRUCIBLE MATERIALS

$$1/2\ Al_2O_3 + 3/2\ Fe\ (\mathcal{L}) \overset{K}{\rightleftarrows}a\ 3/2\ FeO + Al\ (\mathcal{L}) \tag{4}$$

$$1/2\ Al_2O_3 + 3/5\ Ta\ (\mathcal{L}) \overset{K}{\rightleftarrows}b\ 3/10\ Ta_2O_5(s) + Al\ (\mathcal{L}) \tag{5}$$

$$1/2\ Al_2O_3 + 3/2\ C\ (\mathcal{L}) \overset{K}{\rightleftarrows}c\ 3/2\ CO(g) + Al\ (\mathcal{L}) \tag{6}$$

where script ($\mathcal{L}$) indicates the metal solution. Since iron is the solvent with approximately unit activity $a_{Fe} \doteq 1$, the equilibrium for Eq. (4) provides

$$a_{Al} = K_a \tag{7}$$

$$a_{Al}(1727^\circ C) = 1.1 \times 10^{-8}. \tag{8}$$

Using this value of the a_{Al}, we can calculate the activity of tantalum if Ta_2O_5 were present, using the equilibrium of Eq. (5)

$$a_{Ta} = (a_{Al}/K_b)^{5/3} \tag{9}$$

$$a_{Ta}(1727^\circ C) = 3.5 \times 10^{-7}. \tag{10}$$

Since this is lower than the activity resulting from TaC dissolution, we note that some Ta_2O_5 will form and tantalum will be depleted by the oxidation side reaction. This side reaction can be checked only by increasing the aluminum activity by additions of aluminum metal to the melt. This has the effect of opposing all three oxidation side reactions, Eqs. (4-6). The a_{Al} necessary to maintain a_{Ta} at the TaC equilibrium level ($a_{Ta} = 1 \times 10^{-3}$), assuming $\gamma_{Ta} = .01$, can be calculated using Eq. (9)

$$\begin{aligned} a_{Al} &= (a_{Ta})^{3/5} K_b \\ a_{Al}(1727^\circ C) &= 1.6 \times 10^{-6} \end{aligned} \tag{11}$$

The activity coefficient of aluminum in dilute liquid iron melts[13] is $\gamma_{Al} = .035$, which requires an aluminum addition of

$$X_{Al} = (1.6 \times 10^{-6})/.035$$

$$X_{Al} = 5 \times 10^{-5} \text{ or } 5 \times 10^{-3} \text{ atomic percent.}$$

Addition of this much aluminum or even somewhat larger amounts to the melt is not expected to impair carbon and tantalum solubilities in iron.

The required CO overpressure can be calculated from the equilibrium for Eq. (6):

$$P_{CO} = (K_c/a_{Al})^{2/3} \; a_C \; . \qquad (12)$$

The CO pressure required to balance the carbon activity at various temperatures and an arbitrary aluminum activity of $a_{Al} = 1 \times 10^{-4}$ is plotted in Figs. 6 and 7. Since the carbon activity depends on the Ta activity coefficient (see Fig. 3), the required CO pressure to stabilize crucible reactions also depends on the Ta activity coefficient.

The free energy of formation data for the oxides, used in determining the reaction equilibria for Eqs. (4-6), were taken from Coughlin.[14]

d. Solvent Side Reactions

Extraneous reactions between the solvent metal and reactants to form carbides or tantalum intermetallic compounds may or may not be undesirable, depending on the melt conditions. If separate tantalum and carbon sources are present, side reactions usually are not harmful, since the reaction products are themselves sources of tantalum and carbon, redissolving to provide a fixed reactant concentration as reactant is used in growing TaC crystals. Side reactions are less desirable when a TaC nutrient is used without separate tantalum and carbon sources. Such solvent side reactions are being considered in the selection of solvents and operating temperatures. Phase diagrams[2-4] are being used for this purpose.

2. Kinetic Considerations

A decrease in reactant concentration sufficient to prevent excessive supersaturation and nucleation may cause transport of reactants within the solution to become the rate-determining step in the crystal growth process. The major parameters affecting transport in the solution are thermal diffusivities, mass diffusivities, thermal gradients, concentration gradients, and stirring speed. An analysis of equilibrium solution growth with a thermal gradient has been made for a stirred melt, using

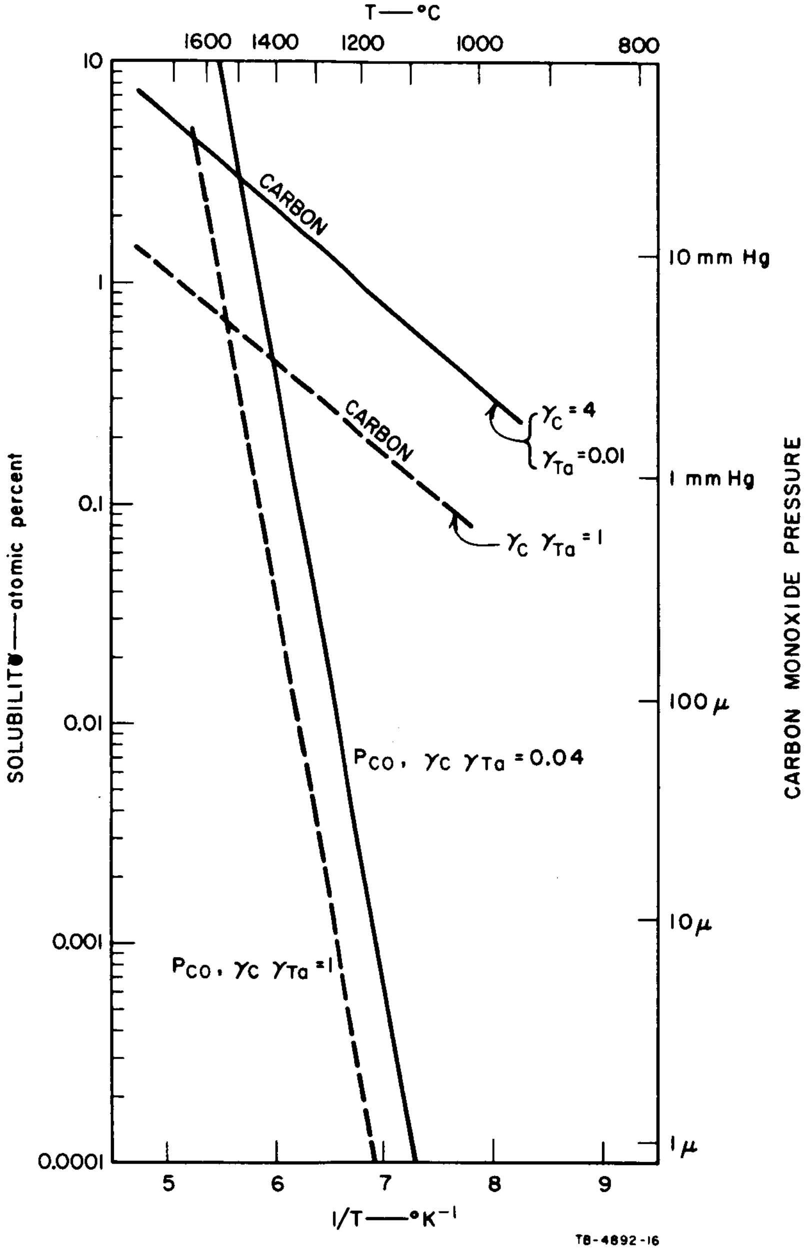

FIG. 6 CARBON AND CARBON MONOXIDE EQUILIBRIA FOR AN IRON MELT CONTAINING EXCESS TaC AND ALUMINUM ($a_{Al} = 1 \times 10^{-4}$) IN EQUILIBRIUM WITH AN Al_2O_3 CRUCIBLE

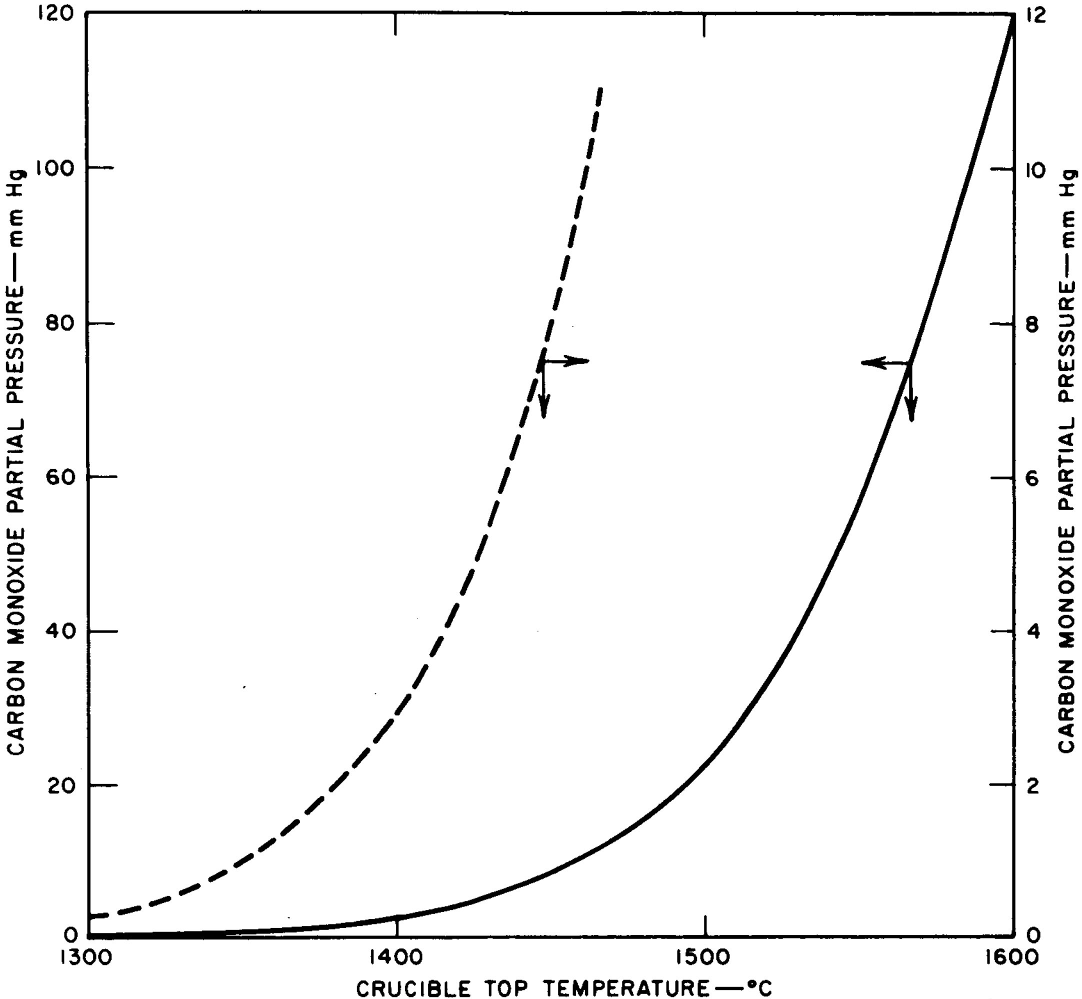

FIG. 7 CARBON MONOXIDE PARTIAL PRESSURE REQUIRED TO PREVENT Al_2O_3 CRUCIBLE SIDE REACTIONS IN AN IRON MELT CONTAINING EXCESS TaC AND ALUMINUM; $a_{Al} = 1 \times 10^{-4}$ (0.0014g Al/g Fe)

boundary-layer theory. This analysis has been applied to SiC growing from a carbon-saturated silicon solution, and reasonable agreement with the experimental results was obtained. The theory may be applicable to equilibrium growth of TaC and HfC from very dilute metal solutions. This particular analysis provides for a calculation of dimensionless (normalized) concentration profiles, velocity profiles, and temperature profiles adjacent to the crucible wall as a function of the distance from the wall upon which growth is initiated. Because of the high thermal diffusivities compared with mass diffusivities in liquid metals, the thermal boundary layer is thicker than the mass (concentration) boundary layer, leaving a supersaturated region near the cold wall, even when equilibrium is attained at the cold wall surface. This situation is shown schematically in Fig. 8. The qualitative results are as follows: crystal growth is promoted within the supersaturated region of the thermal boundary-layer, and the rate of crystal growth is affected by stirring. The transport rate increases with stirring velocity; however, the boundary-layer thickness decreases with stirring velocity. Consequently, at low stirring speeds crystal size is limited by the low mass flux, whereas at high stirring speeds crystal length is limited by a thinner boundary-layer. For a fixed crystal growth period, maximum crystal size will result at stirring speeds that are neither too fast nor too slow. Further consideration of this kinetic treatment will be deferred until an optimum melt system(s) is selected.

3. Experimental Results

Experimental work to establish new solvent systems for solution growth of tantalum carbide was continued during this report period. Pure nickel, tin-10 atomic percent iron, tin-10 atomic percent aluminum, tin-50 atomic percent lead, pure iron, and pure aluminum melts were tested as solvents for tantalum, carbon, and tantalum carbide. Mechanical stirring by a graphite propeller was employed to increase mixing within the melt in some experiments, and alumina crucibles were substituted for graphite crucibles in some instances in an attempt to obtain control over the carbon concentration in the melt.

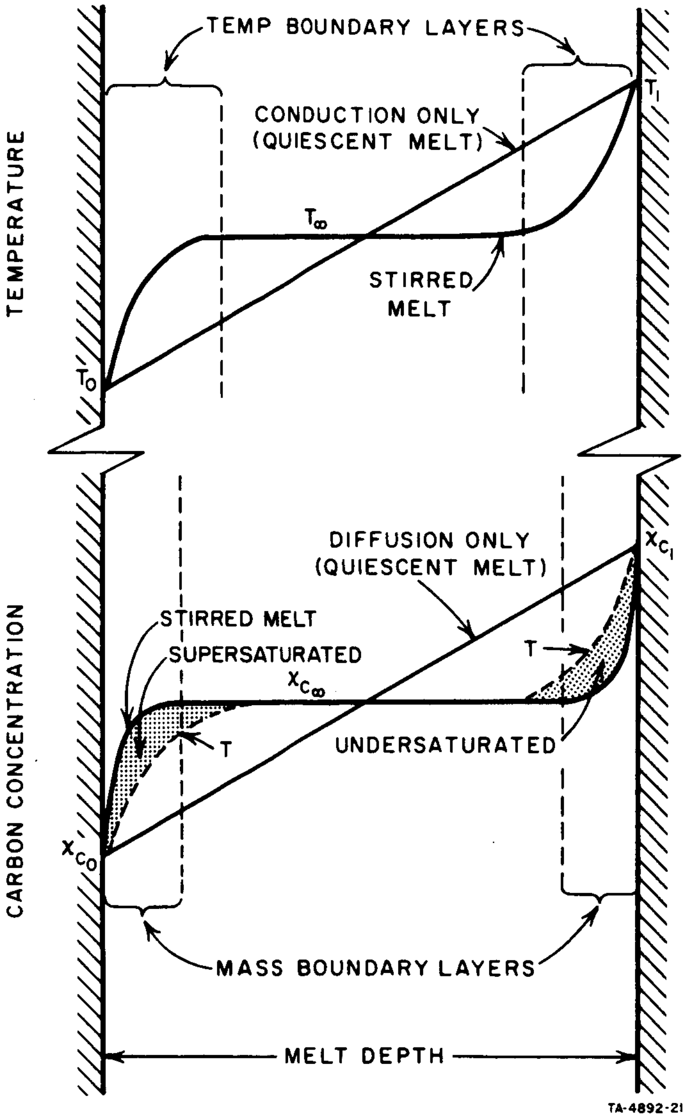

FIG. 8 SCHEMATIC DIAGRAM OF THE TEMPERATURE AND CARBON CONCENTRATION PROFILES DURING SOLUTION GROWTH OF SiC — COMPARING A QUIESCENT MELT WITH A STIRRED MELT

The major parameters of the crystal growth experiments conducted during the report period are presented in Table V. A summary of these experiments follows.

a. New Solvent Experiments

These experiments were usually performed with free tantalum present in a carbon crucible. Dissolution of both tantalum and carbon was indicated by the appearance of TaC. Solubilities were not determined. A solvent experiment using free tantalum was performed with nickel in Run 24. A graphite propeller rotating at 14 rpm in the melt center dissolved during the experiment. The graphite crucible remained intact and a high yield (several grams) of small (<1 mm) cubic crystals of tantalum carbide was obtained. The high carbon concentration in the nickel melt caused the rapid precipitation of TaC. Back reflection lattice constant measurements gave 4.456 Å, indicating these crystals to be stoichiometric TaC. Because tantalum dissolves in nickel but does not dissolve in tin, further experiments were performed with nickel-tin alloy melts. Tantalum wire used as the tantalum source in Run 27 was only partially dissolved in the tin-10 atomic percent nickel melt. The compound Ni_3Sn_4 precipitated as gray plates and needles during cooling. Run 28 was a repeat of Run 27 except that TaC chips were used as the nutrient. A few very small TaC crystallites were obtained, plus polycrystalline Ni_3Sn_4. The tin-10 atomic percent nickel melt is not as effective as the tin-10 atomic percent iron melt in dissolving tantalum.

Another attempt was made to grow TaC crystals either in the upper portion of the crucible or on the propeller shaft, using a tin-50 atomic percent aluminum melt, Run 29. Tantalum foil was used in lieu of the TaC nutrient used in a previous run last quarter. All the graphite surfaces in contact with the melt were found to be coated with a thin polycrystalline layer of TaC, and a few small crystals were obtained from the crucible base. These results were essentially identical with those of the previous experiment in which this melt composition was used.

Experiment 32 was run to determine the solubility of tantalum in a tin-50 atomic percent lead alloy. No measurable amount of tantalum dissolved and crystal growth did not occur.

Table V

SOLUTION CRYSTAL GROWTH CONDITIONS AND RESULTS

SOLVENT	SRI NO.	CRUCIBLE	NUTRIENT TaC	SURFACE TEMP., °C	BASE TEMP., °C	ΔT	TIME, hr	STIRRER	RPM	MELT DEPTH, in.	ATOMIC % Ta	PURPOSE	RESULTS
Nickel	24	C	N.P.*	1410	1475	-65	3-1/4	C	14	2	15.7	Solvent determination	High yield—small crystals
Tin-10 atomic percent Ni	27	C	N.P.	1415	1500	-85	21-1/2	C	180	2	2 wt %	Solvent determination	No TaC—wire partially dissolved
Tin-10 atomic percent Ni	28	C	base	1415	1500	-85	21-1/2	C	180	1-3/4	none	Solvent determination	A few small crystals
Tin-50 atomic percent Al	29	C	N.P.	1385	1500	-115	21-1/2	C	180	2	4 wt %	Solvent determination	A few very small crystals—TaC coating on crucible
Tin-50 atomic percent Pb	32	C (boat)	N.P.	1120	1110	10	18	none	--	1/2	wire	Solvent determination	No solubility
Tin-10 atomic percent Fe	25	C	base	1475	1500	-25	21-1/2	C	180	2	none	TaC Equilibrium growth	A few small crystals
Tin-10 atomic percent Fe	26	C	stir rod	1435	1505	-70	21-1/2	C	180	2	none	TaC Equilibrium growth	A few small crystals
Tin-10 atomic percent Fe	30	C	stir rod	1555	1290	265	20-1/2	C	180	2-1/4	none	TaC Equilibrium growth	A few small crystals—TaC smooth coating on nutrient
Tin-10 atomic percent Fe	31	Al_2O_3	stir rod	1375	1300	75	14	TaC	180	1-3/4	none	TaC Equilibrium growth	No TaC crystals
Iron	33	Al_2O_3	stir rod	1690	1545	145	< 1/2	TaC/C	180	1-1/4	none	TaC Equilibrium growth	Many small TaC crystals—10% nutrient dissolved—Run aborted due to pull rod failure
Iron	34	Al_2O_3	base	1700	1550	150	4	none	--	1-1/2	none	TaC Equilibrium growth	Many small TaC crystals
Aluminum	35	Al_2O_3	N.P.	1100	1000	100	20	C	0	1-5/8	1.3	Low solubility/ irreversible	Many large TaC crystals

*N.P. = not present.

b. Experiments With Modified Tantalum and Carbon Solubilities

A number of experiments were made with known solvents in which separate tantalum and/or carbon sources were deleted. Most of these experiments were done before or concurrently with the analysis presented in the previous section and further work is required before definite conclusions can be drawn.

In Run 25, TaC chips were used as the only source of Ta in order to reduce the rate of TaC nucleation and growth. The melt (tin-10 atomic percent iron) was stirred with a graphite propeller rotating at 180 rpm to aid in dissolving and transporting TaC from the hotter crucible base to the cooler upper portion of the crucible. After 21-1/2 hours, less than 3 wt percent TaC dissolved. Only eight small TaC crystals were recovered from the crucible base after leaching the melt with HCl. Evidently nucleation was retarded, but the tantalum activity, repressed by the high carbon activity from the crucible, was too low to provide adequate growth rates. Experiment 26 was a repeat of experiment 25, with a higher stirring velocity and larger thermal gradient, but there was no increase in crystal size or yield. Run 30 was a repeat of Run 26 except that the gradient was reversed and increased to 265°C in an effort to force the rapidly rotating TaC nutrient in the hotter upper region to recrystallize in the cooler crucible base. Only a few small crystals were obtained. It thus appears that the low tantalum concentration obtained is limiting crystal growth in all of these experiments.

An alumina crucible was used in Run 31 (tin-10 atomic percent iron melt) in place of graphite and a TaC propeller replaced the graphite one. Thus, separate sources of both tantalum and carbon were deleted. Again, less than 1 wt percent of the TaC nutrient dissolved, and crystal growth was not detected.

In order to increase the tantalum and carbon solubilitity in the absence of sources of these elements other than TaC, the next series of experiments employed pure iron melts contained in alumina crucibles. These experiments were the first based on the analysis of the previous section. Run 33 was terminated when the pull rod accidentally slipped into the melt, saturating it with carbon. Nevertheless, many small dendritic TaC crystals were found, indicating that significant amounts of TaC dissolved during this abbreviated experiment. Run 34, which produced many small TaC crystals at the crucible base, had to be terminated after four hours due to suspected crucible cracking. Furthermore, the TaC nutrient was by accident located at the cool base rather than near the hotter surface of the melt as intended. This upset the planned thermal gradient between the nutrient and the growing crystals. Additional experiments are planned.

An alumina crucible containing an aluminum-tantalum solution (Run 35) yielded the most promising results to date. This experiment was based on the low solubility irreversible case of the previous analysis. Carbon was supplied by a one-eighth-inch-diameter graphite rod inserted one-half inch into the melt. The rod completely dissolved during the 20-hour growth period. Many relatively large octahedral crystals of TaC grew on the walls of the crucible in a broad zone from the melt surface down to within one-quarter inch of the crucible base (see Fig. 9). Crystals of $TaAl_3$ grew in the base region below the TaC zone. Depletion of tantalum in this zone may have caused a reduction in the size and number of TaC crystals. The fact that TaC crystals nucleated and grew on the crucible walls in this experiment is encouraging.

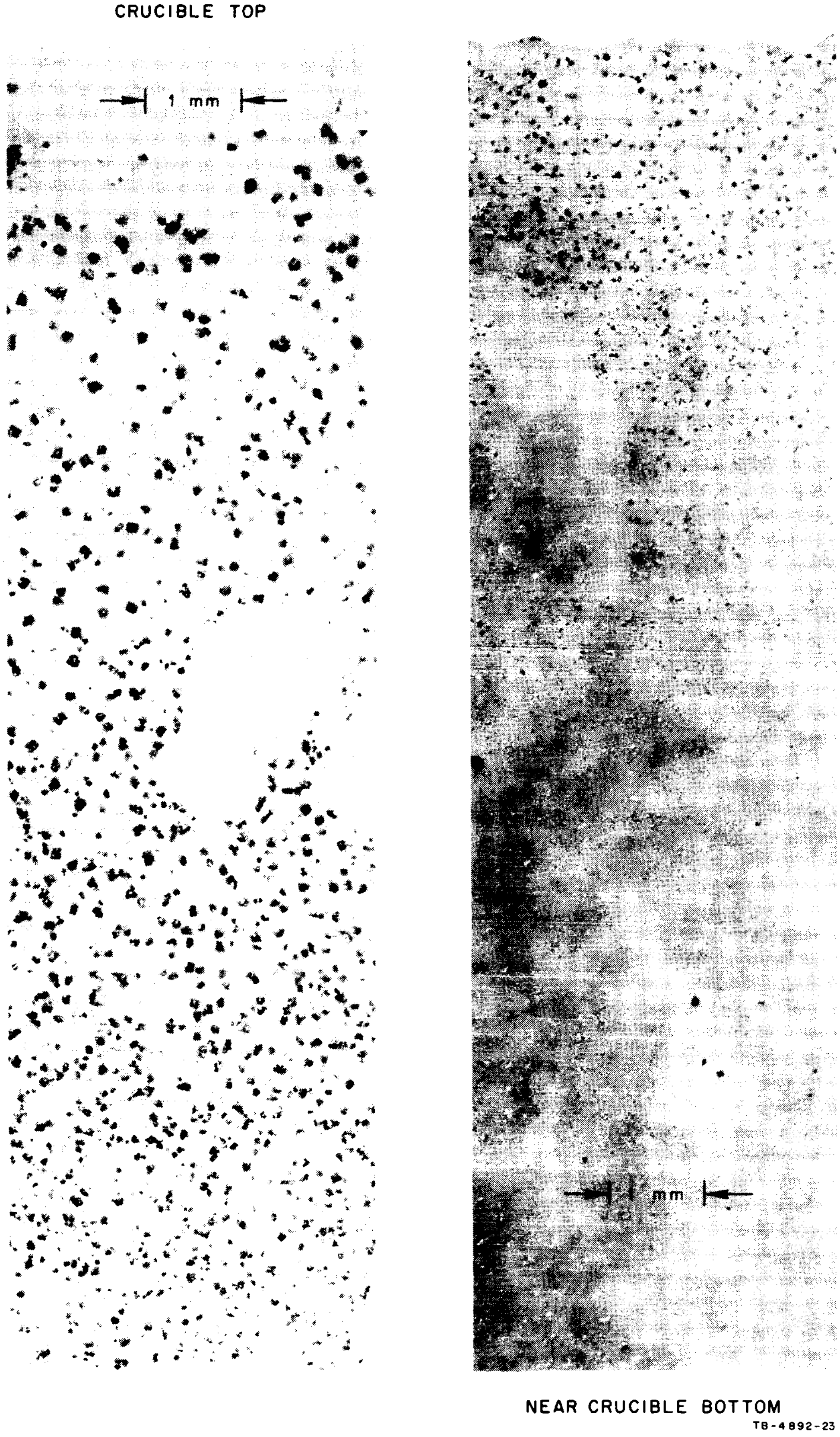

FIG. 9 TaC CRYSTALS FROM RUN NO. 35 (aluminum melt) GROWING ON THE WALLS OF THE Al_2O_3 CRUCIBLE

IV FUTURE WORK

Small TaC crystals have been formed by arc melting and by growth in metal solutions. Further efforts will be directed primarily toward growing larger crystals. Work during the next period will be concentrated on the following:

1. Complete the modifications to the three-electrode arc-Verneuil furnace, and start TaC crystal growing experiments
2. Attempt to grow larger TaC crystals from solution by two methods: (1) using low solubility solvents (aluminum at low temperatures) with separate tantalum and carbon sources; and (2) using high solubility solvents (iron at high temperatures) without sources of tantalum and carbon separate from the TaC nutrient. Lattice constant measurements will be made on crystals grown in both types of solvent systems
3. Investigate further the growth kinetics and morphology of TaC crystals grown from metal solutions, always with the goal of growing larger crystals.

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